

Marine Engine Lubrication

FIELD OF THE INVENTION

This invention relates to the lubrication of 2-stroke and 4-stroke marine diesel internal combustion engines, the former usually being referred to as cross-head engines and the latter as trunk piston engines. Respective lubricants therefor are usually known as marine diesel cylinder lubricants (“MDCL’s”) and trunk piston engine oils (“TPEO’s”).

BACKGROUND OF THE INVENTION

Cross-head engines are slow engines with a high to very high power range. They include two separately-lubricated parts: the piston/cylinder assembly lubricated with total-loss lubrication by a highly viscous oil (an MDCL); and the crankshaft lubricated by a less viscous lubricant, usually referred to as a system oil.

Trunk piston engines may be used in marine, power-generation and rail traction applications and have a higher speed than cross-head engines. A single lubricant (TPEO) is used for crankcase and cylinder lubrication. All major moving parts of the engine, i.e. the main and big end bearings, camshaft and valve gear, are lubricated by means of a pumped circulation system. The cylinder liners are lubricated partially by splash lubrication and partially by oil from the circulation systems that finds its way to the cylinder wall through holes in the piston skirt via the connecting rod and gudgeon pin.

It is known in the art to include brightstock in MDCL’s and TPEO’s, brightstock being a high viscosity oil that is highly refined and dewaxed and that is produced from residual stocks or bottoms. It may, for example, have a kinematic viscosity at 100°C of greater than 25, usually greater than 30, mm²s⁻¹, such as a solvent-extracted, de-asphalted product from vacuum residuum generally having a kinematic viscosity at 100°C of 28-36 mm²s⁻¹.

Brightstock is however expensive and art describes ways of replacing it. WO 99/64543 describes MDCL's formulated without brightstock and US 2008/0287329 describes a TPEO containing little or no brightstock.

A problem in the art is to formulate brightstock-free MDCL's and TPEO's at reduced cost and at the same time provide improved antiwear properties.

SUMMARY OF THE INVENTION

It is now found that the use of olefin copolymers such as an amorphous ethylene-propylene copolymer in an MDCL or a TPEO enables the above problem to be overcome.

Thus, the present invention provides a two-stroke or four-stroke marine engine lubricating oil composition comprising an oil of lubricating viscosity in a major amount and

- (A) additives, in respective minor amounts; and
- (B) a viscosity modifier in the form of an olefin copolymer in an amount in the range of 0.05 - 6 mass %,

wherein the composition includes less than 0.5 mass%, preferably less than 0.1 mass%, of brightstock; preferably brightstock is completely or substantially absent from the composition.

In further aspects the present invention comprises:-

The use of a viscosity modifier (B) to improve the anti-wear properties of a marine diesel cylinder lubricant or of a trunk piston engine oil which includes less than 0.5 mass%, preferably less than 0.1 mass%, of brightstock; preferably brightstock is absent or is substantially absent from the marine diesel cylinder lubricant or the trunk piston engine oil;

A method of lubricating a cross-head marine diesel engine comprising supplying a lubricating oil composition including viscosity modifier (B) to the piston/cylinder assembly of the engine; and

A method of lubricating a trunk piston marine diesel engine comprising supplying the composition to the engine.

In this specification, the following words and expressions, if and when used, have the meanings ascribed below:

“active ingredients” or “(a.i.)” refers to additive material that is not diluent or solvent;

“comprising” or any cognate word specifies the presence of stated features, steps, or integers or components, but does not preclude the presence or addition of one or more other features, steps, integers, components or groups thereof; the expressions “consists of” or “consists essentially of” or cognates may be embraced within “comprises” or cognates, wherein “consists essentially of” permits inclusion of substances not materially affecting the characteristics of the composition to which it applies;

“major amount” means 40 or 50 mass % or more of a composition;

“minor amount” means less than 50 mass % of a composition;

“TBN” means total base number as measured by ASTM D2896.

Furthermore in this specification, if and when used:

“calcium content” is as measured by ASTM 4951;

“phosphorus content” is as measured by ASTM D5185;

“sulphated ash content” is as measured by ASTM D874;

“sulphur content” is as measured by ASTM D2622;

“KV100” means kinematic viscosity at 100°C as measured by ASTM D445.

Also, it will be understood that various components used, essential as well as optimal and customary, may react under conditions of formulation, storage or use and that the invention also provides the product obtainable or obtained as a result of any such reaction.

Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

DETAILED DESCRIPTION OF THE INVENTION

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

OIL OF LUBRICATING VISCOSITY

The lubricant composition contains a major proportion of an oil of lubricating viscosity. Such lubricating oils may range in viscosity from light distillate mineral oils to heavy lubricating oils. Generally, the viscosity of the oil ranges from 2 to 40, such as 3 to 15, mm²/sec, as measured at 100°C, and a viscosity index of 80 to 100, such as 90 to 95. The lubricating oil may comprise greater than 60, typically greater than 70. mass % of the composition.

Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil); liquid petroleum oils and hydrorefined, solvent-treated or acid-treated mineral oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale also serve as useful base oils.

Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymers of olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkybenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulphides and derivative, analogues and homologues thereof.

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, and the alkyl and aryl ethers of polyoxyalkylene polymers (e.g., methyl-polyiso-propylene glycol ether having a molecular weight of 1000 or diphenyl ether of poly-ethylene glycol having a molecular weight of 1000 to 1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C₃-C₈ fatty acid esters and C₁₃ oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of such esters includes dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol esters such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxysilicone oils and silicate oils comprise another useful class of synthetic lubricants; such oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methyl-2-ethylhexyl)silicate, tetra-(p-tert-butyl-phenyl)silicate, hexa-(4-methyl-2-ethylhexyl)disiloxane, poly(methyl)siloxanes and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

Unrefined, refined and re-refined oils can be used in lubricants of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations; petroleum oil obtained directly from distillation; or ester oil obtained directly from esterification and used without further treatment are unrefined oils.

Marine Diesel Cylinder Lubricant ("MDCL")

An MDCL may employ 10-35, preferably 13-30, most preferably 16-24, mass % of a concentrate or additive package, the remainder being base stock. It preferably includes at least 50, more preferably at least 60, even more preferably at least 70, mass % of oil of lubricating viscosity based on the total mass of MDCL. Preferably, the MDCL has a compositional TBN (using ASTM D2896) of 40-100, such as 50-60.

The following may be mentioned as examples of typical proportions of additives in an MDCL.

Additive	Mass% a.i. (Broad)	Mass % a.i. (Preferred)
detergent(s)	1-20	3-15
dispersant(s)	0.5-5	1-3
anti-wear agent(s)	0.1-1.5	0.5-1.3
pour point dispersant	0.03-1.15	0.05-0.1
base stock	balance	balance

Trunk Piston Engine Oil ("TPEO")

A TPEO may employ 7-35, preferably 10-28, more preferably 12-24, mass % of a concentrate or additives package, the remainder being base stock. Preferably, the TPEO has a compositional TBN (using D2896) of 20-60, such as 25-55.

The following may be mentioned as typical proportions of additives in a TPEO.

Additive	Mass% a.i. (Broad)	Mass % a.i. (Preferred)
detergent(s)	0.5-12	2-8
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 dispersant	0.03-1.15	0.05-0.1
base stock	balance	balance

When a plurality of additives is employed it may be desirable, although not essential, to prepare one or more additive packages comprising the additives, whereby several additives can be added simultaneously to the base oil to form the lubricating

oil composition. Dissolution of the additive package(s) into the lubricating oil 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 formulation when the additive package(s) is/are combined with a predetermined amount of base lubricant. Thus, compounds 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.

More detailed description of additive components is given below.

Detergents

A detergent is an additive that reduces formation of 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.

A detergent comprises a polar head with a long hydrophobic tail. Large amounts of a metal base are 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.

The detergent is preferably an alkali metal or alkaline earth metal additive such as an overbased oil-soluble or oil-dispersible calcium, magnesium, sodium or barium salt of a surfactant selected from phenol, sulphonic acid, carboxylic acid, salicylic acid and naphthenic acid, wherein the overbasing is provided by an oil-insoluble salt of the metal, e.g. carbonate, basic carbonate, acetate, formate, hydroxide or oxalate, which is stabilised by the oil-soluble salt of the surfactant. The metal of the oil-soluble surfactant salt may be the same or different from that of the metal of

the oil-insoluble salt. Preferably the metal, whether the metal of the oil-soluble or oil-insoluble salt, is calcium.

The TBN of the detergent may be low, i.e. less than 50 mg KOH/g, medium, i.e. 50-150 mg KOH/g, or high, i.e. over 150 mg KOH/g, as determined by ASTM D2896. Preferably the TBN is medium or high, i.e. more than 50 TBN. More preferably, the TBN is at least 60, more preferably at least 100, more preferably at least 150, and up to 500, such as up to 350 mg KOH/g, as determined by ASTM D2896.

Anti-oxidants

The trunk piston diesel engine lubricant composition may include at least one anti-oxidant. The anti-oxidant may be aminic or phenolic. As examples of amines there may be mentioned secondary aromatic amines such as diarylamines, for example diphenylamines wherein each phenyl group is alkyl-substituted with an alkyl group having 4 to 9 carbon atoms. As examples of anti-oxidants there may be mentioned hindered phenols, including mono-phenols and bis-phenols.

