ADDITIVE COMPOSITION FOR ENGINE OIL

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ABSTRACT
The disclosure relates to an additive composition including:
(a) at least one compound including an azole heterocycle,
(b) at least one alkylbenzene or alkylnapthalene sulphonate not surfisised with an alkali or alkaline-earth metal,
(c) at least one carbodiimide, and
(d) at least one antioxidant
The disclosure also relates to the use thereof as additive composition for engine oil.
ADDITIVE COMPOSITION FOR ENGINE OIL

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a National Phase Entry of International Application No. PCT/IB2010/055964, filed on Dec. 20, 2010, which claims priority to French Patent Application Serial No. 09 59258, filed on Dec. 18, 2009, both of which are incorporated by reference herein.

TECHNICAL FIELD

The present invention relates to additive compositions making it possible to reduce the corrosiveness of engine oils, in particular for diesel engines, vis-à-vis metals and non-ferrous metals, mainly copper, lead, tin, aluminium etc. and their alloys.

BACKGROUND

An engine lubricant comprises a very wide variety of additives, to allow it to reach the high performance levels required by users. Thus, for example, because of environmental concerns, it is increasingly sought to achieve fuel economy in vehicles. The behaviour of the engine lubricant in reducing friction will have a very significant impact on fuel consumption. It is mainly the quality of the lubricant bases, alone or in combination with viscosity index improver polymers and friction modifier additives, which gives the lubricant its properties of reducing friction on the different engine components in operation and hence its "fuel eco" or fuel economy properties. In particular, the formulation of a high-performance fuel eco lubricant always leads to the addition of more friction modifiers to the engine lubricants.

However, this addition of chemical additives can sometimes have adverse effects, such as for example increasing the corrosiveness of the lubricant vis-à-vis certain ferrous or non-ferrous metal parts of the engine. Thus, it has been found that the corrosiveness of the engine oils vis-à-vis copper, lead and tin was increased when they contain organometallic friction modifiers, such as for example the organometallic compounds, so-called molybdenum derivatives, and/or organic friction modifiers without "metal" or without "ash", which are generally fats and can be fatty esters, amines or fatty amides, fatty acids, fatty alcohols, etc. This corrosiveness, in particular at high temperatures, is measured for example according to the standard ASTM D6594, by the "HTCTB" test or "High Temperature Corrosion Bench Test".

The solutions commonly used to remedy these drawbacks involve reducing the organic or organometallc friction modifier content of the lubricants, which greatly limits their "fuel eco" character. Metal deactivating compounds (or metal passivation compounds) such as for example the di- or triazole are also added, without however making it possible to achieve acceptable corrosion levels for the non-ferrous metals.

U.S. Pat. No. 5,614,483 discloses the use of carboxydimides, optionally in combination with a calcium sulphonate, amine or phenolic antioxidants, non-ferrous metal deactivators, anti-wear and extreme-pressure additives, viscosity index improvers, antifoaming agents, dispersants, detergents, in order to reduce the aggressiveness of hydraulic oils containing esters as base oil vis-à-vis lead, zinc, or steel. This document does not disclose a specific combination of carboxydimide with the abovementioned additives, nor the possibility of using such combinations in engine oils containing organic and/or organometallic friction modifiers, in order to reduce their corrosiveness vis-à-vis copper, lead and tin.

Patent Application EP 0992571 describes the combination of a carbodiimide with a specific phenyl-naphthalenylamine (to the exclusion of other diarylamines), and optionally with a copper deactivator which can be a triazole or a thiadiazole, in a base oil which can be mineral or synthetic, for example of ester type, said oil being able to contain additives such as: amine or phenolic antioxidants, VI improvers, sulphur-, phosphor- or phospho sulphur-containing anti-wear or extreme pressure agents, metal thiophosphates or thiocarbamates, rust inhibitors such as carboxylic acids, detergents of metal sulphonate, phenate or carboxylate type, in order to improve the oxidation stability of such oils. This document does not disclose a specific combination of carbodiimide, phenyl-naphthalenylamine, triazole or thiadiazole with said additives, nor their use in engine oils containing organic and/or organometallc friction modifiers, in order to reduce their corrosiveness vis-à-vis copper, lead and tin.

Patent Application WO 2008/095805 discloses additive compositions comprising borated esters and triazoles and optionally amine phosphates in order to reduce the corrosiveness of lubricant compositions containing friction modifiers, which can be glycerol monolactone or an organomolybdenum compound, vis-à-vis copper, lead and tin. The examples of this application do not specify which friction modifiers are contained in the reference oils, the corrosiveness of which is reduced. However, depending on the values of corrosiveness vis-à-vis Cu, Pb, Sn, measured according to ASTM D6594 on the reference oil, it seems that this friction modifier is not of mainly organic type, but much rather predominantly of the MoDTC type. The lowering of the corrosiveness level can also be improved, in particular in the case of copper. Finally, these additive compositions optionally involve an addition of phosphorus which can lead to the production of ash and catalyst poisons detrimental to emission after-treatment systems installed in vehicles (in particular diesel vehicles).

Patent Application EP 2 080 798 discloses the addition of an additive composition comprising an acid amide compound and a benzotriazole, to a lubricant comprising molybdenum dithiocarbamate and organic friction modifiers, which can be fatty acid or aliphatic amine esters. The addition of this additive composition reduces the corrosiveness of said lubricant vis-à-vis copper and lead. However, this effect is only obtained with reduced levels of organic friction modifiers. Said additive compositions have an effect in lubricants to which large quantities of molybdenum friction modifier have been added, increasing the level of metal in the lubricant and therefore its tendency to produce ash, with the abovementioned harmful effects on emissions. Moreover, no effect on the corrosiveness vis-à-vis tin is mentioned.

