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(54) **Marine engine lubrication**

(57) Lubricant additives comprising as overbased metal hydrocarbyl-substituted hydroxybenzoate detergent dispersed in diluent and a polyalkenyl-substituted carboxylic acid anhydride dispersed in a diluent oil 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 or a mixture thereof are blended, in minor amounts, with a high saturates content oil of lubricating viscosity, in a major amount, to give trunk piston marine engine lubricating oil composition for a medium-speed four-stroke compression-ignited marine engine.

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Description**FIELD OF THE INVENTION**

5 **[0001]** This invention relates to trunk piston marine engine lubrication for a medium-speed four-stroke compression-ignited (diesel) marine engine.

BACKGROUND OF THE INVENTION

10 **[0002]** Marine trunk piston engines generally use Heavy Fuel Oil ('HFO') for offshore running. Heavy Fuel Oil is the heaviest fraction of petroleum distillate and comprises a complex mixture of molecules including up to 15% of asphaltenes, defined as the fraction of petroleum distillate that is insoluble in an excess of aliphatic hydrocarbon (e.g. heptane) but which is soluble in aromatic solvents (e.g. toluene). Asphaltenes can enter the engine lubricant as contaminants either via the cylinder or the fuel pumps and injectors, and asphaltene precipitation can then occur, manifested in 'black paint' or 'black sludge' in the engine. The presence of such carbonaceous deposits on a piston surface can act as an insulating layer which can result in the formation of cracks that then propagate through the piston. If a crack travels through the piston, hot combustion gases can enter the crankcase, possibly resulting in a crankcase explosion.

15 **[0003]** It is therefore highly desirable that trunk piston engine oils ('TPEO's) prevent or inhibit asphaltene precipitation, a problem which becomes more acute when the oil of lubricating viscosity has a higher saturates content. The prior art describes ways of doing this, including use of metal carboxylate detergents. See for example, WO 2008/128656, WO 2010/115594 and WO 2010/115595.

20 **[0004]** The art does not, however, concern itself with the influence of the diluent present in additives on the problem of asphaltene precipitation at higher saturate levels in the oil of lubricating viscosity in a TPEO.

SUMMARY OF THE INVENTION

25 **[0005]** It is now surprisingly found that, when the diluent oil in a polyalkenyl carboxylic acid anhydride additive has greater than or equal to 90% saturates and less than or equal to 0.03% sulphur, a TPEO made therefrom and that includes a hydroxybenzoate detergent additive, has improved asphaltene dispersancy performance when the oil of lubricating viscosity in the TPEO is a high saturates content oil.

30 **[0006]** Thus, a first aspect of the invention is a method of preparing a trunk piston marine engine lubricating oil composition for a medium-speed four-stroke compression-ignited marine engine comprising blending (A) a lubricant additive, in a minor amount, comprising an overbased metal hydrocarbyl-substituted hydroxybenzoate detergent dispersed in diluent and (B) an additive comprising a polyalkenyl-substituted carboxylic acid anhydride as active ingredient dispersed in a diluent oil 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 or a mixture thereof with (C) an oil of lubricating viscosity in a major amount that comprises 50, or 60, mass % or more of a basestock containing greater than or equal to 90 % saturates and less than or equal to 0.03 % sulphur.

35 **[0007]** A second aspect of the invention is a trunk piston marine engine lubricating oil composition for a medium-speed four-stroke compression-ignited marine engine obtainable by the method of the first aspect of the invention.

40 **[0008]** A third aspect of the invention is the use of a lubricant additive as defined in the first aspect of the invention in a trunk piston marine lubricating oil composition for a medium-speed compression-ignited marine engine to improve, or provide similar, asphaltene-handling during operation of said engine, fueled by a heavy-fuel oil, and its lubrication by the composition, in comparison with analogous operation when the additive diluent is a Group I basestock.

45 **[0009]** A fourth aspect of the invention is a method of operating a trunk piston medium-speed compression-ignited marine engine comprising

(i) making a lubricating oil composition by the method of the first aspect of the invention;

50 (ii) fueling the engine with a heavy fuel oil; and

(iii) lubricating the crankcase of the engine with said lubricating oil composition.

55 **[0010]** A fifth aspect of the invention is a lubricant additive comprising (B) as defined in the first aspect of the invention, optionally in combination with (A) as defined in the first aspect of the invention.

[0011] 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 or more mass % of a composition; preferably 60 or more mass % of a composition; more preferably 70 or more mass % of a composition;

"minor amount" means less than 50 mass % of a composition; preferably less than 40 mass % of a composition; more preferably less than 30 mass % of a composition;

"TBN" means total base number as measured by ASTM D2896.

[0012] Furthermore in this specification:

"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;

"KV 100" means kinematic viscosity at 100°C as measured by ASTM D445.

[0013] 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.

[0014] 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

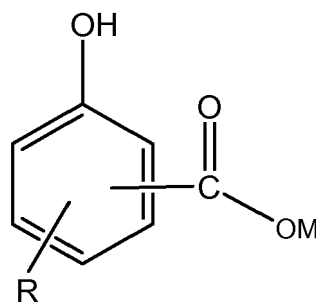
[0015] The features of the invention in its various aspects, if and where applicable, will now be discussed in more detail below.

