(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 049 629 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
08.10.2014 Bulletin 2014/41

(21) Application number: **07799977.9**

(22) Date of filing: **02.08.2007**

(51) Int Cl.:
C10M 129/26 (2006.01)
C10M 129/93 (2006.01)
C10M 163/00 (2006.01)
C10N 20/04 (2006.01)
C10N 20/02 (2006.01)
C10N 30/02 (2006.01)
C10N 30/04 (2006.01)
C10N 40/25 (2006.01)
C10N 40/26 (2006.01)

(86) International application number:
PCT/US2007/075045

(87) International publication number:
WO 2008/021737 (21.02.2008 Gazette 2008/08)

(54) A METHOD OF LUBRICATING AN INTERNAL COMBUSTION ENGINE

VERFAHREN ZUM SCHMIEREN EINER BRENNKRAFTMASCHINE

PROCÉDÉ DE LUBRIFICATION D'UN MOTEUR À COMBUSTION INTERNE

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE SI SK TR

(30) Priority: **07.08.2006 US 821586 P**

(43) Date of publication of application:
22.04.2009 Bulletin 2009/17

(73) Proprietor: **The Lubrizol Corporation**
Wickliffe, OH 44092-2298 (US)

(72) Inventors:
- **MAYHEW, Alexandria**
Belper, Derby DE56 1QN (GB)
- **COOK, Stephen, J.**
Belper, Derby DE56 1QN (GB)

(74) Representative: **Mallalieu, Catherine Louise et al**
D Young & Co LLP
120 Holborn
London EC1N 2DY (GB)

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Printed by Jouve, 75001 PARIS (FR)

Description

FIELD OF INVENTION

[0001] The present invention relates to the use of at least 0.5 wt % of a carboxylic acid or anhydride thereof as an oil thickener for a 2-stroke marine diesel cylinder lubricating composition, wherein the carboxylic acid or anhydride thereof has a hydrocarbyl group of at least 10 carbon atoms.

BACKGROUND OF THE INVENTION

[0002] Lubricant compositions are known to provide a lubricating oil film between different components within an internal combustion engine. The lubricating oil film is known to help provide protection to improve oxidative and thermal stability, to help reduce corrosive and adhesive wear. In addition the lubricant compositions help impart cleanliness to the engine. One of the important features that lubricants have that help in protecting the engine is the lubricating oil film "thickness," i.e., viscosity. However, for a lubricant to perform at an optimum level, the oil film thickness has to provide a balance between being thin enough to spread efficiently over a surface but yet thick enough to provide a continuous film that does not readily evaporate when exposed to engine operating temperatures.

[0003] Control of lubricant thickness has been achieved by employing a wide variety of polymeric viscosity modifiers and/or bright stock. Polymeric viscosity modifiers include, for example, polymethacrylates, polyolefins and polyisobutylenes. International Publication WO 99/64543, for example, discloses diesel cylinder oil having a viscosity index of at least 95 and a total base number of at least 40 mg KOH/g. The oil further contains 1 wt % to 20 wt % of a liquid polyisobutylene having a viscosity from 1500 to 8000 mm^2/s at 100 °C. However, viscosity modifiers are believed to increase piston deposit levels.

[0004] Bright Stock is a lubricating oil component of high viscosity typically obtained from residues of petroleum distillation. Bright stock has been utilized in many lubricants, particularly those requiring SAE 40 or SAE 50 (16.3 mm^2/s to 21.9 mm^2/s) viscosities, bright stock is believed to provide a lubricant with reduced oxidative or thermal stability. However, the availability of bright stock is diminishing, resulting in high volume uses such as those for 2-stroke or 4-stroke marine or stationary power engines requiring alternative solutions to impart the desired viscometrics in lubricants.

[0005] The present invention solves the problem of providing an internal combustion engine with a lubricating composition, especially 2-stroke marine engines capable of providing at Least one property from control of viscometrics, acceptable deposit accumulation, acceptable oxidative stability and a partial or complete replacement for current viscosity modifiers or bright stock.

SUMMARY OF THE INVENTION

[0006] Described herein is a method of lubricating an internal combustion engine with a power output of at least 1600 kilowatts, comprising supplying to the internal combustion engine a lubricating composition comprising (a) an oil of lubricating viscosity and (b) at least 0.5 wt % of a carboxylic acid having a hydrocarbyl group of at least 10, or at least 30 carbon atoms or an anhydride thereof.

[0007] Also described is a method of lubricating a marine-diesel internal combustion engine comprising supplying to the internal combustion engine a lubricating composition comprising (a) an oil of lubricating viscosity and (b) at least 0.5 wt % of a carboxylic acid having a hydrocarbyl group of at least 10, or at least 30 carbon atoms or an anhydride thereof.

[0008] Also described is a lubricating composition comprising (a) an oil of lubricating viscosity, (b) at least 0.5 wt % of a carboxylic acid having a hydrocarbyl group of at least 10, or at least 30 carbon atoms or an anhydride thereof, and (c) at least 5 wt % of an overbased sulphonate detergent.

