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(54) Lubricating oil compositions for marine diesel engines

(57) A residual fuel oil-fuelled diesel engine lubricating oil composition for marine and stationary applications comprising, or made by admixing:

(a) a basestock of lubricating viscosity, in a major amount; and
(b) an oil-soluble or oil-dispersible molybdenum compound, in a minor amount;

wherein the oil composition has a TBN from 20 to 100 as measured according to ASTM D-2896 and a viscosity at 100°C in the range from 9 to 30 mm^2s^{-1} as measured according to ASTM D-445. The lubricating oil compositions of the present invention demonstrate improved cylinder liner wear performance.

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Description

[0001] The present invention concerns improved residual fuel oil-fuelled diesel engine lubricating oil compositions. In particular, the lubricating oil compositions of the present invention demonstrate improved cylinder liner wear performance.

[0002] In large diesel engines of the cross-head type used in marine and heavy stationary applications, the cylinders are lubricated separately from the other engine components. The cylinders are lubricated on a total loss basis with the cylinder oil being injected separately to quills on each cylinder by means of lubricators positioned around the cylinder liner. Oil is distributed to the lubricators by means of pumps, which are, in modern engine designs, actuated to apply the oil directly onto the rings to reduce wastage of the oil. The high stresses encountered in these engines and the use of residual fuels creates the need for lubricants with a high detergency and neutralising capability even though the oils are exposed to thermal and other stresses only for short periods of time. Residual fuels commonly used in these diesel engines typically contain significant quantities of sulfur, which, in the combustion process, combine with water to form sulfuric acid, the presence of which leads to corrosive wear. In particular, in two-stroke engines for ships, areas of the cylinder liners and piston rings can be corroded and worn by the acid. Therefore, it is extremely important for diesel engine lubricating oil to have the ability to resist such corrosion and wear.

[0003] The art describes addition of dispersant and metallic detergent additives, in combination with other co-additives, to lubricating oils to neutralise the sulfuric acid formed and thus protect the cylinder liners and piston rings from corrosion and wear.

[0004] For example, US-A-4842755 describes the incorporation of certain borated dispersants and zinc dialkyldithiophosphates into a marine cylinder lubricating oil composition to provide anti-wear performance in the cylinder liner and piston ring areas.

[0005] US-A-4948522 describes marine diesel cylinder lubricants comprising a borated dispersant and a polybutene and optionally a zinc dialkyldithiophosphate and/or an overbased metal detergent, which lubricants have improved ring wear and linear wear performance and good protection against corrosion.

[0006] US-A-6140280 describes certain succinimide compounds that exhibit corrosion resistance and wear resistance in diesel engines. It also describes that conventional anti-wear agents, such as zinc dithiophosphates and molybdenum dithiocarbamates, may be used as co-additives.

[0007] WO 99/64543 describes cylinder oils of defined characteristics and a liquid polyisobutylene, which provide improved performance including protection against corrosive, friction and abrasive wear.

[0008] A problem in the art is to provide effective or improved cylinder liner protection, particularly in the area of the cylinder prone to corrosive wear. It has now been suprisingly found, as evidenced by the data in this specification, that oil-soluble or oil-dispersible molybdenum compounds meet or alleviate the problem. Molybdenum compounds are known in lubricating oil compositions for automobile engines, but their use in a lubricating oil composition having the base number and viscosity suitable for large residual fuel oil-fuelled diesel engines, such as of the cross-head type used in marine and heavy stationary applications, has neither been disclosed nor suggested.

[0009] Accordingly, in a first aspect, the present invention provides a residual fuel oil-fuelled diesel engine lubricating oil composition for marine and stationary applications comprising.

(a) an oil of lubricating viscosity, in a major amount; and
(b) an oil-soluble or oil-dispersible molybdenum compound, in a minor amount;

wherein the oil composition has a TBN from 20 to 100 as measured according to ASTM D-2896 and a viscosity at 100°C in the range from 9 to 30 $mm^2\ s^{-1}$ as measured according to ASTM D-445.

[0010] In a second aspect, the present invention provides a combination of a cylinder of a two-stroke cross-head marine diesel engine and a lubricating oil composition of the first aspect, wherein the cylinder is characterised by a power output of 4000 or greater, such as 4200 or greater, preferably 4500 or greater, more preferably in the range of 4500 to 6000, kW.

[0011] In a third aspect, the present invention provides the use of an oil-soluble or oil-dispersible molybdenum compound or a composition, such as an oleaginous composition, for example, an additive composition, comprising the molybdenum compound to reduce corrosive wear in a cylinder liner of a residual fuel oil-fuelled diesel engine, preferably a cross-head marine engine.

[0012] In a fourth aspect, the present invention provides a method of reducing corrosive wear in a cylinder liner of a residual fuel oil-fuelled diesel engine, preferably a cross-head marine, comprising supplying to the walls of the cylinder a lubricating oil composition of the first aspect.