A need therefore exists for additives making it possible to further reduce the corrosiveness of lubricant compositions for engines comprising organometallic and/or organic friction modifiers vis-à-vis non-ferrous metals. In particular, there is a need for such additive compositions acting at high levels of friction modifier, preferably at high levels of non-metal friction modifiers, in order to make it possible to formulate "fuel eco" or fuel-economy lubricants, preferably with a low level of ash. More particularly, there is a need for such additive compositions to lead to the addition of a minimum amount of ash-generating compounds.
Surprisingly, the Applicant has found that the introduction of an additive composition comprising one or more carbodiimides, amine or phenolic antioxidants, azole compounds, and anticorrosion additives of neutral sulphonate type to engine oils comprising organic and/or organometallic friction modifiers, made it possible to inhibit the corrosiveness of said oils vis-à-vis non-ferrous metals. The additive compositions according to the invention have a synergistic effect on the reduction of the corrosiveness of these oils vis-à-vis non-ferrous metals. They have the advantage of reducing corrosiveness vis-à-vis non-ferrous metals of engine oils containing a high percentage of friction modifiers, in particular of organic friction modifiers without ash, corresponding to formulae of engine oils with a low ash level and with a "fuel eco" effect.

SUMMARY

A subject of the present invention is additive compositions comprising:

(a) at least one compound comprising an azole heterocycle, chosen from di- or trizole, the azole heterocycle of which optionally comprises a sulphur atom,

(b) at least one non-overbased alkylbenzene or alkylbenzenesulphonate of an alkali or alkaline-earth metal, the alkyl substituent or substituents of which comprise from 7 to 12 carbon atoms, preferably from 8 to 10 carbon atoms,

(c) at least one carbodiimide of formula X—N═C—N=Y, where X and Y are, independently of each other, hydrocarbon radicals comprising from 8 to 60 carbon atoms, of formula (I):

Preferably, the additive compositions according to the invention comprise, as compound (a), at least one benzotriazole of formula (V):

\[
\begin{array}{c}
\text{R}^6 \text{N} \text{N}^+ \text{V} \\
\text{R}^7 \\
\text{N} \text{N}^+ \text{V} \\
\text{R}^8
\end{array}
\]

where R6 and R7 are, independently of each other, linear, branched or cyclic hydrocarbon groups having from 1 to 30 carbon atoms, preferably from 2 to 20 carbon atoms, which can contain an oxygen, sulphur or nitrogen atom.

Preferably, the additive compositions according to the invention comprise, as compound (b), at least one neutral dialkylbenzene or dialkylbenzenesulphonate of an alkali or alkaline-earth metal, the alkyl substituents of which comprise from 7 to 12 carbon atoms. According to a preferred embodiment, in the additive compositions according to the invention, compound (b) has a BN, measured according to the standard ASTM D2892, less than 20, preferably less than 15 mg of KOH/gram.

According to an embodiment, in the additive compositions according to the invention, the secondary amines optionally present as compound (d) are chosen from the secondary amines of formula R8-NH—R9, where R8 and R9 are, independently of each other:

(a) a phenyl group, optionally substituted, preferably in the para position of the amine function, by alkyl or alkenyl groups comprising from 1 to 10 carbon atoms, preferably from 1 to 3 carbon atoms,

(b) a napthyl group, optionally substituted by alkyl or alkenyl groups comprising from 1 to 10 carbon atoms, preferably from 1 to 3 carbon atoms,

where R8 is a phenyl group, and R9 forms, with the nitrogen atom of the amine function and the R8 ring, a C6 heterocycle, optionally substituted by alkyl groups.

Preferably, the secondary amines optionally present as compound (d) in the additive compositions according to the invention are chosen from the diphenylamines, preferably having their phenyl groups substituted in the ortho position by alkyl or alkenyl groups comprising from 1 to 10, preferably from 1 to 3 carbon atoms, the phenylaliphaticamine not substituted, the phenylaliphaticamines substituted by at the most 2 alkyl or alkenyl groups comprising from 1 to 10, preferably from 1 to 3 carbon atoms. According to a preferred embodiment, the additive compositions according to the invention comprise at least one secondary amine as compound (d).

Particularly preferably, in the additive compositions according to the invention, the percentages by mass [a], [b], [c] and [d] of compounds [a], [b], [c] and [d] are present in synergistically effective ratios, and/or comply with:

\[ \text{[c]} \cdot \text{[a]} \text{ is comprised between 10 and 100, preferably between 20 and 50,} \]

\[ \text{[c]} \cdot \text{[b]} \text{ is comprised between 1 and 10, preferably between 2 and 5.} \]

\[ \text{[c]} \cdot \text{[d]} \text{ is comprised between 1 and 10, preferably between 2 and 5.} \]
A subject of the present invention is also lubricant compositions containing such additive compositions. Thus, a subject of the present invention is lubricant compositions for engines, preferably for diesel engines, comprising an additive composition as described above, one or more base oils, and at least one friction modifier, which can be:

(i) at least one organometallic friction modifier, preferably chosen from the organomolybdenum or organotungstate compounds, preferably the molybdenum dithiocarbamates, and/or

(ii) at least one organic friction modifier chosen from the fatty amines, fatty alcohols, fatty acids, fatty acid esters, preferably the glycerol esters such as glycerol mono-, di- or triepoxynates, oleate, stearate, isostearate, linoleate, caprylate, the citrates, tartrates, malates, lactates, mandelates, glycolates, hydroxypropionates, hydroxyglutarates, and their derivatives.

Preferably, the lubricant compositions according to the invention comprise between 0.8% and 5% by mass, preferably between 1 and 1.5% by mass of friction modifiers. According to a preferred embodiment, the lubricant compositions according to the invention comprise at least 0.8% and 5% by mass, preferably between 1 and 1.5% by mass of organic friction modifiers. Preferably, the lubricant compositions according to the invention comprise between 0 and 0.5% by mass, preferably between 0.01% and 0.3% by mass of organometallic friction modifiers. According to particularly preferred embodiment, the lubricant compositions according to the invention, the quantity of additive composition as described above is such that compound (c) represents from 0.5 to 4%, preferably from 0.8 to 3.5% by mass, preferably from 1 to 3% by mass of said lubricant compositions.