OVERBASED METAL DETERGENT ADDITIVE (A)

[0016] A metal detergent is an additive based on so-called metal "soaps", that is metal salts of acidic organic compounds, sometimes referred to as surfactants. They generally comprise a polar head with a long hydrophobic tail. Overbased metal detergents, which comprise neutralized metal detergents as the outer layer of a metal base (e.g. carbonate) micelle, may be provided by including large amounts of metal base by reacting an excess of a metal base, such as an oxide or hydroxide, with an acidic gas such as carbon dioxide.

[0017] In the present invention, overbased metal detergents (A) are overbased metal hydrocarbyl-substituted hydroxybenzoate, preferably hydrocarbyl-substituted salicylate, detergents.

[0018] "Hydrocarbyl" means a group or radical that contains carbon and hydrogen atoms and that is bonded to the remainder of the molecule via a carbon atom. It may contain hetero atoms, i.e. atoms other than carbon and hydrogen, provided they do not alter the essentially hydrocarbon nature and characteristics of the group. As examples of hydrocarbyl, there may be mentioned alkyl and alkenyl. The overbased metal hydrocarbyl-substituted hydroxybenzoate typically has the structure shown:



wherein R is a linear or branched aliphatic hydrocarbyl group, and more preferably an alkyl group, including straight- or branched-chain alkyl groups. There may be more than one R group attached to the benzene ring. M is an alkali metal (e.g. lithium, sodium or potassium) or alkaline earth metal (e.g. calcium, magnesium barium or strontium). Calcium or magnesium is preferred; calcium is especially preferred. The COOM group can be in the ortho, meta or para position with respect to the hydroxyl group; the ortho position is preferred. The R group can be in the ortho, meta or para position with respect to the hydroxyl group. When M is polyvalent, it is represented fractionally in the above formula.

[0019] Hydroxybenzoic acids are typically prepared by the carboxylation, by the Kolbe-Schmitt process, of phenoxides, and in that case, will generally be obtained (normally in a diluent) in admixture with uncarboxylated phenol. Hydroxybenzoic acids may be non-sulphurized or sulphurized, and may be chemically modified and/or contain additional substituents. Processes for sulphurizing a hydrocarbyl-substituted hydroxybenzoic acid are well known to those skilled in the art and are described, for example, in US 2007/0027057.

[0020] In hydrocarbyl-substituted hydroxybenzoic acids, the hydrocarbyl group is preferably alkyl (including straight- or branched-chain alkyl groups), and the alkyl groups advantageously contain 5 to 100, preferably 9 to 30, especially 14 to 24, carbon atoms.

[0021] The term "overbased" is generally used to describe metal detergents in which the ratio of the number of equivalents of the metal moiety to the number of equivalents of the acid moiety is greater than one. The term "low-based" is used to describe metal detergents in which the equivalent ratio of metal moiety to acid moiety is greater than 1, and up to about 2.

[0022] By an "overbased calcium salt of surfactants" is meant an overbased detergent in which the metal cations of the oil-insoluble metal salt are essentially calcium cations. Small amounts of other cations may be present in the oil-insoluble metal salt, but typically at least 80, more typically at least 90, for example at least 95, mole % of the cations in the oil-insoluble metal salt are calcium ions. Cations other than calcium may be derived, for example, from the use in the manufacture of the overbased detergent of a surfactant salt in which the cation is a metal other than calcium. Preferably, the metal salt of the surfactant is also calcium.

[0023] Carbonated overbased metal detergents typically comprise amorphous nanoparticles. Additionally, there are disclosures of nanoparticulate materials comprising carbonate in the crystalline calcite and vaterite forms.

[0024] The basicity of the detergents may be expressed as a total base number (TBN). A total base number is the amount of acid needed to neutralize all of the basicity of the overbased material. The TBN may be measured using ASTM standard D2896 or an equivalent procedure. The detergent may have a low TBN (i.e. a TBN of less than 50), a medium TBN (i.e. a TBN of 50 to 150) or a high TBN (i.e. a TBN of greater than 150, such as 150-500). In this invention, Basicity Index is used. Basicity Index is the molar ratio of total base to total soap in the overbased detergent. The Basicity Index of the detergent (A) in the invention is preferably in the range of 1 to 8, more preferably 3 to 8, such as 3 to 7, such as 3 to 6. The Basicity Index may for example be greater than 3.

[0025] Overbased metal hydrocarbyl-substituted hydroxybenzoates can be prepared by any of the techniques employed in the art. A general method is as follows:

1. Neutralisation of hydrocarbyl-substituted hydroxybenzoic acid with a molar excess of metallic base to produce a slightly overbased metal hydrocarbyl-substituted hydroxybenzoate complex, in a solvent mixture consisting of a volatile hydrocarbon, an alcohol and water;
2. Carbonation to produce colloiddally-dispersed metal carbonate followed by a post-reaction period;
3. Removal of residual solids that are not colloiddally dispersed; and
4. Stripping to remove process solvents.

[0026] Overbased metal hydrocarbyl-substituted hydroxybenzoates can be made by either a batch or a continuous overbasing process.