[0009] Also described is the use of a carboxylic acid having a hydrocarbyl group of at least 10, or at least 30 carbon atoms or an anhydride thereof as an oil thickener for a lubricating composition, wherein the carboxylic acid or anhydride thereof is present at least 0.5 wt % of the lubricating composition.

[0010] The present invention provides the use of a carboxylic acid having a hydrocarbyl group of at least 10, or at least 30 carbon atoms or an anhydride thereof as an oil thickener for a 2-stroke marine cylinder lubricating composition wherein the carboxylic acid or anhydride thereof is present at least 0.5 wt % of the lubricating composition.

[0011] The carboxylic acid as defined above may be written as "at least 0.5 wt % of a carboxylic acid or an anhydride thereof, wherein the carboxylic acid or anhydride thereof has a hydrocarbyl group of at least 10 carbon atoms".

DETAILED DESCRIPTION OF THE INVENTION

[0012] The present invention provides a use as disclosed above.

[0013] As used herein the term "substantially free of, to free of" means that the substance in question (e.g, the bright stock or dispersant) may be present from 0 wt % to 1 wt % of the lubricating composition.

[0014] The method described herein may employ a lubricating composition that may be substantially reduced (e.g., 0 to less than 15 wt %, or 0.1 to 10 wt %) compared with conventional amounts (typically 15 to 40 wt % of a lubricating composition) in amount of bright stock. The lubricating composition may be substantially free of, to free of bright stock.

[0015] The method may employ a lubricating composition that may be substantially reduced (e.g., 0 to less than 3 wt %, or 0 to 2 wt %) compared with conventional amounts (typically 2 to 5 wt % of a lubricating composition) in amount of dispersant

[0016] The method may employ a lubricating composition that may contain 0 to less than 15 wt %, or 0.1 to 10 wt % of bright stock; and 0 to less than 3 wt %, or 0 to 2 wt % of a dispersant.

[0017] The method may employ a lubricating composition that maybe substantially free of, to free of both bright stock and dispersant.

Hydrocarbyl-Substituted Carboxylic Acid or Anhydride

[0018] The lubricant used in the invention comprises a carboxylic acid or an anhydride thereof, wherein the carboxylic acid or anhydride thereof has a hydrocarbyl group of at least 10 carbon atoms, or mixtures thereof. Hereinafter, this acid is sometimes referred to simply as a hydrocarbyl-substituted carboxylic acid, or even as the carboxylic acid. If the hydrocarbyl group containing 10 carbon atoms is attached to a simple mono-carboxylic group, there will accordingly be 11 carbon atoms in the molecule. If the hydrocarbyl group containing 10 carbon atoms is attached to, for instance, succinic acid, there will accordingly be 14 carbon atoms in the molecule. A hydrocarbyl group containing 10 carbon atoms will normally have a molecular weight of about 141, varying depending on the presence of unsaturation, cyclic structures, hetero groups, or other substituents, if any.

[0019] The carboxylic acid or anhydride thereof may be substituted by or derived from a polyolefin. The polyolefin may be a homopolymer, copolymer, or interpolymer. The polyolefin may be prepared from polymerisable monomers containing 2 to 16, or 2 to 8, or 2 to 6 carbon atoms. Often the polymerisable monomers comprise one or more of propylene, isobutene, 1-butene, isoprene, 1,3-butadiene, or mixtures thereof.

[0020] In one embodiment the carboxylic acid or anhydride thereof comprises a succinic acid or anhydride thereof.

[0021] In one embodiment the hydrocarbyl-substituted carboxylic acid or anhydride thereof comprises a polyisobutylene succinic acid or anhydride thereof. A more detailed description of a suitable carboxylic acid or anhydride thereof is described in WO 93/03121, page 33, line 10 to page 37, line 20.

[0022] In view of the synthesis routes commercially employed to prepare the hydrocarbyl-substituted carboxylic acid or anhydride thereof, there may be a portion of unreacted hydrocarbyl group (typically polyisobutylene) present. The amount of the unreacted hydrocarbyl group may as high as about 25 wt %, or as low as 0 wt % of the hydrocarbyl-substituted carboxylic acid or anhydride thereof.

[0023] The hydrocarbyl-substituted carboxylic acid or anhydride thereof may be present at 0.5 to 20 wt % or 1 to 10 wt % of the lubricating composition.

[0024] Typically the hydrocarbyl-substituted carboxylic acid or anhydride thereof is a polyisobutylene succinic acid or anhydride.

[0025] The hydrocarbyl group of the carboxylic acid or anhydride thereof may typically contain 10 to 400, or 20 to 200, or 30 to 200, or 40 to 150 carbon atoms.

[0026] The hydrocarbyl group of the hydrocarbyl-substituted carboxylic acid or anhydride thereof may have a number average molecular weight of 450 to 20,000, or 550 to 10,000, or 750 to 5000, or 1500 to 3000.

[0027] In one embodiment the hydrocarbyl group of the hydrocarbyl-substituted carboxylic acid or anhydride thereof may have number average molecular weight of 450 to 1500. The acid or anhydride having such a group may, in one embodiment, be present at 2 to 20 wt % or 4 to 10 wt % of the lubricating composition.