The present invention also relates to the use of an additive composition as described above in order to reduce corrosiveness vis-à-vis copper, lead and tin, measured according to ASTM D6594, of an engine oil, preferably for diesel engines, comprising at least one friction modifier which can be:

(i) at least one organometallic friction modifier, preferably chosen from the organomolybdenum or organotungstate compounds, preferably the molybdenum dithiocarbamates, and/or

(ii) at least one organic friction modifier chosen from the fatty amines, fatty alcohols, fatty acids, fatty acid esters, preferably the glycerol esters such as glycerol mono-, di- or triepoxynates, oleate, stearate, isostearate, linoleate, caprylate, the citrates, tartrates, malates, lactates, mandelates, glycolates, hydroxypropionates, hydroxyglutarates, and their derivatives. Finally, the present invention relates to a use as described above, where the engine oil is an engine oil, preferably for diesel engines, comprising the friction modifier or modifiers described above.

DETAILED DESCRIPTION

Carbodiimides (c):

The additive compositions according to the invention comprise one or more carbodiimides of formula: \( X-N=C=N-Y \), where \( X \) and \( Y \) are, independently of each other, hydrocarbon radicals comprising from 8 to 60 carbon atoms, of formula (I):

where \( R_1 \) is an aliphatic or monoaromatic group, substituted or not, comprising from 2 to 20 carbon atoms, \( R_2 \) is either hydrogen, or an aliphatic or monoaromatic group, substituted or not, comprising from 2 to 20 carbon atoms, \( R_3 \) is either hydrogen, or an aliphatic or monoaromatic group, substituted or not, condensed or not, comprising from 2 to 20 carbon atoms.

Preferably, particularly, \( X \) and \( Y \) are substituted in the two ortho positions starting from the carbodiimide group, and optionally in the para position of said group. The substituents can be C2-C20 alkyl or cycloalkyl groups, such as the ethyl, propyl, isopropyl, butyl, tert-butyl, cyclohexyl, dodecyl groups, or aryl or aralkyl groups with 6 to 15 carbon atoms such as phenyl, tolyl, benzyl, naphthyl, etc. Preferably, these substituents are aliphatic substituents comprising at least 3 carbon atoms, branched or cyclic. The carbodiimides where \( X \) and \( Y \) each bear 2 or 3 substituents, in the ortho, or ortho and para positions with respect to the carbodiimide group, and where at least one of these substituents is a branched aliphatic chain having at least 3 carbon atoms or a cycloaliphatic substituent having from 5 to 6 carbon atoms are particularly preferred.

As particularly preferred compounds, \( NN'\text{-di}(2,6\text{-disopropylphenyl})\text{-carbodiimide} \) or \( NN'\text{-di}(2,4,6\text{-trisopropylphenyl})\text{-carbodiimide} \) may be mentioned. The carbodiimides used can also be carbodiimide dimers, oligomers or polymers, of formula:

\[ X=\overset{(-N=C=N)}{-N-Y}=N=C=N-Y, \]

where \( X \) and \( Y \) are as defined above, with the substituents defined above, and \( p \) is an integer comprised between 0 and 100, preferably between 0 and 50, preferably between 0 and 40.

The carbodiimides, their dimers, oligomers and polymers can be used alone or in a mixture.

Azole Compounds (a):

The additive compositions according to the invention comprise one or more compounds comprising an azole heterocycle, optionally comprising a sulphur atom (thiazoles). These are preferably diazoles or triazoles (1,2,4- or 1,2,3-triazoles), or thiazoles such as the benzothiazoles, mercaptobenzothiazoles, thiadiazoles, thiazadiazoles, etc.

The 1,2,4-triazoles can be for example the metal deactivators described in U.S. Pat. No. 4,734,209, column 1, and column 2 lines 1 to 35, of formula (II):
where \( R_4 \) and \( R_5 \) are, independently of each other, C1-C20 alkyl, C3-C20 alkenyl, C5-C12 cycloalkyl, C6-C10 aryl groups, or form both with the nitrogen atom to which they are attached a C5, C6, or C7 heterocycle, or \( R_4 \) and \( R_5 \) are groups of formula (II): \( R_3 X \{ \text{alkylene} \} O \{ \text{alkylene} \} \), with:

\[
X = \text{O, S, or N}
\]

Alkylene — C1-C12 alkylene radical, 

\( n \) is either 0 or an integer between 1 and 6, 

or \( R_4 \) is as described above and \( R_5 \) is a radical of formula (III)

\[
(\text{III})
\]

or \( R_5 \) is a radical of formula (III) and \( R_4 \) a radical of formula (IV):

\[
(\text{IV})
\]

with, \( m = 0 \) or 1 and if \( m = 0 \), \( A \) is a radical of formula (III) and, when \( m = 1 \), \( A \) is an alkylene or a C6-C10 arylene.

[0034] The preferred triazoles are for example the benzotriazoles of formula (V):

\[
(\text{V})
\]

where \( R_6 \) and \( R_7 \) are, independently of each other, linear, branched or cyclic hydrocarbon groups having from 1 to 30 carbon atoms, preferably from 2 to 20 carbon atoms, which can contain an oxygen, sulphur or nitrogen atom.

[0035] Amine or Phenolic Antioxidants (d):

[0036] The compounds (d) are phenols, or secondary amines, the amine and phenol function of which is sterically hindered, well known to a person skilled in the art for their antioxidant action in lubricants. The phenolic antioxidants of the compositions according to the invention are phenols substituted in at least one of their ortho positions, preferably both, by alkyl groups comprising from 1 to 10 carbon atoms, for example methyl, isopropyl or tert-butyl groups, preferably from 1 to 3 carbon atoms. They can also be used in the form of dimers.

[0037] The amine antioxidants of the compositions according to the invention are secondary amines the nitrogen atom of which is linked to at least one aryl group. Preferably, these are secondary amines of formula R8-\( \text{NH} \)-R9, where R8 and R9 are, independently of each other:

[0038] a phenyl group, optionally substituted, preferably in the para position of the amine function, by alkyl or alkenyl groups comprising from 1 to 10 carbon atoms, preferably from 1 to 3 carbon atoms,

[0039] a naphthyl group, optionally substituted by alkyl or alkenyl groups comprising from 1 to 10 carbon atoms, preferably from 1 to 3 carbon atoms.

or \( R_8 \) is a phenyl group, and \( R_9 \) forms, with the nitrogen atom of the amine function and the R8 ring, a C6 heterocycle, optionally substituted by alkyl groups.

