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(54) Marine engine lubrication

(57) Marine engine (two-or four-stroke) lubrication is effected by a composition comprising a major amount of an oil of lubricating viscosity blended with minor amounts of one or more additives and a star polymer or olefin copolymer viscosity modifier dispersed in a heavy basestock diluent oil.

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Description

FIELD OF THE INVENTION

[0001] This invention relates to the lubrication of two-stroke and four-stroke marine diesel internal combustion engines, the former usually being referred to as cross-head engines and the latter as trunk piston engines. Respective lubricants therefor are usually known as marine diesel cylinder lubricants ("MDCL's") and trunk piston engine oils ("TPEO's").

BACKGROUND OF THE INVENTION

[0002] Cross-head engines are slow engines with a high to very high power range. They include two separately-lubricated parts: the piston/cylinder assembly lubricated with total-loss lubrication by a highly viscous oil (an MDCL); and the crankshaft lubricated with a less viscous lubricant, usually referred to as a system oil.

[0003] Trunk piston engines may be used in marine, power-generation and rail traction applications, and have a higher speed than cross-head engines. A single lubricant (TPEO) is used for crankcase and cylinder lubrication. All major moving parts of the engine, i.e. the main and big end bearings, camshaft and valve gear, are lubricated by means of a pumped circulation system. The cylinder liners are lubricated partially by splash lubrication and partially by oil from the circulation systems that finds its way to the cylinder wall through holes in the piston skirt via the connecting rod and gudgeon pin.

[0004] It is known in the art to include brightstock in MDCL's and TPEO's, brightstock being a high viscosity oil that is highly refined and dewaxed and that is produced from residual stocks or bottoms. It may, for example, have a kinematic viscosity at 100°C of greater than 25, usually greater than 30, mm^2s^{-1}, such as a solvent-extracted, de-asphalted product from vacuum residuum generally having a kinematic viscosity at 100°C of 28-36 mm^2s^{-1}.

[0005] Brightstock is however expensive and art describes ways of replacing it. WO 99/64543 describes MDCL's formulated without brightstock and US 2008/0287329 describes a TPEO containing little or no brightstock. Both use liquid, oil-miscible polyisobutylene ('PIB').

[0006] A problem with brightstock-free MDCL's and TPEO's is that they give rise to evaporation debits (i.e. lubricating oil evaporation and consumption). As discussed in US 2008/0287329, the degradation of polyisobutylene leads to the formation of volative products that escape from the engine, which results in lube oil consumption.

[0007] The aim of the invention is to overcome the problems of the prior art. In particular, an aim of the present invention is to reduce lubricating oil consumption.

SUMMARY OF THE INVENTION

[0008] It is now found that the use of star polymers (such as an amorphous styrene-diene copolymer) or olefin copolymers (such as an ethylene-propylene copolymer) dispersed in a heavy diluent oil in an MDCL or a TPEO enables the above problem to be overcome.

[0009] Thus, the present invention provides a two-stroke or four-stroke marine engine lubricating oil composition comprising an oil of lubricating viscosity in a major amount, and blended with

> (A) one of more additives, in respective minor amounts; and
>
> (B) a viscosity modifier in the form of either (i) a polymer comprising a core and a plurality of polymeric arms extending therefrom, or (ii) an olefin copolymer, the viscosity modifier being dispersed in a heavy diluent oil of kinematic viscosity at 100 °C in the range of 6-15, such as 7-14, $mm^2\ s^{-1}$

wherein the two-stoke marine engine lubricating oil composition has a TBN of 10 to 100 such as 40 to 100 using ASTM D2896 and the four-stroke marine engine lubricating oil composition has a TBN of 25 to 60 using ASTM D2896.

[0010] In further aspects the present invention comprises:-

> a method of making a two-stroke or four-stroke marine engine lubricating oil composition comprising blending an oil of lubricating viscosity in a major amount with:
>
> > (A) one or more additives, in respective minor amounts; and
> > (B) a viscosity modifier in the form of either (i) a polymer comprising a core and a plurality of polymeric arms extending therefrom, or (ii) an olefin copolymer, the viscosity modifier being dispersed in a heavy diluent oil of kinematic viscosity at 100 °C in the range of 6-15, such as 7-14, $mm^2\ s^{-1}$, wherein the two-stoke marine engine lubricating oil composition has a TBN of 10 to 100 such as 40 to 100 using ASTM D2896 and the four-stroke

marine engine lubricating oil composition has a TBN of 25 to 60 using ASTM D2896;

a two-stroke or four-stroke marine engine lubricating oil composition obtainable by the above method of this invention.

a method of lubricating a cross-head marine diesel engine comprising supplying the composition of the invention to the piston/cylinder assembly of the engine;

a method of lubricating a trunk piston marine diesel engine comprising supplying the composition to the engine; and

the use of a viscosity modifier (B) as defined in the first aspect of the invention to improve the carbon deposition properties of a marine diesel cylinder lubricant of TBN 10-100 such as 40 to 100 using ASTM D2896 or a trunk piston engine oil having a TBN of 25-60 using ASTM D2896.