[0028] In one embodiment the hydrocarbyl group of the hydrocarbyl-substituted carboxylic acid or anhydride thereof may have a number average molecular weight of greater than 1500 to 5000. The acid or anhydride having such a group may, in one embodiment, be present at 0.5 to less than 10 wt % or 1 to 5 wt % of the lubricating composition.

Detergent

[0029] In one embodiment the lubricating composition further comprises at least one detergent selected from the group consisting of sulphonates, salicylates, salixarates, phenates and hybrid detergent, such as sulphonate-phenate compositions, phenate-salicylate compositions or phenate-stearate compositions.

[0030] The total amount of detergent in the lubricating composition may be 0 wt % to 50 wt %, or at least 5 wt % to 35 wt %, or 6.5 wt % to 32 wt %, or 9 wt % to 30 wt %, or 12 wt % to 28 wt % of the lubricating composition.

[0031] In one embodiment the detergent may be an overbased sulphonate detergent.

[0032] The sulphonate detergent of the composition includes compounds represented by the formula:

$$(R^1)_k\text{-A-SO}_3\text{M} \qquad \text{(I)}$$

wherein each R^1 may be a hydrocarbyl group, typically each hydrocarbyl group may contain 6 to 40, or 8 to 35 or 12 to 30 carbon atoms; A may be independently a cyclic or acyclic divalent hydrocarbon group; M may be hydrogen, a valence of a metal ion, an ammonium ion or mixtures thereof; and k may be an integer of 0 to 5, for example 0, 1, 2, 3, 4, 5. In one embodiment k may be 1, 2 or 3, or 1 or 2. In one embodiment M may be hydrogen and typically present on less than 30%, or less than 20%, or less than 10% or less than 5% of the available M entities, the balance of the M entities being a metal or ammonium ion.

[0033] In one embodiment k is 1 and R^1 may be a branched alkyl group with 6 to 40 carbon atoms. In one embodiment k may be 1 and R^1 is a linear alkyl group with 6 to 40 carbon atoms.

[0034] Examples of suitable sulphonic acids capable of forming the overbased sulphonate detergent include polypropene benzene sulphonic acid, undecyl benzene sulphonic acid, dodecyl benzene sulphonic acid, tridecyl benzene sulphonic acid, tetradecyl benzene sulphonic acid, pentadecyl benzene sulphonic acid, hexadecyl benzene sulphonic acid and mixtures thereof. In one embodiment the sulphonic acid includes tridecyl benzene sulphonic acid, tetradecyl benzene sulphonic acid, octadecyl benzene sulphonic acid, tetraeicosyl benzene sulphonic acid or mixtures thereof. In one embodiment of the invention the sulphonic acid is a polypropene benzene sulphonic acid, where the polypropene contains 18 to 30 carbon atoms.

[0035] In one embodiment of the invention the sulphonate components may be calcium polypropene benzenesulphonate and calcium monoalkyl and dialkyl benzenesulphonates wherein the alkyl groups contain at least 10 or 12 carbons, for example 11, 12, 13, 14, 15, 18, 24 or 30 carbon atoms.

[0036] When M is a valence of a metal ion, the metal may be monovalent, divalent, trivalent or mixtures of such metals. When monovalent, the metal M includes an alkali metal such as lithium, sodium, or potassium and when divalent, the metal M includes an alkaline earth metal such as magnesium, calcium or barium. In one embodiment the metal may be an alkaline earth metal. In one embodiment the metal is calcium.

[0037] When A is cyclic hydrocarbon group, suitable groups include phenylene or fused bicyclic groups such as naphthylene, indenylene, indanylene, bicyclopentadienylene or mixtures thereof. In one embodiment A comprises a benzene ring.

[0038] When A is an acyclic divalent hydrocarbon group, the carbon chain may be linear or branched. In one embodiment A may be an acyclic linear hydrocarbon group.

[0039] The overbased sulphonate detergent in one embodiment has a TBN (total base number) of at least 350, or at least 400, or at least 425, or at least 450, or at least 475. In one embodiment the overbased sulphonate detergent has a TBN of between 400 and 500.

[0040] A sulphonate detergent with 500 TBN and its preparation are disclosed in U.S. Patent 5,792,732. In Example 2 thereof, a 500 TBN all-linear alkylbenzene sulphonate is prepared by reacting an alkyl benzene sulphonate from Witco Corp. (now known as Chemtura) with $Ca(OH)_2$ and CaO in n-heptane and methanol and bubbling with CO_2. It is also reported in the aforementioned patent (col. 5) that a 500 TBN overbased sulphonate containing highly branched alkylbenzene sulphonate is available from Witco Corp. (now known as Chemtura) as Petronate® C-500. Another method for preparing an overbased sulphonate detergent of high metal ratio is disclosed in U.S. Patent 6,444,625 (see, for instance, column 3, bottom).

[0041] Optionally the lubricating composition further includes a phenate detergent. The phenate detergent is known and includes neutral and overbased metal salts of a sulphur-containing phenate, a non-sulphurised phenate or mixtures thereof. Suitable metal salts are the same as those described for the sulphonate detergent.