[0027] Metal base (e.g. metal hydroxide, metal oxide or metal alkoxide), preferably lime (calcium hydroxide), may be

charged in one or more stages. The charges may be equal or may differ, as may the carbon dioxide charges which follow them. When adding a further calcium hydroxide charge, the carbon dioxide treatment of the previous stage need not be complete. As carbonation proceeds, dissolved hydroxide is converted into colloidal carbonate particles dispersed in the mixture of volatile hydrocarbon solvent and non-volatile hydrocarbon oil.

[0028] Carbonation may be effected in one or more stages over a range of temperatures up to the reflux temperature of the alcohol promoters. Addition temperatures may be similar, or different, or may vary during each addition stage. Phases in which temperatures are raised, and optionally then reduced, may precede further carbonation steps.

[0029] The volatile hydrocarbon solvent of the reaction mixture is preferably a normally liquid aromatic hydrocarbon having a boiling point not greater than about 150°C. Aromatic hydrocarbons have been found to offer certain benefits, e.g. improved filtration rates, and examples of suitable solvents are toluene, xylene, and ethyl benzene.

[0030] The alkanol is preferably methanol although other alcohols such as ethanol can be used. Correct choice of the ratio of alkanol to hydrocarbon solvents, and the water content of the initial reaction mixture, are important to obtain the desired product.

[0031] Oil may be added to the reaction mixture; if so, suitable oils include hydrocarbon oils, particularly those of mineral origin. Oils which have viscosities of 15 to 30 mm²/sec at 38°C are very suitable.

[0032] After the final treatment with carbon dioxide, the reaction mixture is typically heated to an elevated temperature, e.g. above 130°C, to remove volatile materials (water and any remaining alkanol and hydrocarbon solvent). When the synthesis is complete, the raw product is hazy as a result of the presence of suspended sediments. It is clarified by, for example, filtration or centrifugation. These measures may be used before, or at an intermediate point, or after solvent removal.

[0033] The products are used as a diluent (or oil) dispersion. If the reaction mixture contains insufficient oil to retain an oil solution after removal of the volatiles, further oil should be added. This may occur before, or at an intermediate point, or after solvent removal.

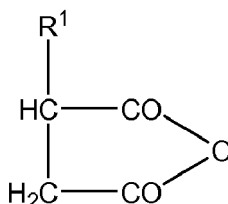
[0034] Preferably, the diluent used for (A) comprises a basestock containing greater than or equal to 90% saturates and less than or equal to 0.03% sulphur. (A) may contain up to 20, 30, 40, 50, 60, 70, 80 or 90, mass% or more (such as all) of said basestock. An example of said basestock is a Group II basestock.

POLYALKENYL-SUBSTITUTED CARBOXYLIC ACID ANHYDRIDE (B)

[0035] The anhydride may constitute at least 1 to 7, such as 1.5 to 5, mass % of the lubricating oil composition. Preferably it constitutes 2 to 5, for example 3 to 5, mass %.

[0036] The anhydride may be mono or polycarboxylic, preferably dicarboxylic. The polyalkenyl group preferably has from 8 to 400, such as 8 to 100, carbon atoms.

[0037] General formulae of exemplary anhydrides may be depicted as



where R¹ represents a C₈ to C₁₀₀ branched or linear polyalkenyl group:

[0038] The polyalkenyl moiety may have a number average molecular weight of from 200 to 3000, preferably from 350 to 950.

[0039] Suitable hydrocarbons or polymers employed in the formation of the anhydrides of the present invention to generate the polyalkenyl moieties include homopolymers, interpolymers or lower molecular weight hydrocarbons. One family of such polymers comprise polymers of ethylene and/or at least one C₃ to C₂₈ alpha-olefin having the formula H₂C=CHR¹ wherein R¹ is straight or branched chain alkyl radical comprising 1 to 26 carbon atoms and wherein the polymer contains carbon-to-carbon unsaturation, preferably a high degree of terminal ethenylidene unsaturation. Preferably, such polymers comprise interpolymers of ethylene and at least one alpha-olefin of the above formula, wherein R¹ is alkyl of from 1 to 18 carbon atoms, and more preferably is alkyl of from 1 to 8 carbon atoms, and more preferably still of from 1 to 2 carbon atoms. Therefore, useful alpha-olefin monomers and comonomers include, for example, propylene, butene-1, hexene-1, octene-1, 4-methylpentene-1, decene-1, dodecene-1, tridecene-1, tetradecene-1, pentadecene-1, hexadecene-1, heptadecene-1, octadecene-1, nonadecene-1, and mixtures thereof (e.g., mixtures of propylene and butene-1, and the like). Exemplary of such polymers are propylene homopolymers, butene-1 homopolymers, ethylene-propylene copolymers, ethylene-butene-1 copolymers, propylene-butene copolymers and the like, wherein the

polymer contains at least some terminal and/or internal unsaturation. Preferred polymers are unsaturated copolymers of ethylene and propylene and ethylene and butene-1. The interpolymers may contain a minor amount, e.g. 0.5 to 5 mole % of a C₄ to C₁₈ nonconjugated diolefin comonomer. However, it is preferred that the polymers comprise only alpha-olefin homopolymers, interpolymers of alpha-olefin comonomers and interpolymers of ethylene and alpha-olefin comonomers. The molar ethylene content of the polymers employed is preferably in the range of 0 to 80 %, and more preferably 0 to 60 %. When propylene and/or butene-1 are employed as comonomer(s) with ethylene, the ethylene content of such copolymers is most preferably between 15 and 50 %, although higher or lower ethylene contents may be present.