[0040] Alkali and Alkaline-Earth Metal Sulphonates (b):

[0041] The metal sulphonates used in the additive compositions according to the present invention are well known to a person skilled in the art for their ferrous metal corrosion inhibiting action in lubricants. These are alkyl benzene or alkyl naphthalene sulphonates of alkali and alkaline-earth metals, the alkyl chain or chains of which comprise from 7 to 12 carbon atoms, preferably from 8 to 10 carbon atoms. The preferred sulphonates are dialkyl benzene or dialkyl naphthalenes the alkyl chains of which comprise from 7 to 12 carbon atoms, preferably from 8 to 10 carbon atoms. The preferred alkali and alkaline-earth metals are calcium, barium, magnesium, zinc, preferably calcium.

[0042] These sulphonates act on the surface of metal parts by creating a protective film by reaction with the metal surfaces. They are distinguished from the sulphonates used as detergents in oils, for example engine oils, or marine engine oils, which themselves act, within the oil, by means of their micellar structure and their reserve of basicity provided by overbasing, for example with metal carbonates.

[0043] The basicity provided is characterized by the BN or “Base Number”, measured according to the standard ASTM D2896, in mg KOH/gm of detergent. The detergents typically have a BN greater than 80 mg KOH/gm of detergent or also greater than 150, which can be up to 4000 mg KOH/gm of detergent or beyond. The sulphonates in themselves have only very low intrinsic basicity and have to be overbased when they are used as detergents.

[0044] When they are used as anticorrosion additives, by contrast, the sulphonates should not be overbased (they should be “neutral”), in order to be able to act on the surface and bind to the metal surfaces of the parts to be protected. When they are used as anticorrosion additives, the sulphonates have a basicity according to ASTM D2896 of virtually zero, less than 30, preferably less than 20, or even less than 15 mg of KOH/gm of sulphonates.

[0045] The sulphonates used as detergents typically have alkyl chains containing from 18 to 24 carbon atoms, longer than those of the sulphonates of the compositions according to the invention. These long chains make it possible to maintain the micelles of overbased detergents in suspension in the oil, which distinguishes them from the anticorrosion sulphonates according to the invention.

[0046] Preferably, compounds (a), (b), (c) and (d) are present in synergistically effective quantities in the additive compositions according to the invention. Preferably, in the additive compositions according to the invention, the ratios between the percentages by mass of compounds (a), (b), (c) and (d), denoted [a], [b], [c] and [d] respectively comply with the following three conditions:

[0047] [c]:[a] is comprised between 10 and 100, preferably between 20 and 50,

[0048] [c]:[b] is comprised between 1 and 10, preferably between 2 and 5,

[0049] [c]:[d] is comprised between 1 and 10, preferably between 2 and 5.

[0050] An advantage of the additive compositions according to the invention is a reduction in corrosiveness vis-à-vis copper, lead or tin of lubricant compositions containing a high percentage of organic and/or organometallic friction modifiers, for example between 0.8 and 5% by mass, or between 0.8
and 2% by mass, or also between 1 and 1.5% by mass. When the lubricant compositions contain only organic molybdenum friction modifiers, this can also represent between 400 and 2500 ppm of molybdenum, or between 450 and 1000 ppm, or also between 500 and 1500 ppm of molybdenum. Thus, the additive composition reduces the corrosiveness, vis-à-vis the abovementioned non-ferrous metals, of lubricant compositions themselves having a “fuel eco” or fuel economy effect. [0051] Another advantage of the additive compositions according to the invention is a reduction in corrosiveness vis-à-vis copper, lead or tin of lubricant compositions containing a high percentage of organic friction modifiers, for example comprising between 0.5% and 5% by mass, preferably between 0.8 and 5% by mass, or also between 0.7% and 4% by mass, or between 0.9 and 2% by mass, or between 1% and 1.5% by mass of organic friction modifiers. Thus, the additive compositions according to the invention reduce the corrosiveness, vis-à-vis the abovementioned non-ferrous metals, of lubricant compositions the “fuel eco” or fuel economy effect of which is obtained essentially or exclusively with organic friction modifiers, and therefore with a zero or reduced level (for example comprised between 0 and 0.5% by mass or between 0.01% and 0.3% by mass) of ash-generating organometallic friction modifiers.

[0052] Lubricant Compositions:

[0053] The lubricant compositions according to the invention are engine oils, preferably for diesel engines, comprising an additive composition comprising compounds (a), (b), (c), and (d) described above, organic and/or organometallic friction modifiers and all types of lubricant bases, viscosity index improver polymers, and other additives suited to their use. Preferably, the quantity of additive composition is such that compound (c) represents from 0.5 to 4%, preferably from 0.8 to 3.5% by mass, or also from 1 to 3% by mass of said lubricant compositions.

[0054] Friction Modifiers (FM):

[0055] The lubricant compositions according to the invention contain organometallic or organic friction modifiers known to a person skilled in the art and commonly used in the formulation of engine oils. The metal compounds are for example complexes of transition metals such as Mo, W, Fe, Cu, Zn, or also metals such as Sb, Sn, the ligands of which can be hydrocarbon compounds containing oxygen, nitrogen, sulphur or phosphorus atoms. In particular, the organic compounds containing tungsten or molybdenum can be particularly effective, such as for example the molybdenum dihydroxycarbamates or MoDTC and are preferred in the lubricant compositions according to the invention.

[0056] The organic friction modifiers are for example fatty alcohols, fatty acids, fatty amines, fatty esters. These compounds can optionally be mono- or polyethoxylated. Unsaturated fatty acid polyethoxylated ethers are thus used as organic friction modifiers. The boronated fatty ester derivatives can also be used as friction modifiers. The fatty esters can be polyol and fatty acid esters, for example glycerol mono-, di- or trihydroxyester, oleate, stearate, isostearate, linolate, caprate, preferably glycerol monooleate and monostearate.