[0042] The phenate detergent in one embodiment has a TBN from 30 to 450, in another embodiment 30 to 350 or 290, in another embodiment 40 to 265, in another embodiment 50 to 190 and in another embodiment 70 to 175. In one embodiment the sulphur containing phenate detergent has a TBN of 150, in another embodiment a TBN of 225 and in another embodiment 250.

[0043] The detergent may also be a hybrid (or complex) detergent.

[0044] In one embodiment the complex/hybrid may be an overbased phenate-stearate detergent, typically with a TBN of 300 to 450. Methods of preparing overbased phenate-stearate detergents are disclosed in EP 271262 B1 and EP273 588 B1.

[0045] In one embodiment the complex/hybrid may be an overbased phenate-salicylate detergent. Methods of preparing overbased phenate-salicylate detergents are disclosed in EP 123 6791 A1 and EP 123 6792 A1.

[0046] In one embodiment the complex/hybrid may be prepared by reacting, in the presence of the suspension and acidifying overbasing agent, alkyl aromatic sulphonic acid and at least one alkyl phenol (such as, alkyl phenol, aldehyde-coupled alkyl phenol, sulphurised alkyl phenol) and optionally alkyl salicylic acid.

[0047] A hybrid detergent may be prepared by hybrid preparing an overbased calcium detergent composed of a sulphonic acid and an alkyl phenol. A hybrid detergent may be prepared as disclosed in WO97046643 or by the following preparative Example.

[0048] Preparative Example 1: 540 g of toluene, 276 g of methanol and 290 g of the product of lime are mixed at ambient temperature in a vessel. Then 238 g of sulphurised alkyl phenol and 110 g of alkyl sulphonic acid (with molecular weight of 683) are charged along with 22 g of water and an additional 50 g of toluene at 40 °C. After neutralization the vessel is cooled to 28 °C while 62 g of carbon dioxide is injected. The reaction temperature is increased to 60 °C over a period of 1 hour, before cooling to 28 °C. 254 g of lime is added and a second carbonation step carried out, whilst heating to 60 °C over 90 minutes. The product of the reaction is cooled and filtered.

Oils of Lubricating Viscosity

[0049] The oil of lubricating viscosity may have a SAE grade of SAE 30, SAE 40, SAE 50, or SAE 60. In one embodiment the oil of lubricating viscosity may be a SAE 50 oil. Typically a SAE 50 oil has a kinematic viscosity of 16.3 mm^2/s to 21.9 mm^2/s at 100 °C.

[0050] Such oils include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined and re-refined oils and mixtures thereof.

[0051] Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment.

[0052] Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Purification techniques are known in the art and include solvent extraction, secondary distillation, acid or base extraction, filtration, percolation and the like.

[0053] Re-refined oils are also known as reclaimed or reprocessed oils, and are obtained by processes similar to those used to obtain refined oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0054] Natural oils useful in making the inventive lubricants include animal oils, vegetable oils (e.g., castor oil, lard oil), mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types and oils derived from coal or shale or mixtures thereof.

[0055] Synthetic lubricating oils are useful and include hydrocarbon oils such as polymerised and interpolymerised olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), poly(1-decenes), and mixtures thereof; alkyl-benzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); alkylated diphenyl ethers and alkylated diphenyl sulphides and the derivatives, analogs and homologs thereof or mixtures thereof.

[0056] Other synthetic lubricating oils include but are not limited to liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), and polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and typically may be hydroisomerised Fischer-Tropsch hydrocarbons or waxes.

[0057] Oils of lubricating viscosity may also be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows: Group I (sulphur content >0.03 wt %, and/or <90 wt % saturates, viscosity index 80-120); Group II (sulphur content ≤0.03 wt %, and ≥90 wt % saturates, viscosity index 80-120); Group III (sulphur content ≤0.03 wt %, and ≥90 wt % saturates, viscosity index ≥120); Group IV (all polyalphaolefins (PAOs)); and Group V (all others not included in Groups I, II, III, or IV). The oil of lubricating viscosity comprises an API Group I, Group II, Group III, Group IV, Group V oil and mixtures thereof. Often the oil of lubricating viscosity is an API Group I, Group II, Group III, Group IV oil and mixtures thereof. Alternatively the oil of lubricating viscosity is often an API Group I, Group II, Group III oil or mixtures thereof.

Other Performance Additives

[0058] The lubricating composition optionally contains at least one other performance additive. Typically the other performance additives include metal deactivators, dispersant, antioxidants, antiwear agents, corrosion inhibitors, antiscuffing agents, extreme pressure agents, foam inhibitors, demulsifiers, friction modifiers, viscosity modifiers, pour point depressants and mixtures thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives.

Dispersants

[0059] Dispersants are often known as ashless-type dispersants because, prior to mixing in a lubricating oil composition, they do not contain ash-forming metals and they do not normally contribute any ash forming metals when added to a lubricant and polymeric dispersants. Ashless type dispersants are characterised by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include N-substituted long chain alkenyl succinimides. Examples of N-substituted long chain alkenyl succinimides include polyisobutylene succinimide with number average molecular weight of the polyisobutylene substituent in the range 350 to 5000, or 500 to 3000. Succinimide dispersants and their preparation are disclosed, for instance in US Patent 3,172,892 or US Patent 4,234,435. Succinimide dispersants are typically the imide formed from a polyamine, typically a poly(ethyleneamine).