[0040] These polymers may be prepared by polymerizing alpha-olefin monomer, or mixtures of alpha-olefin monomers, or mixtures comprising ethylene and at least one C₃ to C₂₈ alpha-olefin monomer, in the presence of a catalyst system comprising at least one metallocene (e.g., a cyclopentadienyl-transition metal compound) and an alumoxane compound. Using this process, a polymer in which 95 % or more of the polymer chains possess terminal ethenylidene-type unsaturation can be provided. The percentage of polymer chains exhibiting terminal ethenylidene unsaturation may be determined by FTIR spectroscopic analysis, titration, or C¹³ NMR. Interpolymers of this latter type may be characterized by the formula POLY-C(R¹)=CH₂ wherein R¹ is C₁ to C₂₆ alkyl, preferably C₁ to C₁₈ alkyl, more preferably C₁ to C₈ alkyl, and most preferably C₁ to C₂ alkyl, (e.g., methyl or ethyl) and wherein POLY represents the polymer chain. The chain length of the R¹ alkyl group will vary depending on the comonomer(s) selected for use in the polymerization. A minor amount of the polymer chains can contain terminal ethenyl, i.e., vinyl, unsaturation, i.e. POLY-CH=CH₂, and a portion of the polymers can contain internal monounsaturated, e.g. POLY-CH=CH(R¹), wherein R¹ is as defined above. These terminally-unsaturated interpolymers may be prepared by known metallocene chemistry and may also be prepared as described in U.S. Patent Nos. 5,498,809; 5,663,130; 5,705,577; 5,814,715; 6,022,929 and 6,030,930.

[0041] Another useful class of polymers is polymers prepared by cationic polymerization of isobutene, styrene, and the like. Common polymers from this class include polyisobutenes obtained by polymerization of a C₄ refinery stream having a butene content of about 35 to about 75 mass %, and an isobutene content of about 30 to about 60 mass %, in the presence of a Lewis acid catalyst, such as aluminum trichloride or boron trifluoride. A preferred source of monomer for making poly-n-butenes is petroleum feedstreams such as Raffinate II. These feedstocks are disclosed in the art such as in U.S. Patent No. 4,952,739. Polyisobutylene is a most preferred backbone of the present invention because it is readily available by cationic polymerization from butene streams (e.g., using AlCl₃ or BF₃ catalysts). Such polyisobutylenes generally contain residual unsaturation in amounts of about one ethylenic double bond per polymer chain, positioned along the chain. A preferred embodiment utilizes polyisobutylene prepared from a pure isobutylene stream or a Raffinate I stream to prepare reactive isobutylene polymers with terminal vinylidene olefins. Preferably, these polymers, referred to as highly reactive polyisobutylene (HR-PIB), have a terminal vinylidene content of at least 65%, e.g., 70%, more preferably at least 80%, most preferably, at least 85%. The preparation of such polymers is described, for example, in U.S. Patent No. 4,152,499. HR-PIB is known and HR-PIB is commercially available under the tradenames Glissopal™ (from BASF) and Ultravis™ (from BP-Amoco).

[0042] Polyisobutylene polymers that may be employed are generally based on a hydrocarbon chain of from 400 to 3000. Methods for making polyisobutylene are known. Polyisobutylene can be functionalized by halogenation (e.g. chlorination), the thermal "ene" reaction, or by free radical grafting using a catalyst (e.g. peroxide), as described below.

[0043] To produce (B) the hydrocarbon or polymer backbone may be functionalized, with carboxylic anhydride-producing moieties selectively at sites of carbon-to-carbon unsaturation on the polymer or hydrocarbon chains, or randomly along chains using any of the three processes mentioned above or combinations thereof, in any sequence.

[0044] Processes for reacting polymeric hydrocarbons with unsaturated carboxylic, anhydrides and the preparation of derivatives from such compounds are disclosed in U.S. Patent Nos. 3,087,936; 3,172,892; 3,215,707; 3,231,587; 3,272,746; 3,275,554; 3,381,022; 3,442,808; 3,565,804; 3,912,764; 4,110,349; 4,234,435; 5,777,025; 5,891,953; as well as EP 0 382 450 B1; CA-1,335,895 and GB-A-1,440,219. The polymer or hydrocarbon may be functionalized, with carboxylic acid anhydride moieties by reacting the polymer or hydrocarbon under conditions that result in the addition of functional moieties or agents, i.e., acid, anhydride, onto the polymer or hydrocarbon chains primarily at sites of carbon-to-carbon unsaturation (also referred to as ethylenic or olefinic unsaturation) using the halogen assisted functionalization (e.g. chlorination) process or the thermal "ene" reaction.