Preferably, the anti-oxidant, if present, is provided in the composition in an amount of up to 3 mass %, based on the total amount of the lubricant composition.

Other additives such as pour point depressants, anti-foamants, metal rust inhibitors, pour point depressants and/or demulsifiers may be provided, if necessary.

The terms 'oil-soluble' or 'oil-dispersable' as used herein do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible or capable of being suspended in the oil in all proportions. These do mean, however, that they are, for instance, soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

The lubricant compositions of this invention comprise defined individual (i.e. separate) components that may or may not remain the same chemically before and after mixing.

It may be desirable, although not essential, to prepare one or more additive packages or concentrates comprising the additives, whereby the additives can be added simultaneously to the oil of lubricating viscosity to form the lubricating oil composition. Dissolution of the additive package(s) into the lubricating oil 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 formulation when the additive package(s) is/are combined with a predetermined amount of base lubricant.

Thus, the additives 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, preferably from 5 to 75, most preferably from 8 to 60, mass % of additives in the appropriate proportions, the remainder being base oil.

The final formulations may typically contain about 5 to 40 mass % of the additive packages(s), the remainder being base oil.

VISCOSITY MODIFIER

In this invention, as stated above, a viscosity modifier (B) is additionally provided.

Viscosity modifiers impart high and low temperature operability to a lubricating oil and permit it to remain relatively viscous at elevated temperatures and also exhibit acceptable viscosity or fluidity at low temperatures.

In this invention olefin copolymers (OCP's) are used. Examples of ranges in the composition include 0.1-6, 0.1-5, 0.1-4, mass % and lower limits of 1 or 2 mass %.

These may be copolymers of two or more monomers of C₂ to C₃₀, e.g. C₂ to C₈, olefins, including both alpha-olefins and internal olefins, which may be straight or branched, aliphatic, aromatic, alkyl-aromatic, or cycloaliphatic. Frequently, they are of ethylene with C₃ to C₃₀ olefins, particularly preferred being copolymers of ethylene and propylene. They may also be copolymers of C₆ and higher alpha olefins and terpolymers of styrene, e.g. with isoprene and/or butadiene and hydrogenated derivatives thereof.

Preferred OCP's are ethylene copolymers containing 15 to 90, preferably 30 to 80, mass % of ethylene and 10 to 85, preferably 20 to 70, mass % of one or more C₃ to C₂₈, preferably C₃ to C₁₈, more preferably C₃ to C₈, alpha-olefins. Such OCP's may have a degree of crystallinity of less than 25 mass %, as determined by x-ray and differential scanning calorimetry. As indicated above, copolymers of ethylene and propylene are most preferred. Other alpha-olefins suitable in place of propylene, or in combination with ethylene and propylene to form a terpolymer or tetrapolymer, for example, include: 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene; and branched chain alpha-olefins such as 4-methyl-1-pentene, 4-methyl-1-hexene, 4-methyl pentene-1, 4, 4-dimethyl-1-pentene, 6-methylheptene-1, and mixtures thereof.

There may also be included terpolymers and tetrapolymers of ethylene, said C₃ to C₂₈ alpha-olefin, and a non-conjugated diolefin or mixtures of such diolefins. The non-conjugated diolefin is generally present as 0.5 to 20, preferably 1 to 7, mole percent of the total moles of ethylene and alpha-olefin.

EXAMPLES

The present invention is illustrated by, but in no way limited to, the following examples.

MDCL's

A set of MDCL's was formulated, each containing 20.89 mass % of the same additives in the proportions and having a TBN of about 70. The set comprised a control consisting of additives and base oil; a reference consisting of additives, base oil and brightstock; and an inventive MDCL consisting of additives, base oil and viscosity modifier. The additives were additives known in the art and used in proportions known in the art for conferring MDCL properties. The viscosity modifier was an olefin copolymer in the form of amorphous ethylene-propylene copolymer. The brightstock was a Group I bright stock with a kinematic viscosity of >20cSt at 100°C. The base oil was a Group 1 base oil.

TPEO's

A set of TPEO's was formulated, each containing 16 mass % of the same additives in the same proportions and having a TBN of about 40. The set comprised a control consisting of additives and base oil; a reference consisting of additives, base oil and bright stock; and an inventive MDCL consisting of additives, base oil and viscosity modifier. The additives were additives known in the art and used in proportions known in the art for conforming TPEO properties. The viscosity modifier and brightstock were as used in the MDCL's. The base oil was a Group 1 base oil.