[0057] Certain C2-C8 monoalcohols and polyacids esters, such as the citrates, tartrates, malates, lactates, mandelates, glycols, hydroxypropionates, hydroxyglutarates or their borated derivatives, are also used as organic friction modifiers. These organic friction modifiers can also be fatty amides, such as the oleamides, for example used in combination with glycerol esters. The fatty amines used as organic friction modifiers are often derived from natural vegetable oils, for example coconut, palm, olive, peanut, rapeseed, sunflower, soya, cotton or linseed oil, beef tallow etc.

[0058] The preferred organic friction modifiers, in the lubricant compositions according to the invention are the glycerol esters, fatty amines, citrates, as described above. These friction modifiers can be used alone or in a mixture. The lubricant compositions according to the invention can exclusively contain one or more organic FMs, which contribute to their “ashless” character, or exclusively one or more organometallic FMs, or a mixture of one or more organic FMs with one or more organometallic FMs. The friction modifier additives are generally present in engine lubricants at levels comprised between 0.01 and 5%, preferably 0.01 and 1.5%.

[0059] Lubricant Bases:

[0060] The lubricant compositions according to the present invention comprise one or more base oils. These bases generally represent at least 50% by weight of the lubricant compositions, generally more than 70% and may be up to 85% and more. The base oil or oils used in the compositions according to the present invention can be oils of mineral or synthetic origin from Groups I to VI according to the classes defined in the API (American Petroleum Institute) classification alone or in a mixture.

[0061] The mineral base oils according to the invention include all types of bases obtained by atmospheric and vacuum distillation of crude oil, followed by refining operations. The base oils in the compositions according to the present invention can also be synthetic oils, such as certain esters of carboxylic acids and alcohols, or polyalkylcholines. These oils can also be oils of natural, vegetable or animal origin. These different categories of oil can be used alone or in a mixture.

[0062] Viscosity Improver Polymers:

[0063] The viscosity improver polymers make it possible to guarantee good resistance to cold and a minimum high-temperature viscosity, in order to formulate in particular multi-grade oils. The introduction of these compounds into the lubricant compositions allows them to reach viscosity index (VI) values conferring upon them fuel eco or fuel economy properties. Among these compounds the polymeric esters, the Olefin Copolymers (OCP), styrene, butadiene or isoprene homopolymers or copolymers, and polyalkylcholines (PA) may for example be mentioned. They are in a standard fashion present at levels of the order of 0 to 40%, preferably 5 to 15% by weight, in the lubricant compositions for four-stroke engines.

[0064] Other Additives:

[0065] The additives can be added individually, or in the form of additive packages, guaranteeing a certain level of performance to the lubricant compositions, as required, for example for an ACEA (European Automobile Manufacturers' Association) or JASO (Japan Automobile Standards Organisation) diesel lubricant. These are for example and non-limitatively:

[0066] Dispersants, generally representing between 5 and 8% by weight of the lubricant compositions. Dispersants such as for example succinimides, PIB (polyisobutene) succinimides, Mannich bases, ensure that the insoluble solid contaminants constituted by the by-products of oxidation which are formed when the engine oil is in service, are maintained in suspension and removed.

[0067] Antioxidants, generally representing between 0.5 and 2% by weight of the lubricant compositions. The antioxid-
dants slow down the degradation of the oils in service, degradation which can lead to the formation of deposits, the presence of sludge, or an increase in the viscosity of the oil. They act as radical inhibitors or hydroperoxide destroyers. Among the commonly used antioxidants, sterically hindered amino and phenolic type antioxidants are found. Another class of antioxidants is that of oil-soluble copper compounds, for example copper thio- or dithio-phosphates, copper salts of carboxylic acids, copper dithiocarbamates, sulphonates, phenates, acetylacetones. Copper (I) and (II) salts of succinic acid or anhydride are used.

[0068] Anti-wear additives, generally representing between 1 and 2% by weight of the lubricant compositions. Anti-wear additives protect the friction surfaces by forming a protective film adsorbed on these surfaces. The most commonly used is zinc dithiophosphate or DTPZn. Various phosphorus-, sulphur-, nitrogen-, chlorine- and boron-containing compounds are also found in this category.

[0069] Detergents, generally representing between 2 and 4% by weight of the lubricant compositions. The detergents are typically alkali or alkaline-earth metal salts of carboxylic acids, sulphonates, salicylates, naphthenates, as well as phenate salts. They typically have a BN according to ASTM D 2896 greater than 40, or greater than 80 mg KOH/gram of detergent, and are most often overbased, with BN values typically of the order of 150 and more, or even 250 or 400 or more (expressed in mg of KOH per gram of detergent). And also antifoaming agents, pour point depressants, etc.

Example 1

[0070] A reference engine oil (ref. oil), of grade 0W30 according to the SAE J300 (Society of American Engineers) classification was prepared. It contains a mixture of mineral base oils of Group III according to the classification of the API and ATIEL (American Petroleum Institute, Technical Association of the European Lubricants Industry), a package of additives for diesel engine oil comprising dispersants, antiwear additives, detersants, antioxidants, antifoaming agents, providing the performance levels required by the ACEA (European Automobile Manufacturers' Association) or JASO (Japan Automobile Standards Organisation), and a VI improver polymer, alkyl methacrylate copolymer.

[0071] The elemental analysis of the reference oil is given in the following table, by way of illustration, in ppm, as well as other characteristics:

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>B</th>
<th>Zn</th>
<th>P</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>980</td>
<td>300</td>
<td>800</td>
<td>700</td>
<td>130</td>
</tr>
<tr>
<td>2</td>
<td>S</td>
<td>Cl</td>
<td>N</td>
<td>Sulphated ash</td>
<td>TBN, ASTM D2896</td>
</tr>
<tr>
<td>3</td>
<td>2300</td>
<td>30</td>
<td>1100</td>
<td>0.59% by mass</td>
<td>23 mg KOH/g</td>
</tr>
</tbody>
</table>

[0072] An organometallic friction modifier (molybdenum dithiocarbamate), with an organic friction modifier (fatty amine), and with a mixture of these two friction modifiers, were added to this reference engine oil A in order to formulate oils A, B, and C respectively. Amine antioxidants, metallic soaps, carbamides, benzo triazole, alone or in a mixture, were added to these oils A, B and C in order to formulate oils D to M. Oils F, L, and M comprise an additive composition according to the invention.