[0045] Selective functionalization can be accomplished by halogenating, e.g., chlorinating or brominating the unsaturated α -olefin polymer to about 1 to 8 mass %, preferably 3 to 7 mass % chlorine, or bromine, based on the weight of polymer or hydrocarbon, by passing the chlorine or bromine through the polymer at a temperature of 60 to 250°C, preferably 110 to 160°C, e.g., 120 to 140°C, for about 0.5 to 10, preferably 1 to 7 hours. The halogenated polymer or hydrocarbon (hereinafter backbone) is then reacted with sufficient monounsaturated reactant capable of adding the required number of functional moieties to the backbone, e.g., monounsaturated carboxylic reactant, at 100 to 250°C, usually about 180°C to 235°C, for about 0.5 to 10, e.g., 3 to 8 hours, such that the product obtained will contain the desired number of moles of the monounsaturated carboxylic reactant per mole of the halogenated backbones. Alternatively, the backbone and the monounsaturated carboxylic reactant are mixed and heated while adding chlorine to the

hot material.

[0046] While chlorination normally helps increase the reactivity of starting olefin polymers with monounsaturated functionalizing reactant, it is not necessary with some of the polymers or hydrocarbons contemplated for use in the present invention, particularly those preferred polymers or hydrocarbons which possess a high terminal bond content and reactivity. Preferably, therefore, the backbone and the monounsaturated functionality reactant, (carboxylic reactant), are contacted at elevated temperature to cause an initial thermal "ene" reaction to take place. Ene reactions are known.

[0047] The hydrocarbon or polymer backbone can be functionalized by random attachment of functional moieties along the polymer chains by a variety of methods. For example, the polymer, in solution or in solid form, may be grafted with the monounsaturated carboxylic reactant, as described above, in the presence of a free-radical initiator. When performed in solution, the grafting takes place at an elevated temperature in the range of about 100 to 260°C, preferably 120 to 240°C. Preferably, free-radical initiated grafting would be accomplished in a mineral lubricating oil solution containing, e.g., 1 to 50 mass %, preferably 5 to 30 mass % polymer based on the initial total oil solution.

[0048] The free-radical initiators that may be used are peroxides, hydroperoxides, and azo compounds, preferably those that have a boiling point greater than about 100°C and decompose thermally within the grafting temperature range to provide free-radicals. Representative of these free-radical initiators are azobutyronitrile, 2,5-dimethylhex-3-ene-2, 5-bis-tertiary-butyl peroxide and dicumene peroxide. The initiator, when used, typically is used in an amount of between 0.005% and 1% by weight based on the weight of the reaction mixture solution. Typically, the aforesaid monounsaturated carboxylic reactant material and free-radical initiator are used in a weight ratio range of from about 1.0:1 to 30:1, preferably 3:1 to 6:1. The grafting is preferably carried out in an inert atmosphere, such as under nitrogen blanketing. The resulting grafted polymer is characterized by having carboxylic acid (or derivative) moieties randomly attached along the polymer chains: it being understood, of course, that some of the polymer chains remain ungrafted. The free radical grafting described above can be used for the other polymers and hydrocarbons of the present invention.

[0049] The preferred monounsaturated reactants that are used to functionalize the backbone comprise mono- and dicarboxylic acid material, i.e., acid, or acid derivative material, including (i) monounsaturated C₄ to C₁₀ dicarboxylic acid wherein (a) the carboxyl groups are vicinyl, (i.e., located on adjacent carbon atoms) and (b) at least one, preferably both, of said adjacent carbon atoms are part of said mono unsaturation; (ii) derivatives of (i) such as anhydrides or C₁ to C₅ alcohol derived mono- or diesters of (i); (iii) monounsaturated C₃ to C₁₀ monocarboxylic acid wherein the carbon-carbon double bond is conjugated with the carboxy group, i.e., of the structure -C=C-CO-; and (iv) derivatives of (iii) such as C₁ to C₅ alcohol derived mono- or diesters of (iii). Mixtures of monounsaturated carboxylic materials (i) - (iv) also may be used. Upon reaction with the backbone, the monounsaturated of the monounsaturated carboxylic reactant becomes saturated. Thus, for example, maleic anhydride becomes backbone-substituted succinic anhydride, and acrylic acid becomes backbone-substituted propionic acid. Exemplary of such monounsaturated carboxylic reactants are fumaric acid, itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, chloromaleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, and lower alkyl (e.g., C₁ to C₄ alkyl) acid esters of the foregoing, e.g., methyl maleate, ethyl fumarate, and methyl fumarate.

[0050] To provide the required functionality, the monounsaturated carboxylic reactant, preferably maleic anhydride, typically will be used in an amount ranging from about equimolar amount to about 100 mass % excess, preferably 5 to 50 mass % excess, based on the moles of polymer or hydrocarbon. Unreacted excess monounsaturated carboxylic reactant can be removed from the final dispersant product by, for example, stripping, usually under vacuum, if required.

[0051] The diluent used for (B) comprises a basestock containing greater than or equal to 90% saturates and less than or equal to 0.03% sulphur. (B) may contain up to 20, 30, 40, 50, 60, 70, 80 or 90 mass% or more (such as all) of said basestock. An example of said basestock is a Group II basestock.

OIL OF LUBRICATING VISCOSITY (C)

[0052] The 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 mm²/sec, as measured at 100°C.

[0053] 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.

[0054] Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized 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, analogs and homologs thereof.

[0055] 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.

[0056] 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.

[0057] 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.

[0058] 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 phosphorous-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

[0059] 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.

[0060] 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 Table E-1.

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 Table E-1.

