ADDITIVE COMPOSITIONS FOR IMPROVING THE LACQUERING RESISTANCE OF HIGHER GRADE FUELS OF THE DIESEL OR BIODIESEL TYPE

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Abstract
Disclosed are additive compositions for superior quality diesel and biodiesel fuels for improving the lacquering resistance of fuels, in particular those intended for engines provided with Euro 4 to Euro 6 fuel injection systems. The additive compositions include at least one antioxidant of hindered phenol type and at least one metal passivator.
Figure 1

Distribution of percentage areas to be assessed

cylinder 17%  conical portion 8%
ADDITIVE COMPOSITIONS FOR IMPROVING THE LACQUERING RESISTANCE OF HIGHER GRADE FUELS OF THE DIESEL OR BIODIESEL TYPE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a National Phase Entry of International Application No. PCT/EP2012/075863, filed on Dec. 17, 2012, which claims priority to French Patent Application Serial No. 1162225, filed on Dec. 21, 2011, both of which are incorporated by reference herein.

BACKGROUND AND SUMMARY

[0002] The present invention relates to the use of additive compositions for higher grade fuels of the diesel or biodiesel type (Bx) for improving lacquering resistance. Diesel or biodiesel fuels are fuels which can be used for supplying compression ignition engines or diesel engines in automobiles (private cars, commercial vehicles, lorries, etc.).

[0003] Diesel fuels on the market must meet national or supranational specifications (for example standard EN 590 for diesel fuels in the EU). For commercial fuels, there is no legal obligation regarding the incorporation of additives (chemical compounds incorporated in fuels to improve their properties, for example additives for improving cold resistance); the oil companies and the distributors are free to add or not add additives to their fuels. From the commercial standpoint, in the field of distribution of fuels, a distinction is made between the “lowest price” fuels, with little or no additives, and higher-grade fuels, in which one or more additives are incorporated to improve their performance (above the regulation performance). Within the meaning of the present invention, by higher-grade fuel of the diesel or biodiesel type is meant any diesel or biodiesel fuel to which at least 50 ppm w/w of deposit reducer(s)/dispersant(s) has been added.

[0004] It has been noted that higher-grade diesel or biodiesel fuels sometimes cause deposits on the injector needles of injection systems of diesel engines, in particular those of Euro 3 to Euro 6 type. This phenomenon of deposits is also known by the English term lacquering, which will be used hereinafter, or else the acronym IDID (internal diesel injector deposits). Within the meaning of the present invention, the lacquering phenomenon does not refer to deposits outside of the injection system relating to the coking or fouling of injection nozzles as simulated for example by the standard engine test CEC F098-08 DW10B, especially when the fuel tested is contaminated with metallic zinc. The lacquering phenomenon can be localized on the end of the injector needles, both on the head and on the body of the needles of the fuel injection system but also throughout the system controlling the needle lift (valves) of the injection system, for vehicle engines operating on diesel or biodiesel fuel, and can eventually generate a loss of flow rate of fuel injected and therefore a loss of engine power.

[0005] Generally a distinction is made between 2 types of deposits in the lacquering category:

[0006] 1. deposits that are rather whitish and powdery; on analysis, it is found that these deposits consist essentially of soaps of sodium (sodium carboxylate, for example) and/or of calcium (type 1 deposits);

[0007] 2. organic deposits resembling coloured varnishes localized on the needle body (type 2 deposits).

[0008] Regarding the type 1 deposits, there are many possible sources of sodium in fuels of the Bx type:

[0009] catalysts for transesterification of vegetable oils for producing esters of the fatty acid (m)ethyl ester type such as sodium formate;

[0010] another possible source of sodium can be from the corrosion inhibitors used when petroleum products are conveyed in certain pipes, such as sodium nitrite;

[0011] finally, accidental exogenous pollution, via water or air for example, can contribute to the introduction of sodium into fuels (sodium being an element of very wide occurrence). There are many possible sources of acids in fuels of the Bx type, for example:

[0012] residual acids of biofuels (see standard EN14214 which stipulates a maximum permitted level of acids)

[0013] corrosion inhibitors used in the conveyance of petroleum products in certain pipes such as DDSA (dodecenoic/succinic anhydride) or HDSSA (hexadeconoic/succinic anhydride).

[0014] With regard to type 2 organic deposits, some publications state that they may in particular result from reactions between deposit reducers/dispersants (for example of the PIBS type) and acids (which would be present inter alia as impurities of esters of fatty acids in biodiesel). In the publication SAE 880493, Reduced Injection Needle Mobility Caused by Lacquer Deposits from Sunflower Oil, the authors M Ziejewski and H J Goettler describe the lacquering phenomenon and its harmful consequences for the operation of engines operating with sunflower oils as fuel. In the publication SAE 2008-01-0926, Investigation into the Formation and Prevention of Internal Diesel Injector Deposits, the authors J Ullmann, M Geduldig, H Jutztenberger (Robert Bosch GmbH) and R Caprotti, G Balfour (Infinium) also describe the reactions between acids and deposit reducers/dispersants to explain the type 2 deposits.