[0073] The corrosiveness of these different oils vis-à-vis non-ferrous metals was measured according to the HTCTB test carried out according to the standard ASTM D6594. 4 strips of Cu, Pb, Sn and phosphor-bronze are immersed in the oil at 135°C, with a current of air for a well-defined period of time. The contents of the elements copper, lead, tin dissolved in the oil after testing, are measured, in ppm, and similarly the appearance of the Cu strip is evaluated by its colour according to a colour scale. The higher the content of these elements, the more corrosive the oil vis-à-vis corresponding metals and the Cu strip is also rated from 1 (weakly corrosive) to 4 (strongly corrosive).

[0074] Table 1 shows the compositions and properties of these different oils.

[0075] Oil A containing an organometallic friction modifier (MoDTC), without the addition of additives according to the invention, becomes very corrosive vis-à-vis copper with respect to the reference containing no friction modifier (ref. oil). The addition of certain components of the additive composition according to the invention makes it possible to reduce corrosiveness vis-à-vis copper, but has an adverse effect on the corrosiveness vis-à-vis lead (oils D and E, to be compared with oil A). On the other hand, the addition of an additive composition according to the invention (comprising a diphenylamine, a calcium sulphonate, a carbamidamide and a triazole) makes it possible to reduce corrosiveness vis-à-vis copper and lead, while maintaining the absence of corrosiveness vis-à-vis tin (oil F).

[0076] Oil B, containing an organic friction modifier (fatty amine), without the addition of additives according to the invention, becomes very corrosive vis-à-vis copper and lead with respect to the reference containing no FM (ref. oil). The addition of diphenylamine to this oil B also increases corrosiveness vis-à-vis copper and lead (oil G). The addition of calcium sulphonate or of triazole to oil B makes it possible to reduce corrosiveness vis-à-vis copper but greatly increases corrosiveness vis-à-vis lead (oils H and J).

[0077] The addition of carbamidamide to oil B, makes it possible to reduce corrosive vis-à-vis copper, but corrosiveness vis-à-vis lead remains significant, although less than that of the reference B (oil L, to be compared with oil B). The addition of carbamidamide in combination with triazole makes it possible to improve the result (oil K), but corrosiveness vis-à-vis lead remains significant. The addition of an additive composition according to the invention (comprising a diphenylamine, a calcium sulphonate, a carbamidamide and a triazole) makes it possible to obtain excellent results, and brings the corrosiveness of the oil containing an organic FM to the level of that of the reference oil without FM (Oil L, to be compared with the ref. oil).

[0078] Oil C, containing an organic friction modifier (fatty amine) and an organometallic friction modifier (MoDTC), without the addition of additives according to the invention, becomes very corrosive vis-à-vis copper, and its corrosiveness vis-à-vis lead also increases with respect to the reference containing no FM (ref. oil). The addition of an additive composition according to the invention (comprising a diphenylamine, a calcium sulphonate, a carbamidamide and a triazole) makes it possible to obtain excellent results, and brings the corrosiveness of the oil containing an organometallic FM and an organic FM to the level of, or even below that of the reference oil without FM (Oil M, to be compared with the ref. oil).
Example 2

Another engine oil, also of grade 0W30 according to the SAE J300 (Society of American Engineers) classification, was prepared. It contains a mixture of mineral base oils of Groups III and IV according to the API and ATIEL (American Petroleum Institute, Association Technical Association of the European Lubricants Industry) classification, an additive package for diesel engine oil comprising dispersants, antiwear additive, detergents, antioxidants, antifoaming agents, providing the performance levels required by the ACEA (European Automobile Manufacturers’ Association) or the JASO (Japan Automobile Standards Organisation), and a VI improver polymer, copolymer of alkyl methacrylates L77418A.

An organic friction modifier (fatty amine), amino antioxidants, metallic soaps, carbodiimides, benzotriazole, alone or in a mixture, were added to this oil in order to formulate oils N to R. Oil R comprises an additive composition according to the invention. The corrosiveness of these different oils vis-à-vis non-ferrous metals was measured according to the HTCTB test carried out according to the standard ASTM D6594. Table 2 shows the compositions and properties of these different oils. Oils N to R have an equivalent corrosiveness vis-à-vis copper and tin. On the other hand, the corrosiveness vis-à-vis lead of oil R comprising a composition according to the invention is substantially less than that of oils N, O, P, and Q.

Table 2

<table>
<thead>
<tr>
<th>Composition % by mass</th>
<th>N</th>
<th>O</th>
<th>P</th>
<th>Q</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group III mineral base</td>
<td>43.00</td>
<td>41.65</td>
<td>41.65</td>
<td>41.95</td>
<td>41.35</td>
</tr>
<tr>
<td>Group IV base</td>
<td>30.50</td>
<td>29.80</td>
<td>29.80</td>
<td>30.00</td>
<td>29.60</td>
</tr>
<tr>
<td>VI improver polymer</td>
<td>13.50</td>
<td>13.50</td>
<td>13.50</td>
<td>13.50</td>
<td>13.50</td>
</tr>
<tr>
<td>Package</td>
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<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
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<tr>
<td>Fatty amine</td>
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<td>1.00</td>
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<tr>
<td>Diphenylamine</td>
<td>x</td>
<td>0.50</td>
<td>x</td>
<td>x</td>
<td>0.5</td>
</tr>
<tr>
<td>Neutral Cs dialkylbenzene sulphonate</td>
<td>x</td>
<td>x</td>
<td>0.5</td>
<td>x</td>
<td>0.5</td>
</tr>
<tr>
<td>Carbodiimide</td>
<td>x</td>
<td>1.50</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Benzotriazole</td>
<td>x</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
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<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

HTCTB ASTM D6594

| Cu ppm | 18 | 17 | 18 | 20 | 22 |
| Pb ppm  | 319 | 94 | 110 | 107 | 76 |
| Sn ppm  | 0 | 0 | 0 | 0 | 0 |
| Cu Strip Rating | 1b | 1b | 1b | 1b | 1b |