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 Table E-1.

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.

[0061] Analytical Methods for Base Stock are tabulated below:

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

(continued)

PROPERTY	TEST METHOD
	ASTM D 4927
	ASTM D 3120

[0062] The present invention embraces 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 basestocks 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 basestock may be referred to as gas-to-liquid ("GTL") base oil; or from gasification of biomass, when the basestock may be referred to as biomass-to-liquid ("BTL" or "BMTL") base oil; or from gasification of coal, when the basestock may be referred to as coal-to-liquid ("CTL") base oil.

[0063] Preferably, the oil of lubricating viscosity in this invention contains 50 mass % or more said basestocks. It may contain 60, such as 70, 80 or 90, mass % or more of said basestock or a mixture thereof. The oil of lubricating viscosity may be substantially all of said basestock or a mixture thereof.

[0064] It may be desirable, although not essential, to prepare one or more additive packages or concentrates comprising additives, whereby additives (A) and (B) can be added simultaneously to the oil of lubricating viscosity (C) to form the TPEO.

[0065] 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. When the TBN is high, for example 45-55, the concentration of (A) may be higher. When the TBN is lower, for example 30 to below 45, the concentration of (A) may be lower.

[0066] The treat rate of additives (A) and (B) 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 %.

CO-ADDITIVES

[0067] The lubricating oil composition of the invention may comprise further additives, different from and additional to (A) and (B). Such additional additives may, for example include ashless dispersants, other metal detergents, anti-wear agents such as zinc dihydrocarbyl dithiophosphates, anti-oxidants and demulsifiers.

EXAMPLES

[0068] The present invention is illustrated by but in no way limited to the following examples.

COMPONENTS

[0069] The following components and oils were used:

Component (A):

[0070] A set of overbased calcium salicylate detergents comprising a mixture of a detergent having a basicity index of 8.0 and a detergent having a basicity index of 3.0 where the diluents were respectively SN 150 (Group I, as a reference), and various Group II basestocks as identified in the RESULTS tables below.

[0071] The detergents were made by solvent exchange between the solvent present in production (e.g. xylene) and the above-mentioned diluents.

Component (B):

[0072] A set of polyisobutene succinic anhydrides ("PIBSA") derived from a polyisobutene having a number average molecular weight of 950, comprising 20% diluent in the form of SN150 (Group I as a reference) and various Group II

basestocks as identified in the RESULTS tables below.

Oils of Lubricating Viscosity (C):

[0073]

Oil I: an API Group I base oil known as XOM 600

Oil II: an API Group II 600R basestock from Chevron

Heavy Fuel Oil:

[0074] A heavy fuel oil, ISO-F-RMK 380.

LUBRICANTS

[0075] Selections of the above components were blended with a major proportion of oil of lubricating viscosity (C) to give a range of trunk piston marine engine lubricants. Some of the lubricants are examples of the invention; others are reference examples for comparison purposes. The compositions of the lubricants tested when each contained HFO are shown in the tables below under the "Results" heading

TESTING

Light Scattering

[0076] The test lubricants were evaluated for asphaltene dispersancy using light scattering according to the Focused Beam Reflectance Method ("FBRM"), which predicts asphaltene agglomeration and hence 'black sludge' formation.

[0077] The FBRM test method was disclosed at the 7th International Symposium on Marine Engineering, Tokyo, 24th - 28th October 2005, and was published in 'The Benefits of Salicylate Detergents in TPEO Applications with a Variety of Base Stocks', in the Conference Proceedings. Further details were disclosed at the CIMAC Congress, Vienna, 21st - 24th May 2007 and published in "Meeting the Challenge of New Base Fluids for the Lubrication of Medium Speed Marine Engines - An Additive Approach" in the Congress Proceedings. In the latter paper it is disclosed that by using the FBRM method it is possible to obtain quantitative results for asphaltene dispersancy that predict performance for lubricant systems based on base stocks containing greater than or less than 90% saturates, and greater than or less than 0.03% sulphur. The predictions of relative performance obtained from FBRM were confirmed by engine tests in marine diesel engines.

[0078] The FBRM probe contains fibre optic cables through which laser light travels to reach the probe tip. At the tip, an optic focuses the laser light to a small spot. The optic is rotated so that the focussed beam scans a circular path between the window of the probe and the sample. As particles flow past the window they intersect the scanning path, giving backscattered light from the individual particles.

[0079] The scanning laser beam travels much faster than the particles; this means that the particles are effectively stationary. As the focussed beam reaches one edge of the particle there is an increase in the amount of backscattered light; the amount will decrease when the focussed beam reaches the other edge of the particle.

[0080] The instrument measures the time of the increased backscatter. The time period of backscatter from one particle is multiplied by the scan speed and the result is a distance or chord length. A chord length is a straight line between any two points on the edge of a particle. This is represented as a chord length distribution, a graph of numbers of chord lengths (particles) measured as a function of the chord length dimensions in microns. As the measurements are performed in real time the statistics of a distribution can be calculated and tracked. FBRM typically measures tens of thousands of chords per second, resulting in a robust number-by-chord length distribution. The method gives an absolute measure of the particle size distribution of the asphaltene particles.