[0015] Furthermore, in the publication SAE International, 2010-01-2242, Internal Injector Deposits in High-Pressure Common Rail Diesel Engines, the authors S Schwab, J Bennett, S Dell, J Galante-Fox, A Kulinowski and Keith T Miller explain that the internal parts of the injectors are generally covered with a slightly coloured deposit that is visible to the naked eye. Their analyses showed that it mainly comprises sodium salts of alkene (hexadecene or dodecene) succinic acids; the sodium originating from dehydrating agents, from caustic solutions used in the refining, from tank bottom water or from seawater, and the succinic diacids being used as corrosion inhibitors or present in multifunctional additive packages. Once formed, these salts are insoluble in low-sulphur diesel fuels, and as they are in the form of fine particles they pass through diesel fuel filters and are deposited inside the injectors. In this publication, the development of an engine test is described, making it possible to reproduce the deposits. This publication emphasizes that only the diacids generate deposits, in contrast to monocarboxylic acids or the neutral esters of organic acids.

[0016] In the publication SAE International, 2010-01-2250, Deposit Control in Modern Diesel Fuel Injection System, the authors, R Caprotti, N Bharti and G Balfour, also investigate the same type of internal deposits in the injectors and assert that the appearance of deposits is not linked specifically to one type of fuel (B0 or containing EMAG/Bx) nor to vehicles of one type (light vehicles or heavy goods vehicles) equipped with modern motorizations (common
rail). They demonstrate the performance of a new deposit reducer/dispersant, effective on all types of deposits (coking and lacquering).

[0017] The deposits due to the lacquering phenomenon are insoluble in low-sulphur diesel fuels and in biodiesel fuels. These deposits are in the form of fine particles and can pass through diesel fuel filters and can then be deposited inside the injectors.

[0018] The accumulation of deposits of the lacquering type as described above can lead to the following problems:

[0019] a slowing of the response of the fuel injector,

[0020] sticking of internal components, which can lead to a loss of control of the injection time as well as of the amount of fuel supplied per injection,

[0021] a loss of manœuvrability of the vehicle,

[0022] power variations,

[0023] an increase in fuel consumption,

[0024] an increase in pollutants,

[0025] a disturbance in combustion, since the amount of fuel injected will not be as envisaged theoretically and the injection profile will be different,

[0026] unstable idle of the vehicle,

[0027] an increase in engine noise,

[0028] a lowering of the quality of combustion over the long term,

[0029] a lowering of the quality of atomization.

If there is a heavy deposit of the lacquering type, the vehicle could have great difficulty starting, or even not start at all, since the needle permitting injection would be blocked. The present invention makes it possible to overcome the problems indicated above.

DETAILED DESCRIPTION

[0030] The present invention proposes additive compositions that can tangibly improve the lacquering resistance of higher-grade diesel and biodiesel fuels, i.e. with the addition of at least 50 ppm by weight of deposit reducer(s)/dispersant(s). The deposit reducer or reducer(s)/dispersants used in higher-grade diesel fuels are generally selected from:

[0031] substituted amines such as N-polyisobutene amine R1-NH2, N-polyisobutene-ethylenediamine R1-NH—R2-NH2,

[0032] or polyisobutene succinimides of formula

$$R_1 - NH_2$$

[0033] where R represents a polyisobutene group of molecular weight between 140 and 5000 and preferably between 500 and 2000 or preferably between 750 and 1250; or their bissuccinimide, succinimic acid, succinimide structural equivalents, and where R2 represents at least one of the following segments —CH2—CH—, CH2—CH2—CH2—, CH2—CH(CH3)— and x represents an integer between 1 and 6.


[0035] the polyethylenamines of formula:

$$R_1 - R_2$$

$$O - CH - CH$$

[0036] where R is an alkyl or aryl group having from 1 to 30 carbon atoms; R1 and R2 are each independently a hydrogen atom, an alkyl chain with 1 to 6 carbon atoms or —O—CHR1—CHR2—; A is an amine or N-alkylamine with 1 to 20 carbon atoms in the alkyl chain, an N,N-dialkyamine having from 1 to 20 carbon atoms in each alkyl group, or a polyamine with 2 to 12 nitrogen atoms and from 2 to 40 carbon atoms and x is in the range from 5 to 30.

Such polyethylenamines are marketed for example by the companies BASF, HUNSTMAN or CHEVRON.

[0037] the products of reaction between a phenol substituted with a hydrocarbon chain, an aldehyde and an amine or polyamine or ammonia. The alkyl group of the alkylated phenol can comprise from 10 to 110 carbon atoms. This alkyl group can be obtained by polymerization of olefinic monomer containing from 1 to 10 carbon atoms (ethylene, propylene, 1-butene, isobutylene and 1-decene). The polyolefins that are used in particular are polyisobutene and/or polypropylene. The polyolefins generally have a weight-average molecular weight Mw between 140 and 5000 and preferably between 500 and 2000 or preferably between 750 and 1250.

[0038] The alkyl phenols can be prepared by an alkylation reaction between a phenol and an olefin or a polyolefin such as polyisobutylene or polypropylene. The aldehyde used can contain from 1 to 10 carbon atoms, generally formaldehyde or paraformaldehyde.

[0039] The amine used can be an amine or a polyamine including the alkanolamines having one or more hydroxy groups. The amines used are generally selected from ethanolamine, diethanolamines, methylamine, dimethylamine, ethylenediamine, dimethylaminopropylamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine and/or 2-(2-aminoethoxy)ethanol. This dispersant can be prepared by a Mannich reaction by reacting an alkylphenol, an aldehyde and an amine as described in patent U.S. Pat. No. 5,697,988.