[0060] In one embodiment the invention further comprises at least one dispersant derived from polyisobutylene succinimide with number average molecular weight in the range 350 to 5000, or 500 to 3000. The polyisobutylene succinimide may be used alone or in combination with other dispersants.

[0061] In one embodiment the invention further comprises at least one dispersant derived from polyisobutylene succinic anhydride, an amine and zinc oxide to form a polyisobutylene succinimide complex with zinc. The polyisobutylene succinimide complex with zinc may be used alone or in combination.

[0062] Another class of ashless dispersant is Mannich bases. Mannich dispersants are the reaction products of alkyl phenols with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines). The alkyl group typically contains at least 30 carbon atoms.

[0063] The dispersants may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron, urea, thiourea, dimercaptothiadiazoles, carbon disulphide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds.

[0064] The dispersant may be present from 0 wt % to 5 wt %, or 0 wt % to 3 wt %, or 0 wt % to 2 wt %, or 0.1 wt % to 2 wt %.

Antioxidants

[0065] Antioxidant compounds are known and include for example, sulphurised olefins, alkylated diphenylamines (typically di-nonyl diphenylamine, octyl diphenylamine, di-octyl diphenylamine), hindered phenols, molybdenum compounds (such as molybdenum dithiocarbamates), or mixtures thereof. Antioxidant compounds may be used alone or in combination.

[0066] The hindered phenol antioxidant often contains a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group is often further substituted with a hydrocarbyl group and/or a bridging group linking to a second aromatic group. Examples of suitable hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol or 4-butyl-2,6-di-tert-butylphenol, or 4-dodecyl-2,6-di-tert-butylphenol. In one embodiment the hindered phenol antioxidant is an ester and may include, e.g., Irganox™ L-135 from Ciba. A more detailed description of suitable ester-containing hindered phenol antioxidant chemistry is found in US Patent 6,559,105.

[0067] Suitable examples of molybdenum dithiocarbamates which may be used as an antioxidant include commercial materials sold under the trade names such as Molyvan 822™ and Molyvan™ A from R. T. Vanderbilt Co., Ltd., and Adeka Sakura-Lube™ S-100, S-165 and S-600 from Asahi Denka Kogyo K. K and mixtures thereof.

Viscosity Modifiers

[0068] Viscosity modifiers include hydrogenated copolymers of styrene and butadiene, ethylene-propylene copolymers, polyisobutenes, hydrogenated styrene-isoprene polymers, hydrogenated isoprene polymers, polymethacrylates, polyacrylates, polyalkyl styrenes, hydrogenated alkenyl aryl conjugated diene copolymers, polyolefins, esters of maleic anhydride-styrene copolymers.

Antiwear Agents

[0069] The lubricant composition optionally further comprises at least one antiwear agent (other than the various other components mentioned herein that may also impart some antiwar functionality). The antiwear agent may be present in ranges including 0 wt % to 15 wt %, or 0.1 wt % to 10 wt % or 1 wt % to 8 wt % of the lubricating composition. Examples of suitable antiwear agents include a boron-containing compound such as borate esters or borate alcohols, phosphate esters, sulphurised olefins, sulphur-containing ashless antiwear additives are metal dihydrocarbyldithiophosphates (such as zinc dialkyldithiophosphates or molybdenum dialkyldithiophosphates), thiocarbamate-containing compounds, such as thiocarbamate esters, alkylene-coupled thiocarbamates, and bis-(S-alkyldithiocarbamyl) disulphides.

[0070] The borate esters or borate alcohols may be substantially the same except the borate alcohol has at least one hydroxyl group that is not esterified. Therefore, as used herein the term "borate ester" is used to refer to either borate ester or borate alcohol. The borate esters or borate alcohols may have a formula $B(OR')_3$ or be a derivative thereof containing a >B-O-B< group, wherein R' may be hydrogen or a hydrocarbyl group, typically containing 1 to 40, or 1 to 20 carbon atoms on each R'. When R' is hydrogen, the boron-containing compound is a borate alcohol. When R' is hydrogen, the boron-containing compound is a borate alcohol. When R' is hydrocarbyl, the boron-containing compound is a borate ester.

[0071] The borate ester may be prepared by the reaction of a boron compound and at least one compound selected from epoxy compounds, halohydrin compounds, epihalohydrin compounds, alcohols and mixtures thereof. The alcohols include dihydric alcohols, trihydric alcohols or higher alcohols, with the proviso for one embodiment that hydroxyl groups are on adjacent carbon atoms i.e. vicinal.

[0072] The borate ester may be prepared by blending the boron compound and the epoxy compounds or alcohols described above and heating them at a suitable temperature, such as at 80°C to 250°C, 90°C to 240°C, or 100°C to 230°C, until the desired reaction has occurred. The molar ratio of the boron compounds to the epoxy compounds is typically 4:1 to 1:4, or 1:1 to 1:3, or 1:2. An inert liquid may be used in performing the reaction. The liquid may be, for instance, toluene, xylene, chlorobenzene, dimethylformamide and mixtures thereof. Water is typically formed and is distilled off during the reaction. Alkaline reagents may be used to catalyze the reaction.