[0013] In a fifth aspect, the present invention provides an additive composition comprising:

(a) an oil-soluble or oil-dispersible molybdenum compound; and

(b) one or more co-additives;

wherein the additive composition contains (a) and (b) in an amount to provide a lubricating oil composition having a TBN from 20 to 100 as measured according to ASTM D-2896 and a viscosity at 100°C in the range from 9 to 30 $mm^2 s^{-1}$ as measured according to ASTM D-445, when the lubricating oil composition contains 5 to 40 mass % of the additive composition.

[0014] In this specification, the following words and expressions shall have the meanings ascribed below:

"major amount" means in excess of 50 mass % of the composition;

"minor amount" means less that 50 mass % of the composition, both in respect of the stated additive and in respect of the total mass % of all the additives present in the lubricant, reckoned as active ingredient of the additive or additives;

"active ingredient (a.i.)" refers to additive material that is not diluent or solvent.

"comprises or comprising" or cognate words specifies the presence of stated features, steps, integers or components, but does not preclude the presence or addition of one or more other features, steps, integers, components, or groups thereof;

"TBN" - Total Base Number as measured by ASTM D2896;

"oil-soluble or oil-dispersible" - does not necessarily indicate solubility, dissolvability, miscibility or capability of suppression in oil in all proportions. They do mean, however, solubility or stable dispersibility sufficient to exert the intended effect in the environment in which the oil is employed. Moreover, additional incorporation of other additives may permit incorporation of higher levels of a particular additive, if desired.

[0015] It will be understood that the various components of the lubricating oil composition, essential as well as optimal and customary, may react under the conditions of formulation, storage or use and that the invention also provides the product obtainable or obtained as a result of any such reaction.

[0016] The features of the invention will now be discussed in more detail below.

Diesel Engines

[0017] Diesel fuel oils can in general be divided into two main categories - distillates and heavy or residual fuels. Distillates consist of one or more distillate fractions. Heavy or residual fuels are fuels which comprise at least a proportion of a residual oil, i.e. oil that remains after the distilled fractions have been removed from unrefined oil. The composition of the residual fuel will vary with the composition of the starting oil, usually a crude oil, and will also vary depending upon the distillation conditions. However, by its nature, residual fuel oil is of high molecular weight, contains significant quantities of sulfur and has a high boiling point. The term "residual oil" is understood by those skilled in the art; it is defined according to the standards ISO 8217, ISO RME25 and ISO RME35.

[0018] The present invention is suitable for large residual fuel oil-fuelled diesel engines, such as diesel engines of the cross-head type used in marine and heavy stationary applications, and of the trunk piston type found in marine applications. Large diesel engines are mainly employed for marine propulsion and power generation. Diesel engines suitable in the present invention can also be fuelled by a mixture of distillate and residual fuels.

[0019] Cross-head engines tend to be two-stroke, whereas trunk piston engines tend to be four-stroke. Four-stroke trunk piston engines may have a speed of 100 to 2,000, preferably 300 to 1,800, more preferably 350 to 1500, rpm, and the cylinder is characterised by power output of 50 to 10000, preferably 100 to 6000, more preferably 150 to 5000, kW. Two-stroke cross-head engines may have a speed of 40 to 600, preferably 60 to 500, such as 80 to 300, rpm and the cylinder is characterised by a power output of 4000 or greater, such as 4200 or greater, preferably 4500 or greater, more preferably in the range of 4500 to 6000, kW. Further, the engines may, for example, have from 6 to 12 cylinders and their total output may, for example, be in the range of 18,000 to 70,000 kW. The bore of the cylinder may, for example, be 850 or greater, such as 900 or greater, preferably in the range of 900 to 1000, cm.

[0020] The lubricating oil compositions of the present invention are particularly useful in cross-head engines, such as two-stroke cross-head engines for marine propulsion and stationary power generation.

Lubricating Oil Composition

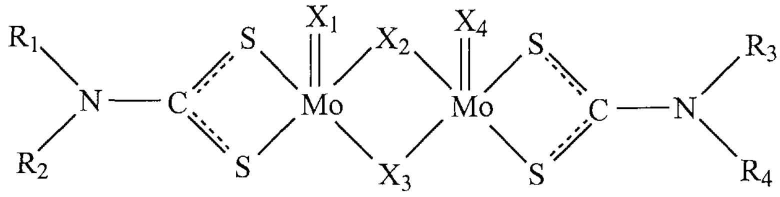
[0021] In respect of each aspect of the present invention, the total base number (TBN) of the lubricating oil composition, independent of the viscosity at 100 °C, is preferably 30 to 95, more preferably 40 to 90, especially 65 to 90.
[0022] In respect of each aspect of the present invention, the viscosity at 100 °C of the lubricating oil composition, independent of the TBN, is preferably 9 to 25, more preferably 12 to 25, especially 16 to 25, such as 18 to 22, $mm^2 s^{-1}$.
[0023] In respect of each aspect of the present invention, the viscosity index, as defined by ASTM D2270, of the lubricating oil composition is preferably at least 90, more preferably at least 95, especially at least 100, for example in the range from 90 to 110.
[0024] Lubricating oil compositions used in large residual-fuelled diesel engines can become contaminated with residual fuel during use, particularly in four-stroke trunk piston engines. Therefore, the lubricating oil compositions of the invention can also contain a residual fuel oil.
[0025] The lubricating oil compositions of the present invention will typically be monograde, i.e. compositions which exhibit little or no viscosity index improvement properties, for example, an SAE30, SAE 40, SAE 50 or higher lubricant. Thus, lubricating oil compositions of the present invention preferably do not comprise a viscosity index modifier.