[0040] other dispersants, such as:

[0041] carboxylic dispersants such as those described in U.S. Pat. No. 3,219,666;

[0042] the amine dispersants resulting from reaction between halogenated aliphatics of high molecular weight with amines or polyamines, preferably polyalkylene polyamines, described for example in U.S. Pat. No. 3,565,804;

[0043] polymeric dispersants obtained by polymerization of alkyl acrylates or alkyl methacrylates (C8 to C30 alkyl chains), aminoalkyl acrylates or acrylamides and acrylates substituted with poly(oxyethylene) groups. Examples of polymeric dispersants are described for example in U.S. Pat. No. 3,329,658 and U.S. Pat. No. 3,702,500;

[0044] dispersants containing at least one aminotriazol group such as described for example in U.S. Patent Publication No. 2009/0282731 resulting from reaction of a dicar-
boylic acid or anhydride substituted with a hydrocarbyl and an amine compound or salt of the (amino)guanidine type;  

[0045] oligomers of PIBSA and/or of DDSA and of hydrazine monohydrate, such as those described in EP 1,887,074;  

[0046] oligomers of ethoxylated naphthol and of PIBSA, such as those described in EP 1,884,556;  

[0047] quaternized ester, amide or imide derivatives of PIBSA, such as those described in WO2010/132259;  

[0048] mixtures of Mannich bases, for example dodecylphenol/ethylene diamine/formaldehyde, and of PIBSA, such as those described in WO2010/097624 and WO 2009/040582;  

[0049] quaternized terpolymers of ethylene, of alkoxynaphthylene(s) and of monoesters with at least one ethylenic unsaturation and containing an at least partially quaternized tertiary nitrogen, such as those described in WO2011/134923.  

[0050] The present invention relates to the use of additive compositions for improving the lacquering resistance of higher-grade diesel and biodiesel fuels, said compositions comprising at least one antioxidant of the hindered phenol type (alkylphenol) at and at least one metal passivator b/. The additive compositions for fuels, in particular of the diesel or biodiesel type, used in the invention for improving lacquering resistance, comprise:  

[0051] at least one antioxidant of the hindered phenol type (alkylphenol) at  

[0052] at least one metal passivator b/.  

[0053] The improvement in lacquering resistance provided by the additive compositions of the present invention is totally different from the improvement in the oxidation resistance of biodiesels as described for example in EP 2,087,074, EP 2,132,285 or EP 2,173,838. In fact, the oxidation phenomenon described in these documents takes place under the action in particular of light and air. Now, the deposits due to the lacquering phenomenon are produced actually inside the engine, on the injector, i.e. in an environment away from the light. Moreover, as indicated above, the lacquering phenomenon causes the appearance of deposits that appear specifically on the injectors and that result in particular from the chemical reaction of an acidic friction modifier and a deposit reducer/dispersant forming notably salts.  

[0054] The antioxidant or antioxidants a/ of the hindered phenol type can be selected from molecules comprising at least one hindered phenol group (alkylphenols). As examples of antioxidants of the hindered phenol type, there may be mentioned di-t-butyl-2,6-methyl-4-phenol (BHT), t-butyl hydroquinone (TBHQ), 2,6- and 2,4-di-t-butyl phenol, 2,4-dimethyl-6-t-butyl phenol, pyrogallol, tocopherol, 4,4’-methylen bis(2,6-di-t-butyl) phenol (CAS No. 118-82-1), alone or in a mixture. The preferred antioxidants of the hindered phenol type a/ comprise one or more of the following molecules comprising at least one hindered phenol group, alone or in a mixture: di-t-butyl-2,6-methyl-4-phenol (BHT), t-butyl hydroquinone (TBHQ), 2,6- or 2,4-di-t-butyl phenol, 2,4-dimethyl-6-t-butyl phenol alone or in a mixture.  

[0055] The metal passivator or passivators b/ can be selected from amines substituted with triazole groups (benzotriazole, tolyltriazole, etc.) such as N,N-bis(2-ethylhexyl)-1,2,4-triazol-1-ylmethanamine (CAS 12173-04-0), N,N-bis(2 ethylhexyl)-4-methyl-1H-benzotriazol-1-methylamine (CAS 80584-90-3), N,N-bis(hexyl)-ar-methyl-1H-benzotriazole-1-methanamine, N,N-bis(nonyl)-ar-methyl-1H-benzotriazole-1-methanamine, N,N-bis(dodecyl)-ar-methyl-1H-benzotriazole-1-methanamine, N,N-bis(undecyl)-ar-methyl-1H-benzotriazole-1-methanamine, N,N-bis(dodecyl)-ar-methyl-1H-benzotriazole-1-methanamine, N,N-bis(2-ethylhexyl)-ar-methyl-1H-benzotriazole-1-methanamine, 1,2,4-triazoles, benzimidazoles, 2-alkylthiobenzimidazoles; 2-alkylthiobenzothiazoles; 2-(N,N-dialkylthiocarbamoyl)benzothiazoles; 2-bis(alkylthio)-1,3,4-thiadiazoles such as 2,5-bis(tert-octylthio)-1,3,4-thiadiazole, 2,5-bis(tert-nonylthio)-1,3,4-thiadiazole, 2,5-bis(tert-decylthio)-1,3,4-thiadiazole, 2,5-bis(tert-undecylthio)-1,3,4-thiadiazole, 2,5-bis(tert-dodecylthio)-1,3,4-thiadiazole, 2,5-bis(tert-tridecylthio)-1,3,4-thiadiazole, 2,5-bis(tert-tetradecylthio)-1,3,4-thiadiazole, 2,5-bis(tert-pentadecylthio)-1,3,4-thiadiazole, 2,5-bis(tert-hexadecylthio)-1,3,4-thiadiazole, 2,5-bis(tert-heptadecylthio)-1,3,4-thiadiazole, 2,5-bis(tert-octadecylthio)-1,3,4-thiadiazole, 2,5-bis(tert-nonadecylthio)-1,3,4-thiadiazole, 2,5-bis(tert-eicosylthio)-1,3,4-thiadiazole, 2,5-bis(N,N-dialkylthiocarbamoyl)-1,3,4-thiadiazoles; 2-alkylthio-5-mercaptotriazoles; alone or in a mixture. Preferably the metal passivator or passivators b/ are selected from N,N-bis(2-ethylhexyl)-1,2,4-triazol-1-ylmethanamine (CAS 91273-04-0) and/or N,N-bis(2-ethylhexyl)-4-methyl-1H-benzotriazol-1-methylamine (CAS 80584-90-3), alone or in a mixture with other known metal passivators usually encountered in engines, in particular passivators of copper, of zinc.  