[0081] The Focused beam Reflectance Probe (FBRM), model Lasentec D600L, was supplied by Mettler Toledo, Leicester, UK. The instrument was used in a configuration to give a particle size resolution of 1 μm to 1mm. Data from FBRM can be presented in several ways. Studies have suggested that the average counts per second can be used as a quantitative determination of asphaltene dispersancy. This value is a function of both the average size and level of agglomerate. In this application, the average count rate (over the entire size range) was monitored using a measurement time of 1 second per sample.

[0082] The test lubricant formulations were heated to 60°C and stirred at 400rpm; when the temperature reached 60°C the FBRM probe was inserted into the sample and measurements made for 15 minutes. An aliquot of heavy fuel oil

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(10% w/w) was introduced into the lubricant formulation under stirring using a four blade stirrer (at 400 rpm). A value for the average counts per second was taken when the count rate had reached an equilibrium value (typically overnight).

RESULTS

Light Scattering

[0083] Results of the FBRM tests are summarized in the tables below (TABLES 1 and 2).

[0084] In TABLE 1, each TPEO had a BN of 30 and comprised 0.56% of calcium salicylate of BI 8.0, 0.51% of calcium salicylate of BI 3.0, 0.73% of a Group I diluent (for the detergent), and 0.03% Zn.

TABLE 1

Ex	PIBSA (% active matter)	PIBSA Diluent and % Saturates	Oil of Lubricating Viscosity (C) (Group II)	Lasentec (Counts)
1	4.00	RLOP100/96	83.10	1894.94
2	4.00	Etro 4/96	83.10	1903.50
3	4.00	Nexbase 3043/95	83.10	2026.35
4	4.00	Durasyn 41/98	83.10	2144.54
5	4.00	Yubase 4/98	83.10	2222.15
6	4.00	Jurong 150/95	83.10	2862.79
7	4.00	Spectrasyn 4/98	83.10	2913.87
8	4.00	Priolube 3970/100	83.10	2982.07
Ref 1	4.00	SN150/70	83.10	3233.67
Control 1	-	-	88.10	6793.31

[0085] The results are given in particle counts where a lower value indicates better performance. The Control (lacking PIBSA) gave the worst result. Ref 1, using PIBSA in a Group I diluent, gave a better result. Best results were exhibited by Examples 1-8, each of which used PIBSA in a high saturate diluent.

[0086] In Table 2, each TPEO had a BN of 40 and comprised 0.75% of calcium salicylate of B1 8.0, 0.68% of calcium salicylate of B1 3.0, and 0.04% Zn. The total additive diluent was 0.98% and was either entirely Group I (SN150) or entirely high saturate (Jurong 150 or Chevron 100).

TABLE2

Ex	PIBSA (% active matter)	Oil of Lubricating (C)	Lasentec (counts)	
			Group I diluent	High saturate diluent
Ref2	0	84.10	7578.11	4027.04
9	0.80	83.10	8231.84	4096.64
10	1.60	82.10	6248.28	1544.70
11	2.40	81.10	3608.86	2338.28
12	3.20	80.10	2704.36	907.70
13	4.00	79.10	2395.59	484.70
14	4.80	78.10	1972.86	262.10

[0087] The results show that performance generally improves as the PIBSA active matter % increases, but that the improvement is much more significant when the additive diluent is a high saturate oil.

Claims

1. A method of preparing a trunk piston marine engine lubricating oil composition for a medium-speed four-stroke compression-ignited marine engine comprising blending (A) a lubricant additive, in a minor amount, comprising an overbased metal hydrocarbyl-substituted hydroxybenzoate detergent dispersed in diluent and (B) an additive comprising a polyalkenyl-substituted carboxylic acid anhydride as active ingredient dispersed in a diluent oil 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 or a mixture thereof with (C) an oil of lubricating viscosity in a major amount that comprises 50, or 60, mass % or more of a basestock containing greater than or equal to 90 % saturates and less than or equal to 0.03 % sulphur.
2. The method of claim 1 where the metal is calcium.
3. The method of claim 1 or claim 2 where the hydrocarbyl-substituted hydroxybenzoate is a salicylate.
4. The method of any of claims 1 to 3 where the hydrocarbyl group has from 8 to 400, such as 12 to 100, especially 16 to 64, carbon atoms.
5. The method of any of claims 1 to 4 where the diluent oil in which (B) is dispersed comprises 60 mass % or more of the basestock containing greater than or equal to 90 % saturates and less than or equal to 0.03 % sulphur or a mixture thereof.
6. The method of claim 5 where the diluent oil in which (B) is dispersed consists of or consists essentially of the basestock containing greater than or equal to 90 % saturates and less than or equal to 0.03 % sulphur or a mixture thereof.
7. The method of any of claims 1 to 6 where the basestock is a Group II, III, IV or V basestock.
8. The method as claimed in any of claims 1 to 7 where the polyalkenyl substituent in (B) has from 8 to 400, such as 12 to 100, especially 16 to 64, carbon atoms.
9. The method as claimed in any of claims 1 to 8 where the polyalkenyl substituent in (B) has a number average molecular weight of from 350 to 1000, such as from 500 to 1000.
10. The method as claimed in any of claims 1 to 9 where the polyalkenyl-substituted carboxylic acid anhydride derivative, (B), is a succinic anhydride.
11. The method as claimed in claim 10 where (B) is a polyisobutene succinic acid or anhydride.
12. The method of any of claims 1 to 11 where the diluent in (A) comprises 50, or 60, mass % or more of a basestock containing greater than or equal to 90 % saturates and less than or equal to 0.03 % sulphur.
13. The method of any of claims 1 to 12 where the composition has a TBN of 20 to 60, such as 25 to 55.
14. The method of any of claims 1 to 13 where the basestock in the oil of lubricating viscosity (C) is a Group II, III, IV or V basestock.
15. A trunk piston marine engine lubricating oil composition for a medium-speed four-stroke compression-ignited marine engine obtainable by the method of any of claims 1 to 14.
16. The use of an additive as defined in any of claims 1 to 14 in a trunk piston marine lubricating oil composition for a medium-speed compression-ignited marine engine to provide asphaltene-handling during operation of said engine.
17. The use of an additive as defined in any of claims 1 to 14 in a trunk piston marine lubricating oil composition for a medium-speed compression-ignited marine engine to provide asphaltene-handling during operation of said engine, fueled by a heavy-fuel oil, and its lubrication by the composition, in comparison with analogous operation when the additive diluent is a Group I basestock.