Oil of Lubricating Viscosity

[0026] The oil of lubricating viscosity (sometimes referred to as lubricating oil) may be any oil suitable for the lubrication of a large diesel engine, such as a cross-head engine or a trunk piston engine. The lubricating oil may suitably be an animal, a vegetable or a mineral oil. Suitably the lubricating oil is a petroleum-derived lubricating oil, such as a naphthenic base, paraffinic base or mixed base oil. Alternatively, the lubricating oil may be a synthetic lubricating oil. Suitable synthetic lubricating oils include synthetic ester lubricating oils, which oils include diesters such as di-octyl adipate, di-octyl sebacate and tri-decyl adipate, or polymeric hydrocarbon lubricating oils, for example liquid polyisobutene and poly-alpha olefins. Commonly, a mineral oil is employed.
[0027] Another class of lubricating oils is hydrocracked oils, where the refining process further breaks down the middle and heavy distillate fractions in the presence of hydrogen at high temperatures and moderate pressures. Hydrocracked oils typically have kinematic viscosity at 100 °C of from 2 to 40, for example from 3 to 15, mm^2s^{-1} and a viscosity index typically in the range of from 100 to 110, for example from 105 to 108.
[0028] The term 'brightstock' as used herein refers to base oils which are solvent-extracted, de-asphalted products from vacuum residuum, which generally have a kinematic viscosity at 100 °C of from 28 to 36 mn^2s^{-1} and are typically used in a proportion of less than 30, preferably less than 20, more preferably less than 15, most preferably less than 10, such as less than 5, mass %, based on the mass of the lubricating oil composition.

Molybdenum Compound

[0029] Molybdenum compounds suitable in the present invention include any oil-soluble or oil-dispersible molybdenum compounds, such as organic molybdenum compounds.
[0030] Examples of organic molybdenum compounds include molybdenum xanthates, thioxanthates, alkoxides, carboxylates, dialkyldithiocarbamates, dialkyldithiophosphinates and dialkyldithiophosphates.
[0031] The molybdenum compound may, for example, be mononuclear, dinuclear, trinuclear or tetranuclear.
[0032] Dinuclear molybdenum compounds can be represented by the formula $MoO_xS_{4-x}L_2$, where L is a ligand such as dialkyldithiocarbamate and dialkyldithiophosphate, and x is an integer from 0 to 4. An example of dinuclear (or dimeric) molybdenum dialkyldithiocarbamate is expressed by the following formula:



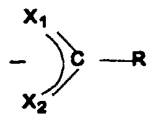
where R_1 to R_4 independently denote a straight chain, branched chain or aromatic hydrocarbyl group having 1 to 24 carbon atoms; and X_1 to X_4 independently denote an oxygen atom or a sulfur atom. The four hydrocarbyl groups, R_1

to R_4, may be identical or different from one another.

[0033] Another group of organo-molybdenum compounds useful in the lubricating compositions of this invention are trinuclear (or trimeric) molybdenum compounds, especially those of the formula $Mo_3S_kL_nQ_z$ and mixtures thereof wherein the L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble in the oil, n is from 1 to 4, k varies from 4 to 7, Q is selected from the group of neutral electron donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. At least 21 total carbon atoms should be present among all the ligands' organo groups, such as at least 25, at least 30, or at least 35 carbon atoms.

[0034] The ligands may be selected from the group consisting of

-X-R 1,



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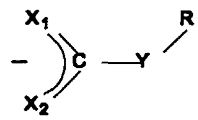

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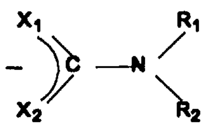

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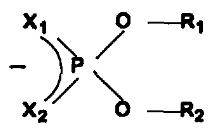


5,

and mixtures thereof, wherein X, X_1, X_2, and Y are selected from the group consisting of oxygen and sulfur, and wherein R_1, R_2, and R are selected from hydrogen and organo groups that may be the same or different. Preferably, the organo groups are hydrocarbyl groups such as alkyl (e.g., in which the carbon atom attached to the remainder of the ligand is primary or secondary), aryl, substituted aryl and ether groups. More preferably, each ligand has the same hydrocarbyl group.

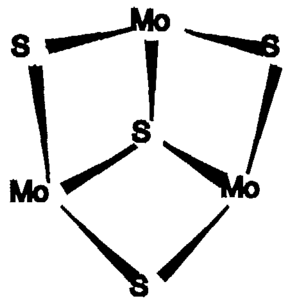
[0035] The term "hydrocarbyl" as used herein denotes a substituent having carbon atoms directly attached to the remainder of the ligand and is predominantly hydrocarbyl in character. Such substituents include the following:

1. Hydrocarbon substituents, that is, aliphatic (for example alkyl or alkenyl), alicyclic (for example cycloalkyl or cycloalkenyl) substituents, aromatic-, aliphatic- and alicyclic-substituted aromatic nuclei, as well as cyclic substituents wherein the ring is completed through another portion of the ligand (that is, any two indicated substituents may together form an alicyclic group).