[0073] Boron compounds suitable for preparing the borate ester include the various forms selected from the group consisting of boric acid (including metaboric acid, HBO_2, orthoboric acid, H_3BO_3, and tetraboric acid, $H_2B_4O_7$), boric oxide, boron trioxide and alkyl borates. The borate ester may also be prepared from boron halides.

[0074] In one embodiment suitable borate ester compounds include tripropyl borate, tributyl borate, tripentyl borate, trihexyl borate, triheptyl borate, trioctyl borate, trinonyl borate and tridecyl borate.

[0075] The dithiocarbamate-containing compounds may be prepared by reacting a dithiocarbamate acid or salt with an unsaturated compound. The dithiocarbamate containing compounds may also be prepared by simultaneously reacting an amine, carbon disulphide and an unsaturated compound. Generally, the reaction occurs at a temperature of 25 °C to 125 °C. US Patents 4,758,362 and 4,997,969 describe dithiocarbamate compounds and methods of making them.

[0076] Examples of suitable olefins that may be sulphurised to form an the sulphurised olefin include propylene, butylene, isobutylene, pentene, hexane, heptene, octane, nonene, decene, undecene, dodecene, undecyl, tridecene, tetradecene, pentadecene, hexadecene, heptadecene, octadecene, octadecenene, nonodecene, eicosene or mixtures thereof. In one embodiment, hexadecene, heptadecene, octadecene, octadecenene, nonodecene, eicosene or mixtures thereof and their dimers, trimers and tetramers are especially useful olefins. Alternatively, the olefin may be a Diels-Alder adduct of a diene such as 1,3-butadiene and an unsaturated ester, such as, butylacrylate.

[0077] Another class of sulphurised olefin includes fatty acids and their esters. The fatty acids are often obtained from vegetable oil or animal oil and typically contain 4 to 22 carbon atoms. Examples of suitable fatty acids and their esters include triglycerides, oleic acid, linoleic acid, palmitoleic acid or mixtures thereof. Often, the fatty acids are obtained from lard oil, tall oil, peanut oil, soybean oil, cottonseed oil, sunflower seed oil or mixtures thereof. In one embodiment fatty acids and/or ester are mixed with olefins.

[0078] In an alternative embodiment, the ashless antiwear agent (which may also be described as a friction modifier) may be a monoester of a polyol and an aliphatic carboxylic acid, often an acid containing 12 to 24 carbon atoms. Often the monoester of a polyol and an aliphatic carboxylic acid is in the form of a mixture with a sunflower oil or the like, which may be present in the ashless antiwear agent mixture include 5 to 95, or in other embodiments 10 to 90, or 20 to 85, or 20 to 80 weight percent of said mixture. The aliphatic carboxylic acids (especially a monocarboxylic acid) which form the esters are those acids typically containing 12 to 24 or 14 to 20 carbon atoms. Examples of carboxylic acids include dodecanoic acid, stearic acid, lauric acid, behenic acid, and oleic acid.

[0079] Polyols include diols, triols, and alcohols with higher numbers of alcoholic OH groups. Polyhydric alcohols include ethylene glycols, including di-, tri- and tetraethylene glycols; propylene glycols, including di-, tri- and tetrapropylene glycols; glycerol; butane diol; hexane diol; sorbitol; arabitol; mannitol; sucrose; fructose; glucose; cyclohexane diol; erythritol; and pentaerythritols, including di- and tripentaerythritol. Often the polyol is diethylene glycol, triethylene glycol, glycerol, sorbitol, pentaerythritol or dipentaerythritol.

[0080] The commercially available monoester known as "glycerol monooleate" is believed to include 60 ± 5 percent by weight of the chemical species glycerol monooleate, along with 35 ± 5 percent glycerol dioleate, and less than 5 percent trioleate and oleic acid. The amounts of the monoesters, described above, are calculated based on the actual, corrected, amount of polyol monoester present in any such mixture.

Extreme Pressure Agents

[0081] Extreme Pressure (EP) agents that are soluble in the oil include sulphur- and chlorosulphur-containing EP agents, chlorinated hydrocarbon EP agents and phosphorus EP agents. Examples of such EP agents include chlorinated wax; organic sulphides and polysulphides such as dibenzyldisulphide, bis-(chlorobenzyl) disulphide, dibutyl tetrasulphide, sulphurised methyl ester of oleic acid, sulphurised alkylphenol, sulphurised dipentene, sulphurised terpene, and sulphurised Diels-Alder adducts; phosphosulphurised hydrocarbons such as the reaction product of phosphorus sulphide with turpentine or methyl oleate; phosphorus esters such as the dihydrocarbon and trihydrocarbon phosphites, e.g., dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite; metal thiocarbamates such as zinc dioctyldithiocarbamate and barium heptylphenol diacid; amine salts of alkyl and dialkylphosphoric acids, including, for example, the amine salt of the reaction product of a dialkyldithiophosphoric acid with propylene oxide; and mixtures thereof.