[0056] Preferably, the additive compositions according to the invention comprise:  

[0057] a/ at least one antioxidant of the hindered phenol type (alkylphenol) containing one or more alkylphenols selected from di-t-butyl-2,6-methyl-4-phenol (BHT), t-butyl hydroquinone (TBHQ), 2,6- or 2,4-di-t-butyl phenol, 2,4-dimethyl-6-t-butyl phenol, alone or in a mixture;  

[0058] b/ at least one metal passivator, preferably comprising N,N-bis(2-ethylhexyl)-1,2,4-triazol-1-ylmethanamine (CAS 91273-04-0) and/or N,N-bis(2 ethylhexyl)-4-methyl-1H-benzotriazol-1-methylamine (CAS 80584-90-3), alone or in a mixture with other metal passivators.  

[0059] According to an embodiment of the invention, the additive compositions comprise a passivator/antioxidant with a weight ratio in the range from 1/10 to 2, preferably in the range from 1/6 to 1, advantageously from 3/5 to 1/2. According to an embodiment, the additive compositions used in the invention comprise di-t-butyl-2,6-methyl-4-phenol (BHT) and N,N-bis(2-ethylhexyl)-1,2,4-triazol-1-ylmethanamine (CAS 91273-04-0). According to an embodiment of the invention, the additive compositions used comprise t-butyl hydroquinone (TBHQ) and N,N-bis(2-ethylhexyl)-1,2,4-triazol-1-ylmethanamine (CAS 91273-04-0). According to an embodiment of the invention, the additive compositions comprise t-butyl hydroquinone (TBHQ) and N,N-bis(2-ethylhexyl)-4-methyl-1H-benzotriazol-1-methylamine (CAS 80584-90-3). According to an embodiment of the invention, the additive compositions comprise t-butyl hydroquinone (TBHQ) and N,N-bis(2-ethylhexyl)-4-methyl-1H-benzotriazol-1-methylamine (CAS 80584-90-3).  

[0060] Besides components a/ and b/ mentioned above, the additive compositions according to the invention can also contain other additives, of a different chemical nature and/or with different functionality or functionalities. Among these other additives different from the antioxidants a/ and the passivators b/, the compositions according to the invention can contain, non-exhaustively:
at least one cold resistance additive,

at least one tracer or marker,

at least one perfuming and/or odor-masking and/or reodorizing agent,

at least one biocide,

at least one metal deactivator,

one or more deposit reducers/dispersants.

According to an embodiment, the additive compositions according to the invention comprise:

at least one antioxidant of the hindered phenol type (alkylphenol),

at least one metal passivator, and

at least one conventional deposit reducer/dispersant.

According to an embodiment of the invention, the additive compositions comprise:

from 1 to 50% by weight, preferably from 5 to 30% by weight of at least one antioxidant of the hindered phenol type 

from 1 to 25% by weight, preferably from 2 to 15% by weight of at least one metal passivator,

at least one conventional deposit reducer/dispersant, preferably in a quantity of up to 80% by weight, more preferably in the range from 30 to 70% by weight.

Examples of deposit reducers/dispersants used conventionally in diesel or biodiesel fuels have already been given. There may in particular be mentioned:

substituted amines such as N-polysobutene amine R1-NH2, N-polysobutene-ethylenediamine R1-NH—R2—NH2,

polyisobutenesuccinimides of formula

where R represents a polyisobutene group of molecular weight between 140 and 5000 and preferably between 500 and 2000 or preferably between 750 and 1250; or their bisuccinimides, succinnamic, succinimide structural equivalents, and where R2 represents at least one of the following segments —CH2—CH3—, CH2—CH2—CH2—, CH—CH(CH3)— and x represents an integer between 1 and 6.

polyethylenamines,

polyethylenamines of formula:

where R is an alkyl or aryl group having from 1 to 30 carbon atoms; R1 and R2 are each independently a hydrogen atom, an alkyl chain with 1 to 6 carbon atoms or —O—CHR1-CHR2—; A is an amine or N-alkylamine with 1 to 20 carbon atoms in the alkyl chain, an N,N-dialkylamine having from 1 to 20 carbon atoms in each alkyl group, or a polyamine with 2 to 12 nitrogen atoms and from 2 to 40 carbon atoms and x is in the range from 5 to 30,