1. An additive composition comprising:
(a) at least one compound comprising an azole heterocycle selected from the group consisting of diazoles, triazoles, diazoles wherein the azole heterocycle of which comprises a sulphur atom and triazoles wherein the azole heterocycle of which comprises a sulphur atom;
(b) at least one non-overbased alkylbenzene or alkynaphthylene sulphonate of an alkali or alkaline-earth metal, the alkyl substituent or substituents of which comprise from 7 to 12 carbon atoms;

Table 1

<table>
<thead>
<tr>
<th>Ref. Oil A</th>
<th>Oil B</th>
<th>Oil C</th>
<th>Oil D</th>
<th>Oil E</th>
<th>Oil F</th>
<th>Oil G</th>
<th>Oil H</th>
<th>Oil I</th>
<th>Oil J</th>
<th>Oil K</th>
<th>Oil L</th>
<th>Oil M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition % by mass</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Group III mineral base</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Package</td>
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<td>12.4</td>
<td>12.4</td>
<td>12.4</td>
<td>12.4</td>
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<td>12.4</td>
</tr>
<tr>
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<td>6.7</td>
<td>6.7</td>
<td>6.7</td>
<td>6.7</td>
<td>6.7</td>
<td>6.7</td>
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<td>6.7</td>
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</tr>
<tr>
<td>MoDTC</td>
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<td>—</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.3</td>
</tr>
<tr>
<td>Fatty amine</td>
<td>—</td>
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<td>1</td>
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<td>—</td>
<td>0.3</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Diphenylamine</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.5</td>
<td>1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.5</td>
</tr>
<tr>
<td>Neutral Cs dialkylbenzene sulphonate</td>
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<td>—</td>
<td>—</td>
<td>0.03</td>
<td>0.09</td>
<td>0.5</td>
<td>—</td>
<td>1</td>
<td>—</td>
<td>—</td>
<td>0.5</td>
</tr>
<tr>
<td>Carbodiimide</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.5</td>
<td>—</td>
<td>—</td>
<td>1</td>
<td>—</td>
<td>1.5</td>
</tr>
<tr>
<td>Benzotriazole</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.08</td>
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<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

ASTM D445

| Cu ppm | 4 | 220 | 89 | 73 | 18 | 16 | 41 | 114 | 30 | 10 | 50 | 12 | 11 |
| Pb ppm | 105 | 50 | 490 | 124 | 120 | 113 | 34 | 1540 | 664 | 360 | 1418 | 152 | 102 |
| Sn ppm | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Cu Strip Rating | 1b | 4b | 2c | 4b | 1b | 2c | 2c | 4b | 1b | 1b | 2c | 1b | 1b |
(c) at least one carbodiimide of formula \( \text{X--N=C=N--Y} \), where \( \text{X} \) and \( \text{Y} \) are, independently of each other, hydrocarbon radicals comprising from 8 to 60 carbon atoms, of formula (I):

\[
\text{(I)}
\]

where \( \text{R}_1 \) is selected from the group consisting of an aliphatic group, a monoaromatic group, an aliphatic group substituted, a monoaromatic group substituted comprising from 2 to 20 carbon atoms;

\( \text{R}_2 \) is selected from the group consisting of either hydrogen, an aliphatic group, a monoaromatic group, an aliphatic group substituted, a monoaromatic group, comprising from 2 to 20 carbon atoms;

\( \text{R}_3 \) is selected from the group consisting of either hydrogen, an aliphatic group, a monoaromatic group, an aliphatic group substituted, a monoaromatic group substituted, a monoaromatic group, condensed, comprising from 2 to 20 carbon atoms; and

(d) at least one antioxidant chosen from the secondary amine the nitrogen atom of which is linked to at least one aryl group, or from the phenols substituted on at least one of their ortho positions, by alkyl groups comprising from 1 to 10 carbon atoms and their dimers.

2. The additive composition according to claim 1 comprising, as compound (c), at least one carbodiimide where \( \text{X} \) and \( \text{Y} \) each have 2 or 3 substituents, in the ortho, or ortho and para positions with respect to the carbodiimide group, and where at least one of these substituents is a branched aliphatic chain having at least 3 carbon atoms or a cycloaliphatic substituent having from 5 to 6 carbon atoms.

3. The additive composition according to claim 1 comprising, as compound (a), at least one benzotriazole of formula (V):

\[
\text{(V)}
\]

where \( \text{R}_6 \) and \( \text{R}_7 \) are, independently of each other, linear, branched or cyclic hydrocarbon groups having from 1 to 30 carbon atoms, which can contain an oxygen, sulphur or nitrogen atom.

4. The additive composition according to claim 1 comprising, as compound (b), at least one neutral dialkylenzene or dialkynaphthalene sulphonate of an alkali or alkaline-earth metal, the alkyl substituents of which comprise from 7 to 12 carbon atoms.

5. The additive composition according to claim 1 wherein compound (b) has a BN, measured according to the standard ASTM D2892, less than 20 mg of KOH/gram.

6. The additive composition according to claim 1 wherein the secondary amines present as compound (d) are chosen from the secondary amines of formula \( \text{R}_8\text{-NH--R}_9 \), where \( \text{R}_8 \) and \( \text{R}_9 \) are, independently of each other:

- a phenyl group, a phenyl group substituted by alkyl or alkenyl groups comprising from 1 to 10 carbon atoms;
- a naphthyl group, a naphthyl group substituted by alkyl or alkenyl groups comprising from 1 to 10 carbon atoms or \( \text{R}_8 \) is a phenyl group, and \( \text{R}_9 \) forms, with the nitrogen atom of the amine function and the \( \text{R}_8 \) ring, a \( \text{C}_6 \) heterocycle or a \( \text{C}_5 \) heterocycle substituted by alkyl groups.

7. The additive composition according to claim 6 wherein the secondary amines present as compound (d) are chosen from the group consisting of diphenylenamines, diphenylenamines having their phenyl groups substituted in the ortho position by alkyl or alkenyl groups comprising from 1 to 10 carbon atoms, non substituted phenyl-naphthylamine, phenyl-naphthylamines substituted by at the most 2 alkyl or alkenyl groups comprising from 1 to 10.