[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 40 or 50 mass % or more of a composition, preferably 60 mas % or more, even more preferably 70 mass% or more;

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

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

[0012] Furthermore in this specification, if and when used:

"calcium content" is as measured by ASTM 4951;

"phosphorus content" is as measured by ASTM D5185;

"sulphated ash content" is as measured by ASTM D874;

"sulphur content" is as measured by ASTM D2622;

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

[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 will now be discussed in more detail below.

OIL OF LUBRICATING VISCOSITY

[0016] The lubricant composition contains a major proportion of an oil of lubricating viscosity. Such lubricating oils may range in viscosity from light distillate mineral oils to heavy lubricating oils. Generally, the viscosity of the oil ranges from 2 to 40, such as 3 to 15, mm^2/sec, as measured at 100°C, and a viscosity index of 80 to 100, such as 90 to 95.

The lubricating oil may comprise greater than 60, typically greater than 70, mass % of the composition.

[0017] 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.

[0018] 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, analogues and homologues thereof.

[0019] 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 C_3-C_8 fatty acid esters and C_{13} oxo acid diester of tetraethylene glycol.

[0020] 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.

[0021] Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol esters such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0022] Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxysilicone oils and silicate oils comprise another useful class of synthetic lubricants; such oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methyl-2-ethylhexyl)silicate, tetra-(p-tert-butyl-phenyl) silicate, hexa-(4-methyl-2-ethylhexyl)disiloxane, poly(methyl)siloxanes and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

[0023] Unrefined, refined and re-refined oils can be used in lubricants of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations; petroleum oil obtained directly from distillation; or ester oil obtained directly from esterification and used without further treatment are unrefined oils.

[0024] 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.

[0025] 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
	ASTM D 4927
	ASTM D 3120

[0026] The present invention preferably 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.

[0027] 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.

Marine Diesel Cylinder Lubricant ("MDCL")

[0028] An MDCL may employ 10-35, preferably 13-30, most preferably 16-24, mass % of a concentrate or additive package, the remainder being base stock. It preferably includes at least 50, more preferably at least 60, even more preferably at least 70, mass % of oil of lubricating viscosity based on the total mass of MDCL. Preferably, the MDCL has a compositional TBN (using ASTM D2896) of 10-100, such as 40-100, preferably 60-90, more preferably 70-80.

[0029] The following may be mentioned as examples of typical proportions of additives in an MDCL.

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

Trunk Piston Engine Oil ("TPEO")

[0030] A TPEO may employ 7-35, preferably 10-28, more preferably 12-24, mass % of a concentrate or additives package, the remainder being base stock. Preferably, the TPEO has a compositional TBN (using D2896) of 25-60, such as 25-55.

[0031] The following may be mentioned as typical proportions of additives in a TPEO.

Additive	Mass% a.i. (Broad)	Mass % a.i. (Preferred)
detergent(s)	0.5-12	2-8
dispersant(s)	0.5-5	1-3
anti-wear agent(s)	0.1-1.5	0.5-1.3
oxidation inhibitor	0.2-2	0.5-1.5
rust inhibitor	0.03-0.15	0.05-0.1
pour point dispersant	0.03-1.15	0.05-0.1

(continued)

Additive	Mass% a.i. (Broad)	Mass % a.i. (Preferred)
base stock	balance	balance

ADDITIVES (A)

[0032] More detailed description of additive components is given below.

Detergents

[0033] A detergent is an additive that reduces formation of deposits, for example, high-temperature varnish and lacquer deposits, in engines; it has acid-neutralising properties and is capable of keeping finely divided solids in suspension. It is based on metal "soaps", that is metal salts of acidic organic compounds, sometimes referred to as surfactants.

[0034] A detergent comprises a polar head with a long hydrophobic tail. Large amounts of a metal base are included by reacting an excess of a metal compound, such as an oxide or hydroxide, with an acidic gas such as carbon dioxide to give an overbased detergent which comprises neutralised detergent as the outer layer of a metal base (e.g. carbonate) micelle.

[0035] The detergent is preferably an alkali metal or alkaline earth metal additive such as an overbased oil-soluble or oil-dispersible calcium, magnesium, sodium or barium salt of a surfactant selected from phenol, sulphonic acid, carboxylic acid, salicylic acid and naphthenic acid, wherein the overbasing is provided by an oil-insoluble salt of the metal, e.g. carbonate, basic carbonate, acetate, formate, hydroxide or oxalate, which is stabilised by the oil-soluble salt of the surfactant. The metal of the oil-soluble surfactant salt may be the same or different from that of the metal of the oil-insoluble salt. Preferably the metal, whether the metal of the oil-soluble or oil-insoluble salt, is calcium.

[0036] The TBN of the detergent may be low, i.e. less than 50 mg KOH/g, medium, i.e. 50-150 mg KOH/g, or high, i.e. over 150 mg KOH/g, as determined by ASTM D2896. Preferably the TBN is medium or high, i.e. more than 50 TBN. More preferably, the TBN is at least 60, more preferably at least 100, more preferably at least 150, and up to 500, such as up to 350 mg KOH/g, as determined by ASTM D2896.