TESTING & RESULTS

Samples of the above formulations were tested using a PCS Instruments high frequency reciprocating rig (HFRR) on a standard protocol comprising the following conditions:

- 120 minutes
- 20 Hz reciprocation of 1mm stroke length
- 200g load using standard equipment manufacturer supplied steel substrates.

Each test was repeated two further times and the recorded wear measurement was the average of these values.

The HFRR data for the compositions are summarized in the table below.

Table

<u>TPEO</u>	<u>Additive</u> (mass %)	<u>Base oil</u> (mass %)	<u>Brightstock</u> (mass %)	<u>OCP</u> (mass %)	<u>Result</u> (wear vol m ³)
Control	16	84	-	-	5,584
Reference	16	75.5	8.5	-	8,279
1	16	82.67	-	1.33	5,359

MDCL

Control	20.89	79.11	-	-	33,960
Reference	20.89	58.89	20.22	-	3,940
2	20.89	77.61	-	3.17	2,953

The above results show that the use of an amorphous olefin copolymer additive gives advantageous results when compared with brightstock at much lower additive treatment levels in the formulation.

CLAIMS:

1. A two-stroke or four-stroke marine engine lubricating oil composition comprising an oil of lubricating viscosity in a major amount and
 - (A) additives, in respective minor amounts; and
 - (B) a viscosity modifier in the form of an olefin copolymer in an amount in the range of 0.05 to 6 mass%;

wherein the composition includes less than 0.5 mass%, preferably less than 0.1 mass%, of brightstock; preferably brightstock is completely or substantially absent from the composition; and wherein the two-stroke marine engine lubricating oil composition has a TBN of 40 to 100 using ASTM D2896, or the four-stroke marine engine lubricating oil composition has a TBN of 25 to 60 using ASTM D2896.

2. The composition as claimed in claim 1, wherein the olefin copolymer is a copolymer of two or more monomers of C₂-C₃₀ olefins.
3. The composition as claimed in claim 2, wherein the olefin copolymer is a copolymer of ethylene with a C₃-C₃₀ olefin.
4. The composition as claimed in claim 3, wherein the olefin copolymer is a copolymer of ethylene with propylene.
5. The composition as claimed in any one of claims 1-4, wherein the copolymer is an ethylene copolymer containing 15-90 mass % of ethylene and 10-85 mass % of one or more C₃-C₂₈ alpha-olefins.
6. The composition as claimed in any one of claims 1-5, wherein the olefin copolymer has a degree of crystallinity of less than 25 mass % as determined by X-ray and differential scanning calorimetry.

7. The composition as claimed in any one of claims 1-6 in the form of a marine diesel cylinder lubricant.
8. The composition as claimed in any one of claims 1-6 in the form of a trunk piston engine oil.
9. The use of a viscosity modifier (B) as defined in any one of claims 1-6 to improve the anti-wear properties of a marine diesel cylinder lubricant or a trunk piston engine oil which includes less than 0.5 mass%, preferably less than 0.1 mass%, of brightstock
10. The use as claimed in claim 9, wherein the marine diesel cylinder lubricant or the trunk piston engine oil is substantially free from brightstock.
11. Use of a viscosity modifier (B) in the form of an olefin copolymer as a replacement, in part or in full, for brightstock in a marine diesel cylinder lubricant or a trunk piston engine oil, so that the marine diesel cylinder lubricant or the trunk piston engine oil includes less than 0.5 mass%, preferably less than 0.1 mass%, of brightstock.
12. A method of lubricating a cross-head marine diesel engine comprising supplying a composition as claimed in any of claims 1-7 to the piston/cylinder assembly of the engine.
13. A method of lubricating a trunk piston marine diesel engine comprising supplying a composition as claimed in any of claims 1-6 or 8 to the engine.
14. A method of reducing the amount of brightstock in a two-stroke or four-stroke marine engine lubricating oil composition comprising an oil of lubricating viscosity in a major amount and (A) additives, in respective minor amounts; the method comprising the step of replacing, in part or in full, the brightstock

with 0.05 to 6 mass % of (B) a viscosity modifier in the form of an olefin copolymer.

15. The method as claimed in claim 14, wherein (B) substantially replaces the brightstock so that the composition includes less than 0.5 mass%, preferably less than 0.1 mass%, of brightstock; preferably so that the composition is completely or substantially free from brightstock.
16. The method as claimed in claim 14, wherein the composition includes less than 0.5 mass%, preferably less than 0.1 mass%, of brightstock; preferably the composition is completely or substantially free from brightstock.
17. The method as claimed in any one of claims 14, 15 or 16, wherein the two-stroke marine engine lubricating oil composition has a TBN of 40 to 100 using ASTM D2896, or the four-stroke marine engine lubricating oil composition has a TBN of 25 to 60 using ASTM D2896.