8. The additive composition according to claim 1 comprising at least one secondary amine as compound (d).

9. The additive composition according to claim 1 wherein the percentages by mass [a], [b], [c] and [d] of compounds (a), (b), (c) and (d) are present in a synergistically effective ratio, and/or comply with:

\[
\begin{align*}
&\text{[c]:[d]} \text{ comprised between 10 and 100}, \\
&\text{[c]:[b]} \text{ is comprised between 1 and 10}; \text{ and} \\
&\text{[c]:[a]} \text{ is comprised between 1 and 10}.
\end{align*}
\]

10. A lubricant composition for engines comprising an additive composition further comprising:

- at least one compound comprising an azole heterocycle selected from the group consisting of diazoles, triazoles, diazoles wherein the azole heterocycle of which comprises a sulphur atom and triazoles wherein the azole heterocycle of which comprises a sulphur atom;
- at least one non overbased alkylbenzene or alkyl-naphthalene sulphonate of an alkali or alkaline-earth metal, the alkyl substituent or substituents of which comprise from 7 to 12 carbon atoms;
- at least one carbodiimide of formula \( \text{X--N=C=N--Y} \), where \( \text{X} \) and \( \text{Y} \) are, independently of each other, hydrocarbon radicals comprising from 8 to 60 carbon atoms, of formula (I):
substituted, a monoaromatic group substituted, a monoaromatic group, condensed, comprising from 2 to 20 carbon atoms;
(d) at least one antioxidant chosen from the secondary amines the nitrogen atom of which is linked to at least one aryl group, or from the phenols substituted on at least one of their ortho positions, by alkyl groups comprising from 1 to 10 carbon atoms and their dimers;
one or more base oils, and at least one friction modifier, comprising:
(i) at least one organometallic friction modifier chosen from the group consisting of the organonobdenum or organonotungstate compounds,
and/or
(ii) at least one organic friction modifier chosen from the group consisting of fatty amines, fatty alcohols, fatty acids, fatty acid esters glycerol esters and their derivatives.
11. The lubricant composition according to claim 10 comprising between 0.8% and 5% by mass of friction modifiers.
12. The lubricant composition according to claim 10 comprising between 1 and 1.5% by mass of organic friction modifiers.
13. The lubricant composition according to claim 10 comprising between 0 and 0.5% by mass of organometallic friction modifier.
14. The lubricant composition according to claim 10, where the quantity of additive composition is such that compound (c) represents from 0.5 to 4% by mass of said lubricant composition.
15. A method of reducing the corrosiveness vis-à-vis copper, lead and tin, measured according to ASTM D6594, of an engine oil, comprising adding an additive composition to an engine oil, the engine oil at least one friction modifier comprising:
(i) at least one organometallic friction modifier chosen from the organonobdenum or organonotungstate compounds,
and/or
(ii) at least one organic friction modifier chosen from the group consisting of fatty amines, fatty alcohols, fatty acids, fatty acid esters glycerol esters and their derivatives;
the additive composition comprising:
(a) at least one compound comprising an azole heterocycle selected from the group consisting of diazoles, triazoles, diazoles wherein the azole heterocycle of which comprises a sulphur atom and triazoles wherein the azole heterocycle of which comprises a sulphur atom;
(b) at least one non overbased alkylbenzene or alkynaphthalene sulphonate of an alkali or alkaline-earth metal, the alkyl substituent or substituents of which comprise from 7 to 12 carbon atoms;
(e) at least one carbodiimide of formula X—N—C=N—Y, where X and Y are, independently of each other, hydrocarbon radicals comprising from 8 to 60 carbon atoms, of formula (I):

\[ R_y-R_s \ \/
\]

where R1 is selected from the group consisting of an aliphatic group a monoaromatic group, an aliphatic group substituted comprising from 2 to 20 carbon atoms;
R2 is selected from the group consisting of either hydrogen, an aliphatic group, a monoaromatic group, an aliphatic group substituted, a monoaromatic group, comprising from 2 to 20 carbon atoms;
R3 is selected from the group consisting of either hydrogen, an aliphatic group, a monoaromatic group, an aliphatic group substituted, a monoaromatic group substituted, a monoaromatic group, condensed, comprising from 2 to 20 carbon atoms;
(d) at least one antioxidant chosen from the secondary amines the nitrogen atom of which is linked to at least one aryl group, or from the phenols substituted on at least one of their ortho positions, by alkyl groups comprising from 1 to 10 carbon atoms and their dimers.
16. (canceled)
17. The additive composition according to claim 6 wherein the secondary amines present as compound (d) are chosen from the secondary amines of formula R8-NH—R9, where R8 and R9 are, independently of each other:
a phenyl group substituted in the para position of the amine function by alkyl or alkenyl groups comprising from 1 to 10 carbon atoms,
a naphthyl group substituted by alkyl or alkenyl groups comprising from 1 to 10 carbon atoms.
18. The additive composition according to claim 1 wherein in the formula (V) R6 and R7 are, independently of each other, linear, branched or cyclic hydrocarbon groups having from 2 to 20 carbon atoms, which can contain an oxygen, sulphur or nitrogen atom.
19. The lubricant composition for engines according to claim 10, wherein the glycerol esters are selected from the group consisting of glycerol mono-, di- or triheptanoate, oleate, stearate, isostearate, linoleate, caprylate, the citrates, tartrates, malates, lactates, mandelates, glycolates, hydroxypropionates, hydroxybutyrates, and their derivatives.
20. The lubricant composition for engine according to claim 10, comprising between 1 and 1.5% by mass of organic friction modifiers and between 0 and 0.5% by mass of organometallic friction modifier.
21. The method according to claim 15, wherein the glycerol esters are selected from the group consisting of as glycerol mono-, di- or trihexanoate, oleate, stearate, isostearate, linoleate, caprylate, the citrates, tartrates, malates, lactates, mandelates, glycolates, hydroxypropionates, hydroxybutyrates, and their derivates.