Anti-oxidants

[0037] The trunk piston diesel engine lubricant composition may include at least one anti-oxidant. The anti-oxidant may be aminic or phenolic. As examples of amines there may be mentioned secondary aromatic amines such as diarylamines, for example diphenylamines wherein each phenyl group is alkyl-substituted with an alkyl group having 4 to 9 carbon atoms. As examples of anti-oxidants there may be mentioned hindered phenols, including mono-phenols and bis-phenols.

[0038] Preferably, the anti-oxidant, if present, is provided in the composition in an amount of up to 3 mass %, based on the total amount of the lubricant composition.

[0039] Other additives such as pour point depressants, anti-foamants, metal rust inhibitors, pour point depressants and/or demulsifiers may be provided, if necessary.

[0040] The terms 'oil-soluble' or 'oil-dispersable' as used herein do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible or capable of being suspended in the oil in all proportions. These do mean, however, that they are, for instance, soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

[0041] The lubricant compositions of this invention comprise defined individual (i.e. separate) components that may or may not remain the same chemically before and after mixing.

[0042] It may be desirable, although not essential, to prepare one or more additive packages or concentrates comprising the additives, whereby the additives can be added simultaneously to the oil of lubricating viscosity to form the lubricating oil composition. Dissolution of the additive package(s) into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The additive package(s) will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration, and/or to carry out the intended function in the final formulation when the additive package(s) is/are combined with a predetermined amount of base lubricant.

[0043] Thus, the additives may be admixed with small amounts of base oil or other compatible solvents together with other desirable additives to form additive packages containing active ingredients in an amount, based on the additive package, of, for example, from 2.5 to 90, preferably from 5 to 75, most preferably from 8 to 60, mass % of additives in the appropriate proportions, the remainder being base oil.

[0044] The final formulations may typically contain about 5 to 40 mass % of the additive packages(s), the remainder being base oil.

VISCOSITY MODIFIER (B)

[0045] In this invention, as stated above, a viscosity modifier (B) is additionally provided in the form of (i) a so-called star polymer, or (ii) an olefin copolymer. Its concentration in the composition may, for example, be in the range of 0.01 to 40 mass %.

(i) Star Polymers

[0046] These are polymers comprising a core and a plurality of polymeric arms extending from the core. Such polymers are known as star-shaped polymers (or star or radial polymers). Examples of ranges of (B) in the composition include 0.1 - 6, 0.1 - 5, 0.1 - 4, 0.1 - 3, mass % and a lower limit of 1 mass %.

[0047] The viscosity modifier may comprise at least one star-shaped, at least partially hydrogenated, polymer derivable, at least in part, from the polymerisation of one or more conjugated diene monomers as defined hereinbefore. Suitably, the star-shaped polymer includes multiple arms extending from a central core; the arms being derived from the polymerisation of one or more conjugated diene monomers as defined hereinbefore, and optionally a vinyl aromatic hydrocarbon monomer as defined hereinbefore.

[0048] The arms of the star polymer may be a homopolymer derived essentially from the polymerisation of a single conjugated diene monomer as defined herein, such as isoprene or 1, 3-butadiene, particularly isoprene.

[0049] Alternatively, the arms of the star polymer may be a copolymer derived essentially from the polymerisation of two or more conjugated diene monomers as defined herein, such as an isoprene and 1,3-butadiene copolymer, or a copolymer derived essentially from the polymerisation of one or more conjugated diene monomers as defined herein and a vinyl aromatic hydrocarbon monomer as defined herein, such as an isoprene-styrene copolymer, a butadiene-styrene copolymer or an isoprene-butadiene-styrene copolymer.

[0050] As used herein in connection with polymer composition, "derived essentially" permits the inclusion of other substances not materially affecting the characteristics of the polymer to which it applies. Preferably, "derived essentially" means the specified monomer and comonomers, in the case of a copolymer, are present in an amount of at least 90 %, more preferably 95 %, even more preferably greater than 99 % by mass of the polymer.

[0051] The arms of the star polymer may also be a block copolymer, preferably a linear block copolymer, more preferably a linear diblock copolymer, such as one represented by the following general formula:

$$A_Z\text{-}(B\text{-}A)_y\text{-}B_X$$

wherein:

A is a polymeric block derived predominantly from vinyl aromatic hydrocarbon monomer;
B is a polymeric block derived predominantly from conjugated diene monomer;
x and z are, independently, a number equal to 0 or 1; and
y is a whole number ranging from 1 to about 15.

[0052] The arms of the star polymer may also be a tapered linear block copolymer such as one represented by the following general formula:

$$A\text{-}A/B\text{-}B$$

wherein:

A is a polymeric block derived predominantly from vinyl aromatic hydrocarbon monomer;

B is a polymeric block derived predominantly from conjugated diene monomer; and

A/B is a tapered segment derived from both vinyl aromatic hydrocarbon monomer and conjugated diolefin monomer.

[0053] Preferably, the arms of the star polymer comprise a hydrogenated isoprene-butadiene copolymer, a hydrogenated styrene-isoprene-butadiene copolymer, a hydrogenated isoprene-styrene copolymer or a hydrogenated butadiene-styrene copolymer.