[0082] Other performance additives such as corrosion inhibitors include those described in paragraphs 5 to 8 of US Application US 2009 156 446 (filed on October 25, 2004 McAtee and Boyer as named inventors), octylamine octanoate, condensation products of dodecenyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine. In one embodiment the corrosion inhibitors include the Synalox® corrosion inhibitor. The Synalox® corrosion inhibitor is typically a homopolymer or copolymer of propylene oxide. The Synalox® corrosion inhibitor is described in more detail in a product brochure with Form No. 118-01453-0702 AMS, published by The Dow Chemical Company. The product brochure is entitled "SYNALOX Lubricants, High-Performance Polyglycols for Demanding Applications."

[0083] Metal deactivators including derivatives of benzotriazoles (typically tolyltriazole), dimercaptothiadiazole derivatives, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, or 2-alkyldithiobenzothiazoles; foam inhibitors including copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers; pour point depressants including esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides.

[0084] Friction modifiers including fatty acid derivatives such as amines, esters, epoxides, fatty imidazolines, condensation products of carboxylic acids and polyalkylene-polyamines and amine salts of alkylphosphoric acids, fatty alkyl tartrates, fatty alkyl tartrimides, fatty alkyl tartramides may also be used in the lubricant composition. Friction modifiers may also encompass materials such as sulphurised fatty compounds and olefins, molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, sunflower oil or monoester of a polyol and an aliphatic carboxylic acid (all these friction modifiers have been described above as antioxidants or antiwear agents).

Industrial Application

[0085] The method and lubricating composition is suitable for 2-stroke internal combustion engines. Typically the 2-stroke engine may be a 2-stroke cross-head engine.

[0086] The power output of the engine may be at least 2000 kilowatts, or at least 3000 kilowatts, or at least 4700 kilowatts.

[0087] The 2-stroke internal combustion engine may be a marine diesel engine or a stationary power engine.

[0088] The engine may be marine-diesel internal combustion engine.

[0089] In one embodiment the 2-stroke engine employs the lubricating composition in a cylinder liner.

EXAMPLES

Marine Diesel Cylinder Lubricants: Invention and Reference Lubricating Oil Compositions

[0090] Lubricating oil compositions are prepared as summarised in Table 1 below. The amounts of sulphonate, phenate and dispersant quoted include the normal amounts of diluent oil associated with additives. Typically the sulphonate, phenate and dispersant contain about 40 wt % of diluent oil.

[0091] Reference oil composition 1 (RF1) is a lubricant containing bright stock (150 BS) and dispersant. Reference oil compositions 2 (RF2) and 3 (RF3) contain polyisobutylene as a thickener, no bright stock. The lubricating oil compositions of the invention 1 (LC1) and 2 (LC2) contain polyisobutylene succinic anhydride, no dispersant and no bright stock.

Table 1

	RF1	RF2	RF3	LC1	LC2
Formulation Components	wt %				
Formulated to Kinematic Viscosity at 100°C (ASTM D445) mm^2/s	19.8	19.4	19.5	19.4	19.5
400 TBN sulphonate	10.6	10.6	10.6	10.6	10.6
255 TBN phenate	10.6	10.6	10.6	10.6	10.6
Dispersant	2	0	0	0	0
Polyisobutylene with Mn of approximately 950-1,000	0	9.5	0	0	0
Polyisobutylene with Mn of approximately 2,200-2,300	0	0	5.2	0	0

(continued)

	RF1	RF2	RF3	LC1	LC2
Formulation Components	wt %				
Polyisobutylene succinic anhydride derived from Polyisobutylene with Mn of approximately 950-1,000	0	0	0	5	0
Polyisobutylene succinic anhydride derived from Polyisobutylene with Mn of approximately 2,200-2,300	0	0	0	0	2.3
Esso 600N base oil	57.8	69.3	73.6	73.8	76.5
Esso 150BS bright stock	19	0	0	0	0

[0092] Test 1 Panel Coker: Approximately 233g of sample is placed in a 250 ml Panel Coker apparatus and heated to 325°C. The sample is splashed against a metal plate for 15 seconds and then baked for 45 seconds. The splashing and baking cycle is continued for approximately 3 hours. The sample is cooled to room temperature and the amount of deposits left on the metal plate is weighed. In addition the deposits are analysed using image analysis techniques. The image analysis techniques have a rating scale from 0 to 100, 0 indicating heavy deposits and 100 indicating no or very little deposits. The results are shown in Table 2.

[0093] Test 2 Hot Tube: The reference and lubricating compositions and house air are fed at controlled rates through a heated Pyrex® glass capillary tube. The oil and air are brought together via a Pyrex® glass tee that is connected to the bottom of the capillary tube. As the oil is metered into the glass tee, the air picks up the oil and carries it up through the vertical glass capillary tube which passes through an electrically heated and temperature controlled aluminum block. The heated oil and air mixture then exits from the top of the glass capillary into a collecting beaker for the oxidized oil. At test completion, the glass capillary tubes are removed from the heating block then flushed with hydrocarbon solvent and rated for lacquer and carbon deposits, using reference standards. A rating scale from 0 to 100 is used and evaluated using standard image analysis techniques, 0 indicating heavy deposits and 100 indicating no or very little deposits. The results are shown in Table 2.