2. Substituted hydrocarbon substituents, that is, those containing non-hydrocarbon groups which do not alter the predominantly hydrocarbyl character of the substituent. Those skilled in the art will be aware of suitable groups (e.g., halo, especially chloro and fluoro, amino, alkoxyl, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.).

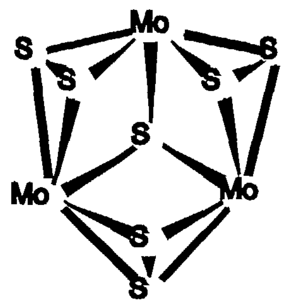
[0036] Importantly, the organo groups of the ligands have a sufficient number of carbon atoms to render the compound soluble in the oil. For example, the number of carbon atoms in each group will generally range between 1 to 100, preferably from 1 to 30, and more preferably between 4 to 20. Preferred ligands include dialkyldithiophosphate, alkylxanthate, carboxylates, dialkyldithiocarbamate ("dtc"), and mixtures thereof. Most preferred are the dialkyldithiocarbamates. Those skilled in the art will realize that formation of the compounds of the present invention requires selection of ligands having the appropriate charge to balance the core's charge (as discussed below).

[0037] Compounds having the formula $Mo_3S_kL_nQ_z$ have cationic cores surrounded by anionic ligands, wherein the cationic cores are represented by structures such as



1,

and



2,

which have net charges of +4. Consequently, in order to solubilize these cores the total charge among all the ligands must be -4. Four monoanionic ligands are preferred. Without wishing to be bound by any theory, it is believed that two or more trinuclear cores may be bound or interconnected by means of one or more ligands and the ligands may be multidentate, i.e., having multiple connections to one or more cores. It is believed that oxygen and/or selenium may be substituted for sulfur in the core(s).

[0038] Oil-soluble trinuclear molybdenum compounds can be prepared by reacting in the appropriate liquid(s)/solvent (s) a molybdenum source such as $(NH_4)_2Mo_3S_{13}\cdot n(H_2O)$, where n varies between 0 and 2 and includes non-stoichiometric values, with a suitable ligand source such as a tetralkylthiuram disulfide. Other oil-soluble trinuclear molybdenum compounds can be formed during a reaction in the appropriate solvent(s) of a molybdenum source such as $(NH_4)_2Mo_3S_{13}\cdot n(H_2O)$, a ligand source such as tetralkylthiuram disulfide, dialkyldithiocarbamate, or dialkyldithiophosphate, and a sulfur-abstracting agent such as cyanide ions, sulfite ions, or substituted phosphines. Alternatively, a trinuclear molybdenum-sulfur halide salt such as $[M']_2[Mo_3S_7A_6]$, where M' is a counter ion, and A is a halogen such as Cl, Br, or I, may be reacted with a ligand source such as a dialkyldithiocarbamate or dialkyldithiophosphate in the appropriate liquid(s)/solvent(s) to form an oil-soluble trinuclear molybdenum compound. The appropriate liquid/solvent may be, for example, aqueous or organic.

[0039] The ligand chosen must have a sufficient number of carbon atoms to render the compound soluble in the lubricating composition.

[0040] Trinuclear molybdenum compounds for use in the compositions of this invention can be those of the formula $Mo_3S_7((alkyl)_2dtc)_4$ where the alkyl has about 8 to 18 carbon atoms and the alkyl being preferably a "coco" alkyl chain which is a mixture of chains of varying even numbers of carbon atoms from typically a C_8 to C_{18} alkyl, mainly C_{10}, C_{12} and C_{14} alkyls derived from coconut oil.

[0041] Other examples of molybdenum compounds include a sulfurized molybdenum containing composition prepared by (i) reacting an acidic molybdenum compound and a basic nitrogen compound selected from the group consisting of succinimide, a carboxylic acid amide, a hydrocarbyl monoamine, a phosphoramide, a thiophosphoramide, a Mannich base, a dispersant viscosity index improver, or a mixture thereof, in the presence of a polar promoter, to form a molybdenum complex, and (ii) reacting the molybdenum complex with a sulfur-containing compound, to thereby form a sulfur- and molybdenum-containing composition.

[0042] In one embodiment of the present invention, the molybdenum compound is preferably dinuclear or trincuclear, more preferably trinuclear.

[0043] In another embodiment of the present invention, the molybdenum compound, irrespective of its nuclearity, is preferably fully sulfurised, i.e. the core contains only sulfur, for example Mo_2S_4, Mo_3S_4 and Mo_3S_7.