[0054] Most preferably, the arms of the star polymer comprise a linear diblock copolymer as defined herein. Preferably, the linear diblock copolymer comprises at least one block derivable predominantly from a vinyl aromatic hydrocarbon monomer as defined herein and at least one block derivable predominantly from one or more conjugated diene monomers as defined herein. Preferably, the vinyl aromatic hydrocarbon monomer comprises styrene. Preferably, the one or more conjugated diene monomers comprise isoprene, butadiene or a mixture thereof. Most preferably, the linear diblock copolymer is at least partially hydrogenated.

[0055] Preferably, the at least one block derivable predominantly from a vinyl aromatic hydrocarbon monomer (e.g. styrene) in the linear diblock copolymer is present in an amount of up to 35 %, even more preferably up to 25 %, most preferably 5 to 25 %, by mass based on the total mass of the linear diblock copolymer.

[0056] Preferably, the at least one block derivable from predominantly from one or more conjugated diene monomers is present in an amount of greater than 65 %, even more preferably greater than or equal to 75 %, most preferably 75 to 95 %, by mass based on the total mass of the linear diblock copolymer.

[0057] Preferably, the linear diblock copolymer comprises at least one polystyrene block and a block derived from isoprene, butadiene, or a mixture thereof. Highly preferred linear diblock copolymers comprise linear diblock copolymers including at least one linear diblock copolymer selected from hydrogenated styrene/isoprene diblock copolymers, hydrogenated styrene/butadiene diblock copolymers and hydrogenated styrene/isoprene-butadiene diblock copolymers.

[0058] Preferably, when the linear diblock copolymer comprises at least one isoprene-butadiene block the block is derived predominantly from 70 to 90 mass % isoprene monomers and 30 to 10 mass % 1,3-butadiene monomers.

[0059] The arms of the star polymer typically comprise a copolymer derived from 70 to 90 mass % isoprene monomers and 30 to 10 mass % 1,3-butadiene monomers. More preferably, the arms of the star polymer further include a vinyl aromatic hydrocarbon monomer as defined herein, particularly styrene. A highly preferred copolymer is derived from isoprene monomers, 1,3-butadiene monomers and a vinyl aromatic hydrocarbon monomer, especially styrene. The vinyl aromatic hydrocarbon monomer may be present in an amount of up to 35 mass %, preferably up to 25 mass %, based on the total mass of the copolymer.

[0060] Preferably, the arms of the star polymer are formed via anionic polymerization to form a living polymer. Anionic polymerization has been found to provide copolymers having a narrow molecular weight distribution (Mw/Mn), such as a molecular weight distribution of less than about 1.2

[0061] As is well known, and disclosed, for example, in U.S. Patent No. 4,116,917, living polymers may be prepared by anionic solution polymerization of a mixture of the conjugated diene monomers in the presence of an alkali metal or an alkali metal hydrocarbon, e.g., sodium naphthalene, as anionic initiator. The preferred initiator is lithium or a mono lithium hydrocarbon. Suitable lithium hydrocarbons include unsaturated compounds such as allyl lithium, methallyl lithium; aromatic compounds such as phenyl lithium, the tolyl lithiums, the xylyl lithiums and the naphthyl lithiums, and in particular, the alkyl lithiums such as methyl lithium, ethyl lithium, propyl lithium, butyl lithium, amyl lithium, hexyl lithium, 2-ethylhexyl lithium and n-hexadecyl lithium. Secondary-butyl lithium is the preferred initiator. The initiator(s) may be added to the polymerization mixture in two or more stages, optionally together with additional monomer. The living polymers are olefinically unsaturated.

[0062] The solvents in which the living polymers are formed are inert liquid solvents, such as hydrocarbons e.g., aliphatic hydrocarbons such as pentane, hexane, heptane, octane, 2-ethylhexane, nonane, decane, cyclohexane, methylcyclohexane, or aromatic hydrocarbons e.g., benzene, toluene, ethylbenzene, the xylenes, diethylbenzenes, propylbenzenes. Cyclohexane is preferred. Mixtures of hydrocarbons e.g., lubricating oils, may also be used.

[0063] The temperature at which the polymerization is conducted may be varied within a wide range, such as from about -50°C to about 150°C, preferably from about 20°C to about 80°C. The reaction is suitably carried out in an inert atmosphere, such as nitrogen, and may optionally be carried out under pressure e.g., a pressure of from about 0.5 to about 10 bars.

[0064] The concentration of the initiator used to prepare the living polymer may also vary within a wide range and is determined by the desired molecular weight of the living polymer.