Table 2

	RF1	RF2	RF3	LC1	LC2
Test 1: Deposit (mg)	229	244	238	94	161
Test 1: Image Analysis Rating	49	51	63	62	65
Test 2: Image Analysis Rating	16	6	14	8	18

[0094] Overall the data indicates that lubricating composition comprising at least 0.5 wt % of a hydrocarbyl-substituted carboxylic acid or anhydride thereof may be more suitable for the engine disclosed herein and capable of producing at least one of fewer deposits and having cleaner ratings than lubricating compositions that contain bright stock or polyisobutylene thickeners, and optionally dispersant.

[0095] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

(i) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);

(ii) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulphoxy);

(iii) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulphur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

[0096] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. The products formed thereby, including the products formed upon employing lubricant composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses lubricant composition prepared by admixing the components described above.

[0097] Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined.

[0098] While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

Claims

1. The use of at least 0.5 wt % of a carboxylic acid or anhydride thereof as an oil thickener for a 2-stroke marine diesel cylinder lubricating composition wherein the carboxylic acid or anhydride thereof has a hydrocarbyl group of at least 10 carbon atoms.

2. The use of claim 1, wherein the hydrocarbyl group of the carboxylic acid or anhydride thereof has number average molecular weight of 450 to 1500, and wherein the carboxylic acid or anhydride thereof is present at 2 to 20 wt %, or 4 to 10 wt % of the lubricating composition.

3. The use of claim 1, wherein the hydrocarbyl group of the carboxylic acid or anhydride thereof has number average molecular weight of greater than 1500 to 5000, and wherein the carboxylic acid or anhydride thereof is present at 0.5 to less than 10 wt % or 1 to 5 wt % of the lubricating composition.

4. The use of claim 1, wherein the carboxylic acid or anhydride thereof is a polyisobutylene-substituted succinic acid or anhydride.

Patentansprüche

1. Verwendung von mindestens 0,5 Gew.-% einer Carbonsäure oder eines Anhydrids davon als Ölverdicker für eine Schmiermittelzusammensetzung für einen Zweitaktschiffsdieselzylinder, wobei die Carbonsäure bzw. das Anhydrid davon eine Hydrocarbylgruppe mit mindestens 10 Kohlenstoffatomen aufweist.

2. Verwendung nach Anspruch 1, wobei die Hydrocarbylgruppe der Carbonsäure bzw. des Anhydrids davon ein zahlenmittleres Molekulargewicht von 450 bis 1500 aufweist und wobei die Carbonsäure bzw. das Anhydrid davon in einer Menge von 2 bis 20 Gew.-% oder 4 bis 10 Gew.-% der Schmiermittelzusammensetzung vorliegt.

3. Verwendung nach Anspruch 1, wobei die Hydrocarbylgruppe der Carbonsäure bzw. des Anhydrids davon ein zahlenmittleres Molekulargewicht von mehr als 1500 bis 5000 aufweist und wobei die Carbonsäure bzw. das Anhydrid davon in einer Menge von 0,5 bis weniger als 10 Gew.-% oder 1 bis 5 Gew.-% der Schmiermittelzusammensetzung vorliegt.

4. Verwendung nach Anspruch 1, wobei es sich bei der Carbonsäure bzw. dem Anhydrid davon um eine polyisobutylensubstituierte Bernsteinsäure oder ein polyisobutylensubstituiertes Bernsteinsäureanhydrid handelt.

Revendications

1. Utilisation d’au moins 0,5% en poids d’un acide carboxylique ou d’un anhydride de celui-ci comme épaississant

d’huile pour une composition lubrifiante de cylindre diesel marin à deux temps, dans laquelle l’acide carboxylique ou l’anhydride de celui-ci possède un groupement hydrocarbyle d’au moins 10 atomes de carbone.

2. Utilisation selon la revendication 1, dans laquelle le groupement hydrocarbyle de l’acide carboxylique ou de l’anhydride de celui-ci possède un poids moléculaire moyen en nombre allant de 450 à 1500, et dans laquelle l’acide carboxylique ou l’anhydride de celui-ci est présent de 2 à 20% en poids, ou de 4 à 10% en poids, de la composition lubrifiante.

3. Utilisation selon la revendication 1, dans laquelle le groupement hydrocarbyle de l’acide carboxylique ou de l’anhydride de celui-ci possède un poids moléculaire moyen en nombre supérieur à de 1500 à 5000, et dans laquelle l’acide carboxylique ou l’anhydride de celui-ci est présent à de 0,5 à moins de 10% en poids, ou de 1 à 5% en poids, de la composition lubrifiante.

4. Utilisation selon la revendication 1, dans laquelle l’acide carboxylique ou l’anhydride de celui-ci est un acide ou anhydride succinique substitué par du polyisobutylène.

REFERENCES CITED IN THE DESCRIPTION

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