[0044] In another embodiment of the present invention, the molybdenum compound is preferably a dithiocarbamate compound, such a dinuclear or trinuclear molybdenum dithiocarbamate; especially effective compounds are molybdenum dialkyldithiocarbamate compounds represented by the formula $Mo_3S_7((alkyl)_2dtc)_4$.

[0045] In each aspect the of present invention, the lubricating oil composition preferably contains 5 to 5000, more preferably 10 to 1000, especially 50 to 750, ppm of molybdenum by mass, based on the mass of the oil composition.

[0046] Oil-soluble or oil-dispersible molybdenum compounds, such as trinuclear molybdenum dithiocarbamates, have been found to be particularly effective in preventing corrosive wear in the cylinder liner.

[0047] The amount of molybdenum is measured according to ASTM D5185.

Dispersant

[0048] In respect of each aspect of the invention, the lubricating oil compositions can also comprise a dispersant. Dispersants maintain oil-insoluble substances, resulting from oxidation during use, in suspension in the fluid, thus preventing sludge flocculation and precipitation or deposition on metal parts.

[0049] So-called ashless dispersants are organic materials, which form substantially no ash on combustion, in contrast to metal-containing (and thus ash-forming) detergents. Borated metal-free dispersants are regarded herein as ashless dispersants.

[0050] Typically, the dispersants comprise amine, alcohol, amide, or ester polar moieties attached to the polymer backbone often via a bridging group. The dispersant may be, for example, selected from oil-soluble salts, esters, amino-esters, amides, imides, and oxazolines of long chain hydrocarbon substituted mono- and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having a polyamine attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine, and Koch reaction products.

[0051] The polymer backbone is typically an olefin polymer, especially polymers comprising a major molar amount (i.e. greater than 50 mole %) of a C_2 to C_{18} olefin (e.g., ethylene, propylene, butylene, isobutylene, pentene, octene-1, styrene), and typically a C_2 to C_5 olefin. The oil-soluble polymeric hydrocarbon backbone may be a homopolymer (e.g., polypropylene or polyisobutylene) or a copolymer of two or more of such olefins (e.g., copolymers of ethylene and an alpha-olefin such as propylene and butylene or copolymers of two different alphaolefins).

[0052] One preferred class of olefin polymers is polybutenes and specifically polyisobutenes (PIB) or poly-n-butenes, such as may be prepared by polymerization of a C_4 refinery stream. Another preferred class of olefin polymers is ethylene alpha-olefin (EAO) copolymers or alpha-olefin homo- and copolymers such as may be prepared using metallocene chemistry having in each case a high degree (e.g. >30%) of terminal vinylidene unsaturation.

[0053] The polymer backbone will usually have number average molecular weight ($\overline{M}n$) within the range of from 100 to 20,000 or 10,000. The $\overline{M}n$ of the backbone is preferably within the range of 250 or 500 to 10,000, more preferably 700 to 5,000. Both relatively low molecular weight ($\overline{M}n$ 500 to 1500) and relatively high molecular weight ($\overline{M}n$ 1500 to 5,000 or greater) polymers are useful to make dispersants. Particularly useful olefin polymers for use in dispersants have $\overline{M}n$ within the range of from 900 to 3000. The olefin polymers used to prepare dispersants preferably have approximately one terminal double bond per polymer chain.

[0054] Suitable dispersants include, for example, derivatives of long chain hydrocarbon-substituted carboxylic acids in which the hydrocarbon groups contain 50 to 400 carbon atoms, examples of such derivatives being derivatives of high molecular weight hydrocarbyl-substituted succinic acid. Such hydrocarbyl-substituted carboxylic acids may be reacted with, for example, a nitrogen-containing compound, advantageously a polyalkylene polyamine, or with an ester. Particularly preferred dispersants are the reaction products of polyalkylene amines with alkenyl succinic anhydrides. Examples of specifications disclosing dispersants of the last-mentioned type are US-A-3 202 678, 3 154 560, 3 172 892, 3 024 195, 3 024 237, 3 219 666, 3 216 936 and BE-A-662 875.

[0055] The dispersant can be further post-treated by a variety of conventional post treatments such as boration, as generally described in US 3,087,936 and 3,254,025. This is readily accomplished by treating an acyl nitrogen-containing dispersant with a boron compound selected from the group consisting of boron oxide, boron halides, boron acids and esters of boron acids or highly borated low Mw dispersant, in an amount to provide a boron to nitrogen mole ratio of 0.01 - 5.0. Usefully the dispersants contain from 0.05 to 2.0, e.g. 0.05 to 1.5 or 0.9, mass % of boron based on the total mass (active ingredient basis) of the borated acyl nitrogen compound.

[0056] Preferred for use in the invention is a polyisobutenyl succinimide dispersant wherein the $\overline{M}n$ of the polyisobutenyl groups is from 750 to 3000, such as 900 to 1200 or 2000 to 2300.

[0057] In one embodiment of the present invention, the amount of dispersant, based on nitrogen derived from the dispersant, in the lubricating oil composition is preferably up to 1.0, more preferably 0.001 to 0.08, such as 0.005 to

0.55 or 0.50, mass %, based on the mass of the lubricating oil composition.