As examples of anti-sedimentation additives and/or wax dispersants, it is in particular possible to use the anti-sedimentation additives selected (but not limitingly) from the group consisting of the copolymers of (meth)acrylic acid/alkyl (meth)acrylate amidated by a polyamine, polyamine alkenyl succinimides, derivatives of phthalic acid and of double-chain fatty amine; alkyl phenol/alkyldiols or -polyol resins; examples of such additives are given in EP 261 959, EP 293 331, EP 674 689, EP 327 423, EP 512 889, EP 832 172; U.S. Patent Publication No. 2005/023636; U.S. Pat. No. 5,989, 530; WO 93/14178. Preferably, the additive compositions according to the invention contain at least one cold resistance additive selected from ethylene/vinyl acetate copolymers (EVA) and/or ethylene/vinyl acetate/vinyl versatate terpolymers (VEOVA) and/or ethylene/vinyl acetate/their ester (2-ethylhexyl acrylate) terpolymers as a cold resistance additive.

The optional perfuming and/or odour-masking and/or reodorizing agent or agents can in particular be selected from the following aliphatic or cycloaliphatic esters:

- 3a,4,5,6,7,10-hexahydro-4,7-methano-1H-inden-5-(or 6)-yl isobutyrate (CAS 67634-20-2).
- Tricyclodecenyl propionate (CAS 17511-60-3).
- cis-3-hexenyl acetate (CAS 3681-71-8).
- Ethyl linalool (CAS 10339-55-6).
- Linalool (CAS 1191-16-8).
- Ethyl myristate (CAS 124-06-1).
- Para-tolyl cyclohexyl acetate (CAS 32210-23-4).
- Butyl acetate (CAS 123-86-4).
- 4,7-methano-1H-inden-6-ol, 3a,4,5,6,7-cyclohexa-
diene-1,4-diol, acetate (CAS 5413-60-5).
- Ethyl caprate (CAS 110-38-3).

The optional perfuming and/or odour-masking and/or reodorizing agent or agents can be selected from:

The organic tricyclic compounds described in EP 1,591,514, which are organic tricyclic compounds of the following formula (I)

![Diagram]

in which the cyclopentane ring is saturated or unsaturated, and R1, R2, R3, which may be identical or different, are selected from hydrogen and hydrocarbon radicals comprising 1 to 10 carbon atoms and optionally having one or more heterocatoms as well as:

- Aliphatic or aromatic aldehydes such as vanillin.
- Aliphatic or aromatic esters, such as benzylic acetate.
- Alcohols, such as linalool, the phenylethyl alcohols.
- Ketones, such as crystallized camphor, ethylmalol, 2,4,5-trimethylphenol.

[0108] essential oils, such as essential oil derived from citrus fruits alone or in a mixture.

Advantageously, it is preferable to use a combination of at least one organic terpene compound and at least one aldehyde, one ester, one hydroxide, one ketone, one essential oil as defined above, as perfuming, odour-masking or reodorizing agent.

[0113] The biocide or biocides can be selected from:

- Mixtures (CAS No. 55965849) of the following compounds: 5-chloro-2-methyl-2H-isothiazol-3-one (CAS: 26172-55-4) and EINECS 247-500-7) and 2-methyl-2H-isothiazol-3-one (CAS No. 26820-20-4 and EINECS 220-239-6).


[0117] Quaternary ammonium salts in the form of chlorides obtained from C12-C18 alkyl benzene or from alkyl dimethyl benzene.

The metal desiccator or deactivators or chelating agents can be selected from amines substituted with N,N'-dialkylcarbamido groups, such as N,N'-dialkylcarbamide 1,2-diaminopropane (MDA).

[0118] Certain components of the compositions according to the invention can have several functionalities, typically marker and perfume agent: one component can be both a marker and a perfuming agent. Besides the components described previously (additives a/ and b/ according to the invention, other additives as defined previously, solvents, co-solvents), the additive compositions for fuel according to the invention can contain other additives such as those required by the regulations (markers, demulsifiers, anti-static additives or additives improving conductivity, lubricity additives, anti-wear agents and/or friction modifiers, combustion improving additives and, in particular, additives for improving the cetane index), anti-foaming additives etc.

[0119] According to a second object, the invention relates to a method of preparing the additive compositions as defined above, by mixing, preferably at room temperature, components a/ and b/ and optionally other additives and/or the solvent or solvents, co-solvents, in one or more steps by any suitable mixing means. According to a third object, the invention relates to the use of at least one additive composition according to the invention incorporated in a fuel of the high-grade diesel or biodiesel type for improving the lacquerability resistance, i.e. fouling on the head and/or on the body of the needles of the fuel injection system but also in the whole needle lift control system (valves) of the injection system, in particular for engines equipped with fuel injection systems of the Euro 4 to Euro 6 type.

[0120] The invention also relates to a method of improving lacquerability resistance, comprising the incorporation of an additive composition in a diesel or biodiesel fuel, said additive composition comprising:

- At least one antioxidant of the hindered phenol type a/.
- At least one metal passivator b/.

Preferably, in the method of improving lacquerability resistance according to the invention, the additive composition is as described in the several variants presented above.
The method of improving lacquering resistance according to the invention makes it possible to avoid and/or reduce and/or delay:

- a slowing of the response of the fuel injector,
- sticking of internal components, which can lead to a loss of control of injection time as well as of the amount of fuel supplied per injection,
- a loss of manoeuvrability of the vehicle,
- variations in power,
- increases in fuel consumption,
- an increase in pollutants,
- a disturbance in combustion, since the amount of fuel injected will not be that envisaged theoretically and the injection profile will be different,
- an unstable idle of the vehicle,
- an increase in engine noise,
- a lowering of the quality of combustion over the long term,
- a lowering of the quality of atomization.