[0065] To form the star polymer, the living polymers formed via the foregoing process are reacted in an additional reaction step, with a polyalkenyl coupling agent. Polyalkenyl coupling agents capable of forming star polymers have been known for a number of years and are described, for example, in U.S. Patent No. 3,985,830. Polyalkenyl coupling agents are conventionally compounds having at least two non-conjugated alkenyl groups. Such groups are usually attached to the same or different electron-withdrawing moiety e.g. an aromatic nucleus. Such compounds have the property that at least of the alkenyl groups are capable of independent reaction with different living polymers and in this respect are different from conventional conjugated diene polymerizable monomers such as butadiene, isoprene, etc. Pure or technical grade polyalkenyl coupling agents may be used. Such compounds may be aliphatic, aromatic or heterocyclic. Examples of aliphatic compounds include the polyvinyl and polyallyl acetylene, diacetylenes, phosphates and phosphates as well as dimethacrylates, e.g. ethylene dimethylacrylate. Examples of suitable heterocyclic compounds include divinyl pyridine and divinyl thiophene.

[0066] The preferred coupling agents are polyalkenyl aromatic compounds and most preferred are the polyvinyl aromatic compounds. Examples of such compounds include those aromatic compounds, e.g. benzene, toluene, xylene, anthracene, naphthalene and durene, which are substituted with at least two alkenyl groups, preferably attached directly thereto. Specific examples include the polyvinyl benzenes e.g. divinyl, trivinyl and tetravinyl benzenes; divinyl, trivinyl and tetravinyl ortho-, meta- and para-xylenes, divinyl naphthalene, divinyl ethyl benzene, divinyl biphenyl, diisobutenyl benzene, diisopropenyl benzene, and diisopropenyl biphenyl. The preferred aromatic compounds are those represented by the formula $A\text{-}(CH{=}CH_2)_x$ wherein A is an optionally substituted aromatic nucleus and x is an integer of at least 2. Divinyl benzene, in particular meta-divinyl benzene, is the most preferred aromatic compound. Pure or technical grade divinyl benzene (containing other monomers e.g. styrene and ethyl styrene) may be used. The coupling agents may be used in admixture with small amounts of added monomers which increase the size of the nucleus, e.g. styrene or alkyl styrene. In such a case, the nucleus can be described as a poly(dialkenyl coupling agent/monoalkenyl aromatic compound) nucleus, e.g. a poly(divinylbenzene/monoalkenyl aromatic compound) nucleus.

[0067] The polyalkenyl coupling agent should be added to the living polymer after the polymerization of the monomers is substantially complete, i.e. the agent should be added only after substantially all the monomer has been converted to the living polymers.

[0068] The amount of polyalkenyl coupling agent added may vary within a wide range, but preferably, at least 0.5 mole of the coupling agent is used per mole of unsaturated living polymer. Amounts of from about 1 to about 15 moles, preferably from about 1.5 to about 5 moles per mole of living polymer are preferred. The amount, which can be added in two or more stages, is usually an amount sufficient to convert at least about 80 mass % to 85 mass % of the living polymer into star-shaped polymer.

[0069] The coupling reaction can be carried out in the same solvent as the living polymerization reaction. The coupling reaction can be carried out at temperatures within a broad range, such as from 0°C to 150°C, preferably from about 20°C to about 120°C. The reaction may be conducted in an inert atmosphere, e.g. nitrogen, and under pressure of from about 0.5 bar to about 10 bars.

[0070] The star polymers thus formed are characterized by a dense centre or nucleus of crosslinked poly(polyalkenyl coupling agent) and a number of arms of substantially linear unsaturated polymers extending outwardly from the nucleus. The number of arms may vary considerably, but is typically between about 4 and 25.

[0071] The resulting star polymers can then be hydrogenated using any suitable means. A hydrogenation catalyst may be used e.g. a copper or molybdenum compound. Catalysts containing noble metals, or noble metal-containing compounds, can also be used. Preferred hydrogenation catalysts contain a non-noble metal or a non-noble metal-containing compound of Group VIII of the periodic Table i.e., iron, cobalt, and particularly, nickel. Specific examples of preferred hydrogenation catalysts include Raney nickel and nickel on kieselguhr. Particularly suitable hydrogenation catalysts are those obtained by causing metal hydrocarbyl compounds to react with organic compounds of any one of the group VIII metals iron, cobalt or nickel, the latter compounds containing at least one organic compound that is attached to the metal atom via an oxygen atom as described, for example, in U.K. Patent No. 1,030,306. Preference is given to hydrogenation catalysts obtained by causing an aluminium trialkyl (e.g. aluminium diethyl ($Al(Et_3)$) or aluminium triisobutyl) to react with a nickel salt of an organic acid (e.g. nickel diisopropyl salicylate, nickel naphthenate, nickel 2-ethyl hexanoate, nickel di-tert-butyl benzoate, nickel salts of saturated monocarboxylic acids obtained by reaction of olefins having from 4 to 20 carbon atoms in the molecule with carbon monoxide and water in the presence of acid catalysts) or with nickel enolates or phenolates (e.g., nickel acetonylacetonate, the nickel salt of butylacetophenone). Suitable hydrogenation catalysts will be well known to those skilled in the art and the foregoing list is by no means intended to be exhaustive.

[0072] The hydrogenation of the star polymer is suitably conducted in solution, in a solvent which is inert during the hydrogenation reaction. Saturated hydrocarbons and mixtures of saturated hydrocarbons are suitable. Advantageously, the hydrogenation solvent is the same as the solvent in which polymerization is conducted. Suitably, at least 50%, preferably at least 70%, more preferably at least 90%, most preferably at least 95% by mass of the original olefinic unsaturation is hydrogenated.