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18. The use of claim 16 or 17 where the lubricating oil composition comprises a major amount of an oil of lubricating viscosity comprising 50 mass % or more of a basestock containing greater than or equal to 90 % saturates and less than or equal to 0.03 % sulphur.

5 **19.** The use of claim 17 where the basestock is a Group II, III, IV or V basestock.

20. A method of operating a trunk piston medium-speed compression-ignited marine engine comprising

- 10 (i) making a lubricating oil composition by the method of any of claims 1 to 14.
(ii) fuelling the engine with a heavy fuel oil; and
(iii) lubricating the crankcase of the engine with said lubricating oil composition.

21. A lubricant additive (B) as defined in any of claims 1, 8, 9 and 10.

15 **22.** A lubricant additive (B) as defined in claim 21 in combination or admixture with a lubricant additive (A) as defined in any of claims 1 to 4.

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EUROPEAN SEARCH REPORT

 Application Number
 EP 14 15 0317

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D A	WO 2010/115594 A1 (INFINEUM INT LTD [GB]; GARNER TERRY [GB]; GREGORY LAURA [GB]; HARTLEY) 14 October 2010 (2010-10-14) * pages 11,12,17 - page 24; claims 1,4,5,6,9,10,11,12,13; tables 1,2,3,4 * -----	15-19, 21,22 1-14,20	INV. C10M169/04
			TECHNICAL FIELDS SEARCHED (IPC)
			C10M
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 18 March 2014	Examiner Pöllmann, Klaus
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

 1
 EPO FORM 1503 03.82 (P04001)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 14 15 0317

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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45

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55

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010115594 A1	14-10-2010	AU 2010234299 A1	27-10-2011
		AU 2010234300 A1	27-10-2011
		CA 2755308 A1	14-10-2010
		CA 2755815 A1	14-10-2010
		CN 102365352 A	29-02-2012
		CN 102365353 A	29-02-2012
		EP 2417233 A1	15-02-2012
		EP 2417234 A1	15-02-2012
		ES 2425957 T3	18-10-2013
		ES 2428237 T3	06-11-2013
		JP 2012522878 A	27-09-2012
		JP 2012522879 A	27-09-2012
		KR 20120006995 A	19-01-2012
		KR 20120027208 A	21-03-2012
		SG 174925 A1	28-11-2011
		SG 175117 A1	28-11-2011
		US 2012028521 A1	02-02-2012
		US 2012028522 A1	02-02-2012
		WO 2010115594 A1	14-10-2010
		WO 2010115595 A1	14-10-2010

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2008128656 A [0003]
- WO 2010115594 A [0003]
- WO 2010115595 A [0003]
- US 20070027057 A [0019]
- US 5498809 A [0040]
- US 5663130 A [0040]
- US 5705577 A [0040]
- US 5814715 A [0040]
- US 6022929 A [0040]
- US 6030930 A [0040]
- US 4952739 A [0041]
- US 4152499 A [0041]
- US 3087936 A [0044]
- US 3172892 A [0044]
- US 3215707 A [0044]
- US 3231587 A [0044]
- US 3272746 A [0044]
- US 3275554 A [0044]
- US 3381022 A [0044]
- US 3442808 A [0044]
- US 3565804 A [0044]
- US 3912764 A [0044]
- US 4110349 A [0044]
- US 4234435 A [0044]
- US 5777025 A [0044]
- US 5891953 A [0044]
- EP 0382450 B1 [0044]
- CA 1335895 [0044]
- GB 1440219 A [0044]

Non-patent literature cited in the description

- Engine Oil Licensing and Certification System. The American Petroleum Institute, December 1996 [0060]
- 7th International Symposium on Marine Engineering, 24 October 2005 [0077]
- The Benefits of Salicylate Detergents in TPEO Applications with a Variety of Base Stocks. *the Conference Proceedings*, 21 May 2007 [0077]
- Meeting the Challenge of New Base Fluids for the Lubrication of Medium Speed Marine Engines - An Additive Approach. *Congress Proceedings* [0077]