The invention further relates to higher-grade diesel or biodiesel fuels with improved lacquering resistance, with the addition of at least 50 ppm w/w of deposit reducer(s)/dispersants and at least one composition comprising at least one antioxidant of the hindered phenol type (alklyphenol) α/ and at least one metal passivator β/ selected from amines substituted with triazole groups. Preferably the concentration of additives α/ and β/ respectively in the final fuel with additives is between 2 and 200 ppm w/w and advantageously between 10 and 50 ppm w/w, i.e. ppmw relative to the total weight of the fuel with additives. Preferably the composition of liquid fuel of the (bio)diesel type according to the invention comprises from 100 to 2000 ppm w/w and advantageously from 500 to 1500 ppm w/w of additive composition(s) according to the invention as defined above.

According to an embodiment of the invention, the diesel or biodiesel fuel according to the invention comprises:

- from 2 to 200 ppm w/w, preferably from 10 to 100 ppm w/w, more preferably from 30 to 80 ppm w/w, advantageously from 10 to 50 ppm w/w, of antioxidant of the hindered phenol type α/ and
- from 2 to 200 ppm w/w, preferably from 5 to 50 ppm w/w, advantageously from 10 to 50 ppm w/w, of metal passivator β/ selected from amines substituted with triazole groups,
- at least 50 ppm w/w, preferably from 50 to 1000 ppm w/w, advantageously from 50 to 500 ppm w/w, and
- ideally from 50 to 250 ppm w/w of at least one conventional deposit reducer/dispersant.

A person skilled in the art will easily adapt the level of incorporation of additive composition(s) according to the invention in relation to the concentration of additives α/ and β/, which may for example depend on the viscosity of additives α/ and β/, and on that of any other additives; in the case when the additive composition according to the invention contains solvents or co-solvents, on the solubility of the additives in these solvents. The optional other additives are generally incorporated in quantities in the range from 50 to 1500 ppm w/w, i.e. ppmw relative to the total weight of the fuel with additives.

By "diesel or biodiesel fuels" is meant mixtures based on liquid hydrocarbons having distillation temperatures comprised between 140 and 380°C, preferably between 180 and 360°C; these mixtures are in general derived from cuts of the middle distillate type, originating from refineries and/or from agrofuels and/or from biofuels and/or from biomass and/or from synthetic fuels, and in particular from cuts rich in paraffins and isoparaffins, with a proportion of naphthenes, or also aromatic molecules such as those contained in gas oils resulting from the pyrolysis of biomass, preferably corresponding to the local specifications for diesel fuels, for example EN 590 in the European Union. The (bio)diesel fuels incorporating at least one additive composition improving lacquering according to the invention can be prepared by doping the hydrocarbon mixture, with the additive composition or compositions according to the invention and with the optional other additive or additives, in one or more steps, generally at room temperature. Separate mixing of the components of the additive composition according to the invention (additives α/ and β/), optionally the other additives, the solvents and/or co-solvents), with the (bio)diesel fuel, also falls within the scope of the invention.

The inventors have also developed a new method that is reliable and robust for evaluating the sensitivity of (bio)diesel fuels, in particular those of higher grade, to lacquering. This method, in contrast to the methods described in the publications cited above, is not a laboratory method but is based on real engine tests and is therefore of industrial interest and makes it possible to quantify the effectiveness of the additives or of the additive compositions against lacquering.

The method of measuring lacquering developed by the inventors is detailed below:

- The engine used is a four-cylinder, 16-valve, high-pressure injection common rail diesel engine with a cylinder capacity of 1500 cm³ and a power of 80 hp: regulation of the fuel injection pressure takes place in the high-pressure part of the pump.

- The power point is 40 h at 4000 rpm: the position of the injector in the chamber has been lowered by 1 mm relative to its nominal position, which on the one hand promotes the release of thermal energy from combustion, and on the other hand brings the injector closer to the combustion chamber.

- The flow rate of fuel injected is adjusted so as to obtain an exhaust temperature of 750°C at the start of the test.

- The injection advance was increased by 1.5° crankshaft relative to the nominal setting (changing from +12.5° to +14° crankshaft) still with the aim of increasing the thermal stresses to which the injector nozzle is subjected.

- Finally, to increase the stresses to which the fuel is subjected, the injection pressure was increased by 10 MPa relative to the nominal pressure (i.e. changing from 140 MPa to 150 MPa) and the temperature is set at 65°C at the inlet of the high-pressure pump.

- The technology used for the injectors requires high fuel return, which promotes degradation of the fuel since it can be subjected to several cycles in the high-pressure pump and the common rail before being injected into the combustion chamber.

- Expression of the results:

- To ensure the validity of the result, various parameters are monitored during the test: power, torque and fuel consumption indicate whether the injector is fouled or whether its operation has deteriorated through formation of deposits, since the operating point is the same throughout the test. The characteristic temperatures of the various fluids (cooling liquid, fuel, oil) allow the validity of the tests to be
monitored. The fuel is adjusted to 65°C at the pump inlet, and the cooling liquid is adjusted to 90°C at the engine outlet.