[0073] The hydrogenated star polymer may then be recovered in solid form from the solvent in which it is hydrogenated by any convenient means, such as by evaporating the solvent. Alternatively, oil e.g. lubricating oil, may be added to the solution, and the solvent stripped off from the mixture so formed to provide a concentrate. Suitable concentrates contain from about 3 mass % to about 25 mass %, preferably from about 5 mass % to about 15 mass % of the hydrogenated star polymer VI improver.

[0074] The star polymers useful in the practice of the present invention can have a number average molecular weight of from about 10,000 to 700,000, preferably from about 30,000 to 500,000. The term "number average molecular weight", as used herein, refers to the number average weight as measured by Gel Permeation Chromatography ("GPC") with a polystyrene standard, subsequent to hydrogenation. It is important to note that, when determining the number average molecular weight of a star polymer using this method, the calculated number average molecular weight will be less than the actual molecular weight due to the three dimensional structure of the star polymer.

[0075] In one preferred embodiment, the star polymer of the present invention is derived from about 75 % to about 90 % by mass isoprene and about 10 % to about 25 % by mass butadiene, and greater than 80 % by mass of the butadiene units are incorporated 1,4-addition product. In another preferred embodiment, the star polymer of the present invention comprises amorphous butadiene units derived from about 30 to about 80 % by mass 1,2-, and from about 20 to about 70 % by mass 1,4-incorporation of butadiene. In another preferred embodiment, the star polymer is derived from isoprene, butadiene, or a mixture thereof, and further contains from about 5 to about 35 % by mass styrene units.

[0076] Typically, the star polymer has a Shear Stability Index (SSI) of from about 1 % to 35 % (30 cycle). An example of a commercially available star polymer VI improver having an SSI equal to or less than 35 is Infineum SV200™, available from Infineum USA L.P. and Infineum UK Ltd. Other examples of commercially available star polymer VI improver having an SSI equal to or less than 35 include Infineum SV250™, Infineum SV261™ and Infineum SV270™, also available from Infineum USA L.P. and Infineum UK Ltd.

[0077] Typically, the viscosity modifier may be provided in an amount of from 0.01 to 20, preferably 1 to 15, mass % based on the mass of the lubricating oil composition.

[0078] Optionally, one or both types of viscosity modifiers used in the practice of the invention can be provided with nitrogen-containing functional groups that impart dispersant capabilities to the VI improver. One trend in the industry has been to use such "multifunctional" VI improvers in lubricants to replace some or all of the dispersant. Nitrogen-containing functional groups can be added to a polymeric VI improver by grafting a nitrogen- or hydroxyl- containing moiety, preferably a nitrogen-containing moiety, onto the polymeric backbone of the VI improver (functionalizing). Processes for the grafting of a nitrogen-containing moiety onto a polymer are known in the art and include, for example, contacting the polymer and nitrogen-containing moiety in the presence of a free radical initiator, either neat, or in the presence of a solvent. The free radical initiator may be generated by shearing (as in an extruder) or heating a free radical initiator precursor, such as hydrogen peroxide.

[0079] The amount of nitrogen-containing grafting monomer will depend, to some extent, on the nature of the substrate polymer and the level of dispersancy required of the grafted polymer. To impart dispersancy characteristics to both star and linear copolymers, the amount of grafted nitrogen-containing monomer is suitably between about 0.4 and about 2.2 mass %, preferably from about 0.5 to about 1.8 mass %, most preferably from about 0.6 to about 1.2 mass %, based on the total weight of grafted polymer.

[0080] Methods for grafting nitrogen-containing monomer onto polymer backbones, and suitable nitrogen-containing grafting monomers are known and described, for example, in U.S. Patent No. 5,141,996, WO 98/13443, WO 99/21902, U.S. Patent No. 4,146,489, U.S. Patent No. 4,292,414, and U.S. Patent No. 4,506,056. (See also J Polymer Science, Part A: Polymer Chemistry, Vol. 26, 1189-1198 (1988); J. Polymer Science, Polymer Letters, Vol. 20, 481-486 (1982) and J. Polymer Science, Polymer Letters, Vol. 21, 23-30 (1983), all to Gaylord and Mehta and Degradation and Crosslinking of Ethylene-Propylene Copolymer Rubber on Reaction with Maleic Anhydride and/or Peroxides; J. Applied Polymer Science, Vol. 33, 2549-2558 (1987) to Gaylord, Mehta and Mehta.

(ii) Olefin Copolymers

[0081] In this invention olefin copolymers (OCP's) may be used. Examples of ranges in the composition include 0.1-6, 0.1-5, 0.1-4, mass % and lower limits of 1 or 2 mass %.

[0082] These may be copolymers of two or more monomers of C_2 to C_{30}, e.g. C_2 to C_8, olefins, including both alpha-olefins and internal olefins, which may be straight or branched, aliphatic, aromatic, alkyl-aromatic, or cycloaliphatic. Frequently, they are of ethylene with C_3 to C_{30} olefins, particularly preferred being copolymers of ethylene and propylene. They may also be copolymers of C_6 and higher alpha olefins and terpolymers of styrene, e.g. with isoprene and/or butadiene and hydrogenated derivatives thereof.

