

MARINE ENGINE LUBRICATION

FIELD OF THE INVENTION

This invention relates to the lubrication of 4-stroke marine diesel internal combustion engines, usually referred to as trunk piston engines. Lubricants therefor are usually known as trunk piston engine oils ("TPEO's").

BACKGROUND OF THE INVENTION

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. Trunk piston engines normally include a centrifuge to clean the TPEO.

Nitrogen-containing ashless dispersants are known in the art as additives for TPEO's. See for example EP-A-2133740; US-A-2009/0203559; US-A-2009/0011966; EP-A-1528099; and EP-A-1209218.

The art does not, however, mention the effect of a nitrogen-containing ashless dispersant on the diminution of base number (BN) during use of the TPEO; nor its effect on viscosity increase.

SUMMARY OF THE INVENTION

It is now found that the use of nitrogen-containing ashless dispersants in defined amounts in a TPEO has a beneficial effect on the BN and viscosity, without adversely affecting deposits performance.

Thus, the present invention provides the use of a nitrogen-containing ashless dispersant additive in an amount providing in the range of 50 to 150, preferably 75 to 125, ppm N by mass in a trunk piston marine lubricating oil composition for a medium-speed compression-ignited marine engine, fueled by a heavy fuel oil, and its lubrication by the composition, the composition having a BN in the range of 20 to 60, preferably 30 to 55, the use being to diminish the loss of BN and to diminish the increase in viscosity without adversely affecting deposits performance, preferably in comparison with analogous use when the amount of nitrogen-containing ashless dispersant falls outside of the above range.

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 50 mass % or more, preferably 60 mass % or more, even more preferably 60 mass % or more, and most preferably 70 mass % or more, of a composition;

“minor amount” means less than 50 mass %, preferably less than 40 mass %, even more preferably less than 30 mass %, and most preferably less than 20 mass %, of a composition;

“TBN” means total base number as measured by ASTM D2896. “BN” has the same meaning.

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.

TRUNK PISTON MARINE ENGINE LUBRICATING OIL COMPOSITION (“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 (oil of lubricating viscosity). Preferably, the TPEO has a compositional TBN (using D2896) of 20-60, preferably 25 or 30-55.

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 or concentrates comprising the additives, whereby several 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, additives 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, preferably from 5 to 75, most preferably from 8 to 60, mass % of additives in the appropriate proportions, the remainder being base oil.

NITROGEN-CONTAINING ASHLESS DISPERSANT

A dispersant is an additive for a lubricating composition whose primary function is to hold solid and liquid contaminants in suspension, thereby passivating them and reducing engine deposits at the same time as reducing sludge depositions. Thus, for example, a dispersant maintains in suspension oil-insoluble substances that result from oxidation during use of the lubricant, thus preventing sludge flocculation and precipitation or deposition on metal parts of the engine.

"Ashless" means that the dispersant is a non-metallic organic material that forms substantially no ash on combustion, in contrast to metal-containing, hence ash-forming, materials. Ashless dispersants comprise a long chain hydrocarbon with a polar head, the polarity being derived from inclusion of, e.g. an O, P or N atom, in this invention, a N atom. The hydrocarbon is an oleophilic group that confers oil-solubility, having, for example 40 to 500 carbon atoms. Thus, ashless dispersants may comprise an oil-soluble polymeric hydrocarbon backbone having functional groups that are capable of associating with particles to be dispersed. Typically, the dispersants comprise amine, alcohol, amide, or ester polar moieties attached to the polymer backbone often via a bridging group. The ashless 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, such as described in US-A-3,442,808.

The oil-soluble polymeric hydrocarbon backbone is typically an olefin polymer or polyene, especially polymers comprising a major molar amount (i.e., greater than 50 mole %) of a C₂ to C₁₈ olefin (e.g., ethylene, propylene, butylene, isobutylene, pentene, octene-1, styrene), and typically a C₂ to C₅ 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 olefin (e.g., copolymers of ethylene and an alpha-

olefin such as propylene or butylene, or copolymers of two different alpha-olefins). Other copolymers include those in which a minor molar amount of the copolymer monomers, e.g., 1 to 10 mole %, is an $\alpha\omega$ -diene; such as a C₃ to O₂₂ non-conjugated diolefin (e.g., a copolymer of isobutylene and butadiene, or a copolymer of ethylene, propylene and 1,4-hexadiene or 5-ethylidene-2-norbornene). Atactic propylene oligomers typically having an Mn of from 700 to 5000 may also be used, as described in EP-A-490454, as well as heteropolymers such as polyepoxides.

A preferred class of olefin polymers is polybutenes, specifically polyisobutenes (PIB) or poly-n-butenes, such as may be prepared by polymerization of a C₄ refinery stream. Other preferred classes of olefin polymers are ethylene alpha-olefin (EAO) copolymers and alpha-olefin homo- and copolymers having in each case a high degree (e.g., >30%) of terminal vinylidene unsaturation, such as described in WO-94/13709, which may be functionalised and aminated to give dispersants.