[0151] The smoke values allow the combustion timing to be monitored at the start of the test (target value 3FSN) and ensure that it is properly repeatable from one test to the next. The injectors are dismantled at the end of the test in order to inspect and assess the deposits formed along the needles. The scoring procedure adopted for assessing the needles is as follows:

[0152] The scale of scores varies from −2.5 (for a heavy deposit) to 10 (for a new needle without any deposit). The final score is a weighted average of the scores for all the needle surfaces assessed.

[0153] Total area: cylindrical portion (immediately after the conical portion) + conical portion: 100%.

[0154] Surface area weighting for the cylindrical portion (immediately after the conical portion): 68%.

[0155] Surface area weighting for the conical portion: 32%.

[0156] See the accompanying FIG. 1, which shows the cylindrical portion and the conical portion which are assessed (the percentages shown correspond to a quarter of the surface area of the needles: thus, the overall surface area weighting is therefore 17.5×4−68%).

[0157] A product performance threshold was determined relative to this assessment procedure: Result <4=Poor, Result >4=Satisfactory.

[0158] The following examples illustrate the invention without limiting it.

EXAMPLES

[0159] The method for evaluating lacquering described above is implemented for various compositions of B0 or B7 fuels complying with standard EN 590 without additives or with one or more petroleum-based additives. The details of each fuel composition tested are shown in Table 1 below together with the overall score for lacquering resistance. Table 2 gives details for the chemical nature of the additives in Table 1.

[0160] The fuels B0 (without VOME) and B7#1 and B7#2 are standard diesel fuels, complying with standard EN 590, and have a sulphur content less than or equal to 10 ppm. Unless stated otherwise, the quantities of the additives shown are expressed in ppm w/w: weight of additive in ppm w/w per total weight of fuel with additives.

<table>
<thead>
<tr>
<th>TABLE 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example No.</td>
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</table>

<table>
<thead>
<tr>
<th>A</th>
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<th>C</th>
<th>D</th>
<th>G</th>
<th>E</th>
</tr>
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<tr>
<td>Type of fuel</td>
<td>B0</td>
<td>B7#1</td>
<td>B7#1</td>
<td>B7#1</td>
<td>B7#1</td>
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<tr>
<td>Deposit reducer 1</td>
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<td>85 ppm</td>
<td>85 ppm</td>
<td></td>
<td></td>
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<td>Deposit reducer 2</td>
<td>165 ppm</td>
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<tr>
<td>Friction modifier</td>
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<td>200 ppm</td>
<td>200 ppm</td>
<td>200 ppm</td>
<td></td>
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<tr>
<td>Compatibilizing agent (co-solvent)</td>
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<td>180 ppm</td>
<td>180 ppm</td>
<td>70 ppm</td>
<td></td>
</tr>
<tr>
<td>Aromatic solvent</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Passivator 1</td>
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<td>30 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Antioxidant 3</td>
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</tr>
<tr>
<td>Antioxidant 4</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lacquering score</td>
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<td>7.0</td>
<td>2.8</td>
<td>−2.5</td>
<td>−2.5</td>
</tr>
</tbody>
</table>

| Example No. |

<table>
<thead>
<tr>
<th>F</th>
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<th>J</th>
<th>K</th>
<th>L</th>
</tr>
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<tr>
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<td>200 ppm</td>
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<td></td>
</tr>
<tr>
<td>Passivator 1</td>
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<td></td>
</tr>
<tr>
<td>Passivator 2</td>
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<tr>
<td>Antioxidant 1</td>
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<td>70 ppm</td>
<td>70 ppm</td>
<td>40 ppm</td>
<td>40 ppm</td>
</tr>
<tr>
<td>Antioxidant 2</td>
<td>40 ppm</td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Lacquering score</td>
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<td>4.4</td>
<td>4.9</td>
<td>6.4</td>
</tr>
</tbody>
</table>
The fuels H to L incorporating an additive composition according to the invention show good, or even excellent, lacquering resistance, in contrast to the comparative fuels with additives C to G.

1. A method of improving a lacquering resistance of higher-grade diesel and biodiesel fuels comprising a step of adding additive compositions into the higher-grade diesel and biodiesel fuels, the compositions comprising at least one antioxidant of a hindered phenol type a/ and at least one metal passivator b/.

2. The method according to claim 1, wherein the antioxidant or antioxidants of the hindered phenol type a/ are selected from di-t-butyl-2,6,6-tetramethyl-4-phenol (BHT), t-butyl hydroquinone (TBHQ), 2,6- and 2,4-di-t-butyl phenol, 2,4-dimethyl-6-t-butyl phenol, pyrocatechol, tocopherol, 4,4'-methylen bis(2,6-di-t-butyl phenol) (CAS No. 118-82-1), alone or in a mixture.

3. The method according to claim 1, wherein the passivator or passivators are selected from amines substituted with triazole groups, alone or in a mixture.