[0058] In another embodiment of the present invention, the amount of dispersant, based on boron derived from the dispersant, in the lubricating oil composition is preferably not more than 0.5, such as not more than 0.25, for example 0.005 to 0.1, mass %, based on the mass of the lubricating oil composition.

[0059] Preferably the dispersant is a borated dispersant, such as a borated succinimide.

[0060] The amount of boron is measured according to ASTM D5185; the amount of nitrogen is measured according to ASTM D5291; the $\overline{M}n$ can be determined by several known techniques - a convenient method for such determination is by gel permeation chromatography (GPC) which additionally provides molecular weight distribution information.

Detergent

[0061] In respect of each aspect of the invention, the lubricating oil compositions can also comprise a detergent composition, which comprises one or more detergents, preferably overbased detergents.

[0062] A detergent is an additive that reduces formation of piston deposits, for example high-temperature varnish and lacquer deposits, in engines; it has acid-neutralising properties and is capable of keeping finely divided solids in suspension. It is based on metal "soaps", that is metal salts of acidic organic compounds, sometimes referred to as surfactants.

[0063] Large amounts of a metal base can be included by reacting an excess of a metal compound, such as an oxide or hydroxide, with an acidic gas such as carbon dioxide to give an overbased detergent which comprises neutralised detergent as the outer layer of a metal base (e.g. carbonate) micelle.

[0064] The metals can be selected from Group 1 and Group 2 metals, e.g., sodium, potassium, lithium, calcium, and magnesium. Calcium and magnesium are preferred; more preferably the metal is calcium.

[0065] Surfactants that may be used include organic carboxylates, for example, aliphatic carboxylates and aromatic carboxylates, such as salicylates, non-sulfurised or sulfurised; sulfonates; phenates, non-sulfurised or sulfurised; thiophosphonates; and naphthenates.

[0066] Examples of suitable detergents include overbased metal phenates, metal sulfonates, metal salicylates and metal carboxylates, where the metal is selected from sodium, calcium and magnesium; preferably the metal is calcium.

[0067] Also suitable in each aspect of the present invention is a detergent in the form of a hybrid complex detergent, wherein the basic material is stabilised by more than one type of surfactant. It will be appreciated by one skilled in the art that a single type of organic acid may contain a mixture of organic acids of the same type. For example, a sulphonic acid may contain a mixture of sulphonic acids of varying molecular weights. Such an organic acid composition is considered as one type. Thus, complex detergents are distinguished from mixtures of two or more separate overbased detergents, an example of such a mixture being one of an overbased salicylate detergent with an overbased phenate detergent.

[0068] The art describes examples of overbased complex detergents. For example, International Patent Application Publication Nos. 9746643/4/5/6 and 7 describe hybrid complexes made by neutralising a mixture of more than one acidic organic compound with a basic metal compound, and then overbasing the mixture. Individual basic micelles of the detergent are thus stabilised by a plurality of surfactant types.

[0069] EP-A-0 750 659 describes a calcium salicylate phenate complex made by carboxylating a calcium phenate and then sulfurising and overbasing the mixture of calcium salicylate and calcium phenate. Such complexes may be referred to as "phenalates"

[0070] Surfactants for the surfactant system of the overbased metal detergent may contain at least one hydrocarbyl group, for example, as a substituent on an aromatic ring. Advantageously, hydrocarbyl groups in surfactants for use in accordance with the invention are aliphatic groups, preferably alkyl or alkylene groups, especially alkyl groups, which may be linear or branched. The total number of carbon atoms in the surfactants should be at least sufficient to impact the desired oil-solubility.

[0071] The proportion of one detergent type (e.g. calcium sulfonate) to another detergent type (e.g. sodium phenate) in the detergent composition is not critical. Similarly, the proportion of one surfactant to another in a complex detergent is not critical.

[0072] The detergent composition may comprise a major proportion of a phenate detergent or comprises a complex hybrid detergent having a major proportion of a phenate surfactant, where the phenate detergent or the complex hybrid detergent is preferably a calcium salt.

[0073] The overbased detergents of the present invention may have a TBN of at least 200, preferably at least 250, especially at least 300, such as up to 600.

[0074] The lubricating oil compositions of the present invention have a sufficient amount of additives, for example, detergents, whether neutral or overbased, to provide the required TBN. For example, the detergent composition may be used up to 30, preferably 2 to 15 or to 20, mass % of detergent composition, based on the mass of the lubricating oil composition.