[0083] Preferred OCP's are ethylene copolymers containing 15 to 90, preferably 30 to 80, mass % of ethylene and 10 to 85, preferably 20 to 70, mass % of one or more C_3 to C_{28}, preferably C_3 to C_{18}, more preferably C_3 to C_8, alpha-olefins. Such OCP's may have a degree of crystallinity of less than 25 mass %, as determined by x-ray and differential scanning calorimetry. As indicated above, copolymers of ethylene and propylene are most preferred. Other alpha-olefins suitable in place of propylene, or in combination with ethylene and propylene to form a terpolymer or tetrapolymer, for example, include: 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene; and branched chain alpha-olefins such as 4-methyl-1-pentene, 4-methyl-1-hexene, 4-methyl pentene-1, 4, 4-dimethyl-1-pentene, 6-methylheptene-1, and mixtures thereof.

[0084] There may also be included terpolymers and tetrapolymers of ethylene, said C3 to C28 alpha-olefin, and a non-conjugated diolefin or mixtures of such diolefins. The non-conjugated diolefin is generally present as 0.5 to 20, preferably 1 to 7, mole percent of the total moles of ethylene and alpha-olefin.

Diluent Oil

[0085] The viscosity modifier is dispersed (e.g. dissolved) in a heavy basestock diluent oil. As stated, the latter has a kinematic viscosity at 100°C in the range of 6-15, preferably 7-14, mm^2s^{-1}. As examples of concentrations of the viscosity modifier in the heavy basestock diluent oil, the following ranges, in mass %, may be mentioned; 0.05 to 5, such as to 4, 3 or 2; 0.01 to 5, 4, 3 or 2, preferably 0.01 to 2; more preferably 1 to 2 such as 1 to 1.5. The main consideration is that the resulting dispersion should have the same or similar kinematic viscosity to that of a brightstock oil.

EXAMPLES

[0086] The present invention is illustrated by, but not limited to, the following examples.

FORMULATIONS

Marine diesel cylinder lubricants (MDCL's)

[0087] Each MDCL comprised a calcium alkylsalicylate detergent package of basicity index 18 and containing 12.4 mass% Ca; 23 mass% of a viscosity modifier or, as a comparison, of a brightstock or polyisobutylene; and 55.6 mass% of an oil of lubricating viscosity (a Group I oil (XOM600)). All MDCL's had a TBN of about 70. The detailed formulations are given in TABLE 1 below.

[0088] The viscosity modifiers used were:

- a star polymer in the form of an amorphous styrene-diene copolymer dispersed either in a heavy oil diluent or a light oil diluent ("star"); and
- an olefin copolymer in the form of an amorphous ethylene-propylene copolymer dispersed either in a heavy oil diluent or a light oil diluent ("OCP")

[0089] The brightstock used was a Group I brightstock with a kinematic viscosity at 100 °C of greater than $20mm^2s^{-1}$.

Trunk piston engine oils (TPEO's)

[0090] Each TPEO comprised a calcium alkylsalicylate detergent package of basicity index 5.8 and containing 8.9 mass% Ca; 7 mass% of a viscosity modifier or, as a comparison, of a brightstock or polyisobutylene; and 77.1 mass% of an oil of lubricating viscosity (a Group II oil (Chevron 600)). All TPEO's had a TBN of 40. The detailed formulations are given in TABLE 2 below. The viscosity modifiers, the brightstock and the polyisobutylene were the same as those in the MDCL's.

TESTING & RESULTS

[0091] Samples of the above formulations were tested for carbon deposition properties using the Panel Coker Test and for evaporation loss using the NOACK volatility tests. The tests are described as follows:

Panel Coker Test

[0092] Lubricating oils may degrade on hot engine surfaces and leave deposits which will affect engine performance; the panel coker test simulates typical conditions and measures the tendency of oils to form such deposits. The oil under test is splashed onto a heated metal plate by spinning a metal comb-like splasher device within a sump containing the oil. At the end of the test period, deposits are measured.

[0093] An overview of the test method is as follows:

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

- The panel is weighed and the deposits are calculated in grams (g).

[0094] **NOACK Volatility Test** determines the evaporation loss of lubricants in high temperature service. It is otherwise known as ASTM D-5800.

TABLE 1- An MDCL including a major amount of a Group I oil (XOM600)

Ex	Star (1.3%) in Diluent having a Kv100 11.21 $mm^2\ s^{-1}$	Star (1.3%) in Diluent having a Kv100 5.21 $mm^2\ s^{-1}$	OCP (1.4%) in Diluent having a Kv100 11.21 $mm^2\ s^{-1}$	OCP (1.4%) in Diluent having a Kv100 5.21 $mm^2\ s^{-1}$	Brightstock	Polyisobutylene 950 Mol. Wt.	Panel Coker (g)	NOACK D5800 Evap. Loss (mass%)
1	√						0.0426	3.8
A		√					0.0736	6.6
2			√				0.0755	4.0
B				√			0.0509	6.7
C					√		0.0988	3.9
D						√	0.0452	4.4

[0095] Table 1 shows that replacing brightstock with either star polymer or an olefin copolymer reduces the amount of deposits in the Panel Coker Test. Table 1 also shows that the use of higher viscosity diluent for the star polymer and the olefin copolymer reduces the evaporation loss (i.e. the lube oil consumption) compared to the use of a lighter viscosity diluent.