4. The method according to claim 3, wherein the metal passivator or passivators are selected from N,N-bis(2-ethylhexyl)-1,2,4-triazole-1-ylmethylamine (CAS 91273-04-0), N,N-bis(2-ethylhexyl)-4-methyl-1H-benzotriazol-1-ylmethylamine (CAS 80584-90-3), N,N-bis[heptyl]-ar-methyl-1H-benzotriazole-1-methanamine, N,N-bis(nonyl)-ar-methyl-1H-benzotriazole-1-methanamine, N,N-bis(heptyl)-4-methyl-1H-benzotriazole-1-methanamine, N,N-bis(nonyl)-4-methyl-1H-benzotriazole-1-methanamine, N,N-bis(undecyl)-ar-methyl-1H-benzotriazole-1-methanamine, N,N-bis(dodecyl)-ar-methyl-1H-benzotriazole-1-methanamine, N,N-bis(2-ethylhexyl)-ar-methyl-1H-benzotriazole-1-methanamine, N,N-bis(2-ethylhexyl)-ar-methyl-1H-benzotriazole-1-methanamine, 1,2,4-triazoles, benzimidazoles, 2-alkylidithiobenzimidazoles, 2-alkylidithiocarbamoylbenzothiazoles, 2-[(alkylidithio)-1,3,4-thiadiazoles such as 2,5-bis(tet-oc-tylidithio)-1,3,4-thiadiazole, 2,5-bis(tet-nonylidithio)-1,3,4-thiadiazole, 2,5-bis(tet-tetradecylidithio)-1,3,4-thiadiazole, 2,5-bis(tet-octylidithio)-1,3,4-thiadiazole, 2,5-bis(tet-hexadecylidithio)-1,3,4-thiadiazole, 2,5-bis(tet-heptadecylidithio)-1,3,4-thiadiazole, 2,5-bis(tet-octadecylidithio)-1,3,4-thiadiazole, 2,5-bis(tet-nona-decyldithio)-1,3,4-thiadiazole, 2,5-bis(tet-eicosyldithio)-1,3,4-thiadiazole, 2,5-bis(N,N-dialkylidithiocarbamoyl)-1,3,4-thiadia-zoles, 2-alkylidithio-5-mercaptopthiadiazoles, alone or in a mixture.

5. The method according to claim 1, wherein the additive compositions additionally contain one or more other additives, selected from:

- at least one cold resistance additive;
- at least one tracer or marker;
- at least one perfuming and/or colour-masking and/or reodorizing agent;
- at least one biocide;
- at least one metal deactivator; and
- one or more deposit reducers/dispersants.

6. The method according to claim 1, wherein the additive compositions additionally contain a solvent.

7. Diesel or biodiesel fuels with improved lacquering resistance, the fuel comprising an addition of at least 50 ppm w/w of deposit reducer(s)/dispersants and at least one composition comprising at least one antioxidant of a hindered phenol type a/ and at least one metal passivator b/ selected from amines substituted with triazole groups.

8. The diesel or biodiesel fuels according to claim 7, wherein their concentration of additives a/ and b/ respectively is between 2 and 200 ppm w/w.

9. The diesel or biodiesel fuels according to claim 7, wherein the antioxidant or antioxidants of the hindered phenol type a/ are selected from di-t-butyl-2,6,6-tetramethyl-4-phenol (BHT), t-butyl hydroquinone (TBHQ), 2,6- and 2,4-di-t-butyl phenol, pyrogallol, tocopherol, 4,4'-methylen bis(2,6-di-t-butyl phenol) (CAS No. 118-82-1), alone or in a mixture.

10. The diesel or biodiesel fuels according to claim 7, wherein the metal passivator or passivators are selected from N,N-bis(2-ethylhexyl)-1,2,4-triazole-1-ylmethylamine (CAS 91273-04-0), N,N-bis(2-ethylhexyl)-4-methyl-1H-benzotriazol-1-ylmethylamine (CAS 80584-90-3), N,N-bis[heptyl]-ar-methyl-1H-benzotriazole-1-methanamine, N,N-bis(nonyl)-ar-methyl-1H-benzotriazole-1-methanamine, N,N-bis(undecyl)-ar-methyl-1H-benzotriazole-1-methanamine, N,N-bis(dodecyl)-ar-methyl-1H-benzotriazole-1-methanamine, N,N-bis(2-ethylhexyl)-ar-methyl-1H-benzotriazole-1-methanamine, 1,2,4-triazoles, benzimidazoles, 2-alkylidithiobenzimidazoles, 2-alkylidithiocarbamoylbenzothiazoles, 2,5-bis(alkylidithio)-1,3,4-thiadiazoles such as 2,5-bis(tet-oc-tylidithio)-1,3,4-thiadiazole, 2,5-bis(tet-nonylidithio)-1,3,4-thiadiazole, 2,5-bis(tet-tetradecylidithio)-1,3,4-thiadiazole, 2,5-bis(tet-octylidithio)-1,3,4-thiadiazole, 2,5-bis(tet-hexadecylidithio)-1,3,4-thiadiazole, 2,5-bis(tet-heptadecylidithio)-1,3,4-thiadiazole, 2,5-bis(tet-octadecylidithio)-1,3,4-thiadiazole, 2,5-bis(tet-nona-decyldithio)-1,3,4-thiadiazole, 2,5-bis(tet-eicosyldithio)-1,3,4-thiadiazole, 2,5-bis(N,N-dialkylidithiocarbamoyl)-1,3,4-thiadia-zoles, 2-alkylidithio-5-mercaptopthiadiazoles, alone or in a mixture.
at least one cold resistance additive;
at least one tracer or marker;
at least one perfuming and/or odour-masking and/or
trocodorizing agent;
at least one biocide;
at least one metal deactivator.

12. The diesel or biodiesel fuels according to claim 7,
further comprising a solvent.

13. The diesel or biodiesel fuels according to claim 12,
further comprising the solvent and a co-solvent.

14. The diesel or biodiesel fuels according to claim 8,
wherein their concentration of additives a/ and b/ respectively
is between 10 and 50 ppm w/w.

15. The method according to claim 6, wherein the additive
compositions contain a solvent and a co-solvent.

* * * * *