Co-Additives

[0075] The lubricants may include an antiwear agent as a co-additive and may also contain other co-additives, for example, antioxidants, antifoaming agents and/or rust inhibitors. Further details of particular co-additives are as follows.
[0076] Oxidation inhibitors, or antioxidants, reduce the tendency of mineral oils to deteriorate in service, evidence of such deterioration being, for example, the production of varnish-like deposits on metal surfaces and of sludge, and viscosity increase. Suitable oxidation inhibitors include sulphurized alkyl phenols and alkali or alkaline earth metal salts thereof; diphenylamines; phenyl-naphthylamines; and phosphosulphurized or sulphurized hydrocarbons.
[0077] Other oxidation inhibitors or antioxidants which may be used in the lubricant comprise oil-soluble copper compounds. The copper may be blended therein as any suitable oil-soluble copper compound. By oil-soluble is meant that the compound is oil-soluble under normal blending conditions in the base stock or an additive package. The copper may, for example, be in the form of a copper dihydrocarbyl thio- or dithio-phosphate. Alternatively, the copper may be added as the copper salt of a synthetic or natural carboxylic acid, for example, a C8 to C18 fatty acid, an unsaturated acid, or a branched carboxylic acid. Also useful are oil-soluble copper dithiocarbamates, sulphonates, phenates, and acetylacetonates. Examples of particularly useful copper compounds are basic, neutral or acidic copper Cu I and/or Cu II salts derived from alkenyl succinic acids or anhydrides.
[0078] Additional detergents and metal rust inhibitors include the metal salts, which may be overbased and have a TBN less than 300, of sulphonic acids, alkyl phenols, sulphurized alkyl phenols, alkyl salicylic acids, thiophosphonic acids, naphthenic acids, and other oil-soluble mono- and dicarboxylic acids. Representative examples of detergents/rust inhibitors, and their methods of preparation, are given in EP-A-208 560. In the case of metal salts of salicylic acids, the TBN of the metal salts may be less than 200.
[0079] Antiwear agents, as their name implies, reduce wear of metal parts. Zinc dihydrocarbyl dithiophosphates (ZDDPs) are very widely used as antiwear agents. Especially preferred ZDDPs are those of the formula $Zn[SP(S)(OR_1)(OR_2)]_2$ wherein R_1 and R_2 represent hydrocarbyl groups such as alkyl groups that contain from 1 to 18, preferably 2 to 12, carbon atoms. Also suitable are ashless or non-metal containing additives, such as sulfur and/or phosphorus containing compounds, for example, sulfurised phenol and amine dithiophosphate.
[0080] The oil compositions of the present invention may contain 0 to 0.2, preferably 0.05 to 0.15, more preferably 0.01 to 0.1, mass % of phosphorus, based on the mass of the oil composition. In a preferred embodiment of the present invention, the oil composition contains less than 150, preferably less than 100, for example 0, ppm of phosphorus.
[0081] Pour point depressants, otherwise known as lube oil flow improvers, lower the minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Foam control may be provided by an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.
[0082] Typical proportions for additives for a four-stroke trunk piston engine oil composition are as follows:

Additive	Mass % a.i.* (Broad)	Mass % a.i.* (Preferred)
Detergent(s)	0.5-10	2-7
Dispersant(s)	0.5-5	1-3
Anti-wear agent(s)	0.1-1.5	0.5-1.3
Oxidation inhibitor	0.2-2	0.5-1.5
Rust inhibitor	0.03-0.15	0.05-0.1
Pour point depressant	0.03-0.15	0.05-0.1
Mineral or synthetic base oil	Balance	Balance

* Mass % active ingredient based on the final oil composition.

[0083] Typical proportions for additives for a two-stroke cross-head oil composition are as follows:

Additive	Mass % a.i.* (Broad)	Mass % a.i.* (Preferred)
Detergent(s)	1-18	3-12
Dispersant(s)	0.5-5	1-3
Anti-wear agent(s)	0.1-1.5	0.5-1.3
Pour point depressant	0.03-0.15	0.05-0.1
Mineral or synthetic base oil	Balance	Balance

* Mass % active ingredient based on the final oil composition.

[0084] When a plurality of additives is employed it may be desirable, although not essential, to prepare one or more additive compositions (also known as packages) or concentrates comprising the additives, whereby several additives can be added simultaneously to the oil of lubricating viscosity to form the lubricant or lubricating oil composition. Dissolution of the additive package(s) into the oil of lubricating vicosity may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The additive package(s) will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration, and/or to carry out the intended function, in the final lubricant when the additive package(s) is/are combined with a predetermined amount of oil of lubricating viscosity.
[0085] Thus, the molybdenum compound in accordance with the present invention may be admixed with small amounts of base oil or other compatible solvents together with other desirable additives to form additive packages containing active ingredients in an amount, based on the additive package, of, for example, from 2.5 to 90 and preferably from 5 to 75 and most preferably from 8 to 60, mass %, the remainder being base oil or other compatible solvents.
[0086] The lubricating oil composition may typically contain 5 to 40, preferably 10 to 38, more preferably 16 to 34, mass % of the additive package(s), based on active ingredient.
[0087] The present invention is illustrated by, but in no way limited to, the following examples.