Dispersants include, for example, derivatives of long chain hydrocarbon-substituted carboxylic acids, examples being derivatives of high molecular weight hydrocarbyl-substituted succinic acid. A noteworthy group of dispersants are hydrocarbyl-substituted succinimides, made, for example, by reacting the above acids (or derivatives) with a nitrogen-containing compound, advantageously a polyalkylene polyamine, such as a polyethylene polyamine. Preferably, the hydrocarbyl group is a polyalkenyl group. Such polyalkenyl (e.g. polybutenyl) moiety may have a number average molecular weight of from 200 to 3000, preferably from 350 to 1000, more preferably from 400 to 960, or 400 to 950. Particularly preferred are the reaction products of polyalkylene polyamines with alkenyl succinic anhydrides, such as described in US-A-3,202,678; -3,154,560; -3,172,892; - 3,024,195, -3,024,237; - 3,219,666; and -3,216,936; and BE-A66,875 that may be post-treated to improve their properties; such as borated (as described in US-A-3,087,936 and -3,254,025); fluorinated and oxylated. For example, boration may be accomplished by treating an acyl nitrogen-containing dispersant with a boron compound selected from boron oxide, boron halides, boron acids and esters of boron acids.

As stated, the dispersants provides the TPEO with 50-150 ppm by mass of N atoms.

The co-additives will now be discussed in further detail.

METAL DETERGENT

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 as 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. 50 TBN or more. 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.

Preferably, the detergent comprises an alkaline earth hydrocarbyl-substituted hydroxyl-benzoate salt such as a calcium alkylsalicylate salt.

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.

OTHER CO-ADDITIVES

The lubricating oil composition of the invention may comprise further additives. Such additional additives may, for example, include other metal detergents, anti-wear agents such as ZDDP's, anti-oxidants such as aminic or phenolic anti-oxidants, and demulsifiers.

OIL OF LUBRICATING VISCOSITY

The lubricating oils present as a major proportion of the TPEO may range in viscosity from light distillate mineral oils to heavy lubricating oils. Generally, the viscosity of the oil ranges from 2 to 40 mm²/sec, as measured at 100°C.

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 such as by esterification or etherification, constitute another class of known synthetic lubricating oil. 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 oil 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 an esterification and used without further treatment would be an unrefined oil. Refined oils are similar to unrefined oils except that the oil is further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art. Re-refined oils are obtained by processes similar to those used to provide refined oils but begin with oil that has already been used in service. Such re-refined oils are also known as reclaimed or reprocessed oils and are often subjected to additional processing using techniques for removing spent additives and oil breakdown products.

The American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998 categorizes base stocks as follows:

- a) Group I base stocks contain less than 90 percent saturates and/or greater than 0.03 percent sulphur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in the table below.
- b) Group II base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater

than or equal to 80 and less than 120 using the test methods specified in the table below.

c) Group III base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater than or equal to 120 using the test methods specified in the table below.

d) Group IV base stocks are polyalphaolefins (PAO).

e) Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

Analytical test methods for base stock, referred to above, are tabulated below:

PROPERTY	TEST METHOD
Saturates	ASTM D 2007
Viscosity Index	ASTM D 2270
Sulphur	ASTM D 2622
	ASTM D 4294
	ASTM D 4927
	ASTM D 3120

As examples of the above oils, there may be mentioned the Group I and Group II oils. Also, there may be mentioned those of the above oils containing greater than or equal to 90% saturates and less than or equal to 0.03% sulphur as the oil of lubricating viscosity, eg Group II, III, IV or V. They also include base stocks derived from hydrocarbons synthesised by the Fischer-Tropsch process. In the Fischer-Tropsch process, synthesis gas containing carbon monoxide and hydrogen (or 'syngas') is first generated and then converted to hydrocarbons using a Fischer-Tropsch catalyst. These hydrocarbons typically require further processing in order to be useful as a base oil. For example, they may, by methods known in the art, be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed. The syngas may, for example, be made from gas such as natural gas or other gaseous hydrocarbons by steam reforming, when the base stock may be referred

to as gas-to-liquid (“GTL”) base oil; or from gasification of biomass, when the base stock may be referred to as biomass-to-liquid (“BTL” or “BMTL”) base oil; or from gasification of coal, when the base stock may be referred to as coal-to-liquid (“CTL”) base oil.

Preferably, the oil of lubricating viscosity in this invention contains 50 mass % or more said base stocks. It may contain 60, such as 70, 80 or 90, mass % or more of said base stock or a mixture thereof. The oil of lubricating viscosity may be substantially all of said base stock or a mixture thereof.

It may be desirable, although not essential, to prepare one or more additive packages or concentrates comprising additives, whereby additives can be added simultaneously to the oil of lubricating viscosity to form the TPEO.