Examples

[0088] Lubricating oil compositions were prepared by methods known in the art. Table 1 shows the compositional details of Example 1 and Comparative Examples 1 and 2. Example 1 and Comparative Examples 1 & 2 were blended so that the resulting lubricating oil composition has a TBN of 70 and viscosity at 100ºC of about 20 mm^2s^{-1}.
[0089] Example 1, an example according to the present invention, is a lubricating oil composition comprising 550 ppm of molybdenum; Comparative Examples 1 and 2 contain the same detergents and dispersant as Example 1, but Comparative Example 1 contains a zinc dithiophosphate additive instead of the molybdenum compound and Comparative Example 2 does not contain the molybdenum compound or the zinc compound. Comparative Example 3 is a commercial lubricating oil composition having a TBN of 70 and viscosity at 100ºC of about 20 mm^2s^{-1}.
[0090] The lubricating oil compositions of Example 1 and Comparative Examples 1 to 3 were tested for cylinder liner wear performance in a slow speed two-stroke cross-head "Bolnes" engine. Such engines are widely used by those skilled in the art for lubricating performance evaluation such as disclosed in a presentation by Nippon Mitsubishi Oil Company on 10 May 2001 at CIMAC conference entitled "The influence of the neutralisation ability of marine lubricants on engine lubrication" Takeshmia et al.
[0091] The cylinder liner wear data for Example 1 and Comparative Examples 1 to 3 are provided in Table 2. The data show that Example 1 provides better wear protection than any one of Comparative Examples 1 to 3, in particular better than Comparative Example 1, which contains ZDDP. This improvement is especially evident in positions 2 to 5 of the cylinder.

Table 1

	Example 1	Comparative Example 1	Comparative Example 2
410 TBN phenate -- sulfonate complex detergent, mass % of active ingredient	7.62	9.60	7.62
250 TBN phenate detergent, mass % of active ingredient	4.71	1.97	4.71
Dispersant[1], based on ppm of B and in parentheses ppm of N	105 (474)	117 (528)	105 (474)
Molybdenum compound[2], based on ppm of Mo	550	-	-
ZDDP[3], based on ppm of P	-	196	-
Brightstock, mass %	18	22	18
basestock	balance	balance	balance

KEY

[1] borated polyisobutenyl succinimide; [2] trinuclear molybdenum compound; [3] zinc dialkyldithiophosphate. A dash indicates absence of the component.

Table 2

Cylinder wear, microns	Example 1*	Comparative Example 1	Comparative Example 2	Comparative Example 3
Position 1, average	0	0	0	0
Position 2, average	16.5	21	25	29
Position 3, average	22	27	31	32
Position 4, average	19	24	26	28
Position 5, average	17	22	20	28
Position 6, average	12	15	14	19
Position 7, average	8.5	7	9	16
Position 8, average	8.5	14	12	17
Average	15	19	20	23
Maximum	29	35	52	37

* average of 2 measurements

Claims

1. A residual fuel oil-fuelled diesel engine lubricating oil composition for marine and stationary applications comprising:

   (a) an oil of lubricating viscosity, in a major amount; and
   (c) an oil soluble or oil-dispersible molybdenum compound, in a minor amount;

   wherein the oil composition has a TBN from 20 to 100 as measured according to ASTM D-2896 and a viscosity at 100°C in the range from 9 to 30 mm^2s^{-1} as measured according to ASTM D-445.

2. The oil composition as claimed in claim 1 in the form of a residual-fuelled cross-head marine diesel engine lubricating oil composition having a TBN from 30 to 95 and a viscosity at 100°C in the range from 9 to 25, such as 12 to 25, mm^2s^{-1}.

3. The composition as claimed in either claim 1 or claim 2 further comprising:

   (c) a detergent composition, which comprises one or more overbased metal detergents.

4. The composition as claimed in any one of claims 1 to 3 further comprising:

   (d) a dispersant, which has a hydrocarbon backbone of molecular weight from 100 to 10000.

5. The composition as claimed in any one of claims 1 to 4, wherein the molybdenum compound is present in an amount from 1 to 10000 ppm of molybdenum by mass, based on the mass of the oil composition.

6. The oil composition as claimed in any one of claims 1 to 5 further comprising a residual fuel oil.

7. A combination of a cylinder of a two-stroke cross-head marine diesel engine and a lubricating oil composition as claimed in any one of claims 1 to 6, wherein the cylinder is **characterised by** a power output of 4000 or greater, such as 4200 or greater, preferably 4500 or greater, more preferably in the range of 4500 to 6000, kW.

8. Use of an oil-soluble or oil-dispersible molybdenum compound or a composition comprising the molybdenum compound to reduce corrosive wear in a cylinder liner of a residual fuel oil-fuelled diesel engine.

9. A method of reducing corrosive wear in a cylinder liner of a residual fuel oil-fuelled diesel engine comprising supplying to the walls of the cylinder a lubricating oil composition as claimed in any one of claims 1 to 6.

10. An additive composition comprising:

    (a) an oil-soluble or oil-dispersible molybdenum compound; and
    (c) one or more co-additives;

    wherein the additive composition contains (a) and (b) in an amount to provide a lubricating oil composition having a TBN from 20 to 100 as measured according to ASTM D-2896 and a viscosity at 100°C in the range from 9 to 30 mm^2s^{-1} as measured according to ASTM D-445, when the lubricating oil composition contains 5 to 40 mass % of the additive composition.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 30 8354

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The present search report has been drawn up for all claims

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MUNICH	20 February 2002	Dötterl, E

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