The final formulations as a trunk piston engine oil may typically contain 30, preferably 10 to 28, more preferably 12 to 24, mass % of the additive package(s), the remainder being the oil of lubricating viscosity. The trunk piston engine oil may have a compositional TBN (using ASTM D2896) of 20 to 60, such as, 30 to 55. For example, it may be 40 to 55 or 35 to 50.

The treat rate of additives contained in the lubricating oil composition may for example be in the range of 1 to 2.5, preferably 2 to 20, more preferably 5 to 18, mass %.

EXAMPLES

The present invention is illustrated by but not limited to the following examples.

TRUNK PISTON ENGINE OILS (TPEO’S)

A set of TPEO’s was formulated comprising two TPEO’s which differed only in that one contained a nitrogen-containing ashless dispersant and the other did not. Each TPEO contained a mixture of overbased calcium salicylate detergents, a mixture

of aminic and phenolic anti-oxidants, and other co-additives. They contained the same base oil to balance. The dispersant was the product of reacting a polyisobutenyl succinic anhydride with a tetraethylene pentamine, and provided the TPEO with 91 ppm by mass of N. The polyisobutenyl moiety had a number average molecular weight of 950.

Each TPEO was tested in a bulk oil oxidation test where the oil was contaminated with 0.5 % HFO (Heavy Fuel Oil) and subjected to oxidising conditions for 120 hours. The test was the DKA oxidation test (CEC L-48-00) in which BN and viscosity change were assessed.

Each TPEO was also tested in the Panel Coker Test which is described as follows:

Panel Coker Test

Lubricating oils may degrade on hot engine surfaces and leave deposits which will affect engine performance; the panel coker test simulates typical conditions and measures the tendency of oils to form such deposits. The oil under test is splashed onto a heated metal plate by spinning a metal comb-like splasher device within a sump containing the oil. At the end of the test period, deposits are measured.

An overview of the test method is as follows:

- 225 ml of the oil is heated in an oil bath to 100°C.
- A heated aluminium panel is located above the oil bath at an incline, maintained at a temperature of 320°C.
- The oil is splashed for 15 seconds against this panel, followed by no splashing for 45 seconds.
- This cycle of intermittent splashing is continued for 1 hour.
- The panel is weighed and the deposits are calculated in grams (g).

Tests were carried out on fresh oil (containing no HFO) and doped oil (containing 2.5 % HFO). Results are expressed on a rating scale of 1-10, where lower values indicate poorer deposits performance.

The results are tabulated below where the example with no dispersant is called “Ref” and the example with the dispersant is called “Inv”.

Example	<u>Panel Coker</u>		<u>DKA</u>	
	Fresh Oil	Doped Oil	BN % Loss	KV100 % Increase
Ref	4.95	3.64	11	17
Inv	6.92	4.29	7	2

The results show that the example of the invention (Inv), which contained dispersant, exhibited both a lower reduction in BN and a lower increase in KV100 than the comparison example (Ref). Also, they show that, where a small amount of dispersant is present, deposit cleanliness in the Panel Coker Test is improved markedly even when the TPEO is contaminated with 2.5% of HFO.

CLAIMS

1. The use of a nitrogen-containing ashless dispersant additive in an amount providing in the range of 50 to 150, preferably 75 to 125, ppm N by mass in a trunk piston marine lubricating oil composition for a medium-speed compression-ignited marine engine, fueled by a heavy fuel oil, and its lubrication by the composition, the composition having a BN in the range of 20 to 60, preferably 30 to 55, the use being to diminish the loss of BN and to diminish the increase in viscosity without adversely affecting deposits performance.
2. The use of a nitrogen-containing ashless dispersant additive in an amount providing in the range of 50 to 150, preferably 75 to 125, ppm N by mass in a trunk piston marine lubricating oil composition for a medium-speed compression-ignited marine engine, fueled by a heavy fuel oil, and its lubrication by the composition, the composition having a BN in the range of 20 to 60, preferably 30 to 55, the use being to diminish the loss of BN and to diminish the increase in viscosity without adversely affecting deposits performance, in comparison with analogous use when the amount of nitrogen-containing ashless dispersant falls outside of the above range.
3. The use of claims 1 or 2, where the composition comprises an oil of lubricating viscosity, containing 50 mass % or more of a basestock containing greater than or equal to 90 % saturates and less than or equal to 0.03 % sulphur.
4. The use of claims 1, 2 or 3, where the composition contains an overbased alkyl-substituted hydroxybenzoate calcium salt detergent additive, such as a calcium salicylate.
5. The use of any of claims 1 to 4, where the composition contains one or more co-additives selected from aminic or phenolic anti-oxidants and from ashless dispersants.

- 6 The use of any of claims 1 to 5, where the dispersant is a hydrocarbyl-substituted succimide, such as a polyalkylene polyamine.
7. The use of claim 6, where the hydrocarbyl group is a polyisobutenyl moiety of number average molecular weight in the range of 400 to 960.