[0096] In the Tables, a tick indicates presence of a particular component and a blank space indicates absence.

TABLE 2- TPEO including a major amount of a Group II oil (Chevron 600)

Ex	Star (1.3%) in Diluent having a Kv100 12.16 $mm^2\ s^{-1}$	Star (1.3%) in Diluent having a Kv100 5.21 $mm^2\ s^{-1}$	OCP (1.4%) in Diluent having a Kv100 12.16 $mm^2\ s^{-1}$	OCP (1.4%) in Diluent having a Kv100 5.21 $mm^2\ s^{-1}$	Brightstock	Polyisobutylene (Mol. Weight 950)	Panel Coker (g)	NOACK D5800 Evap. Loss (mass%)
3	√						0.0191	3.7
W		√					0.0188	4.1
4			√				0.0187	3.2
X				√			0.0166	3.9
Y					√		0.0310	3.1
Z						√	0.0193	3.4

[0097] Table 2 shows that replacing brightstock with either star polymer or an olefin copolymer reduces the amount of deposits in the Panel Coker Test. Table 2 also shows that the use of a higher viscosity diluent for the star polymer and the olefin copolymer reduces the evaporation loss (i.e. the lube oil consumption) compared to the use of a lighter viscosity diluent.

[0098] Examples 1-4 fall within the invention. Examples A-D and W-Z are comparative examples.

Claims

1. A two-stroke or four-stroke marine engine lubricating oil composition comprising an oil of lubricating viscosity in a major amount, and blended with:

   (A) one or more additives, in respective minor amounts; and
   (B) a viscosity modifier in the form of either (i) a polymer comprising a core and a plurality of polymeric arms extending therefrom, or (ii) an olefin copolymer, the viscosity modifier being dispersed in a diluent oil having a kinematic viscosity at 100°C in the range of 6-15, preferably 7-14, $mm^2 s^{-1}$,

   wherein the two-stoke marine engine lubricating oil composition has a TBN of 10 to 100, preferably 40 to 100, using ASTM D2896 and the four-stroke marine engine lubricating oil composition has a TBN of 25 to 60 using ASTM D2896.

2. A method of making a two-stroke or four-stroke marine engine lubricating oil composition comprising blending an oil of lubricating viscosity in a major amount with:

   (A) one or more additives, in relative minor amounts; and
   (B) a viscosity modifier in the form of either (i) a polymer comprising a core and a plurality of polymeric arms extending therefrom, or (ii) an olefin copolymer, the viscosity modifier being dispersed in a diluent oil of kinematic viscosity at 100 °C in the range of 6-15, preferably 7-14, $mm^2 s^{-1}$,

   wherein the two-stoke marine engine lubricating oil composition has a TBN of 10 to 100, preferably 40 to 100, using ASTM D2896 and the four-stroke marine engine lubricating oil composition has a TBN of 25 to 60 using ASTM D2896.

3. A two-stroke or four-stroke marine engine lubricating oil composition obtainable by the method of claim 2.

4. The composition or method of any of claims 1-3, wherein the composition contains less than 0.5, preferably less than 0.1, mass % of brightstock, and more preferably is completely or substantially free of brightstock.

5. The composition or method of any of claims 1-4, wherein the viscosity modifier (B) is present in the composition in an amount in the range of 0.01 to 40 mass %.

6. The composition or method of any claim 1-5, wherein the viscosity modifier (B) comprises the polymer (i), the arms of which comprise a hydrogenated isoprene-butadiene copolymer, a hydrogenated styrene-isoprene-butadiene copolymer, a hydrogenated isoprene-styrene copolymer or a hydrogenated butadiene-styrene copolymer, such as a linear diblock copolymer.

7. The composition or method of any of claims 1-5, wherein the viscosity modifier (B) comprises the olefin copolymer (ii) as a copolymer of two or more monomers of C_2 - C_{30} olefins, such as a copolymer of ethylene with a C_3 - C_{30} olefin such as propylene.

8. The composition or method of any one of claims 1-7, wherein the composition is in the form of a marine diesel cylinder lubricant.

9. The composition or method of any one of claims 1-7, wherein the composition is in the form of a trunk piston engine oil.

10. The use of a viscosity modifier (B) as defined in claim 1 to improve the carbon deposition properties of a marine diesel cylinder lubricant of TBN 10-100, prerably 40-100, using ASTM D2896 or a trunk piston engine oil having a TBN of 25-60 using ASTM D2896.

11. A method of lubricating a cross-head marine diesel engine comprising supplying a composition of any one of claims 1-8 to the piston/cylinder of the engine.

12. A method of lubricating a trunk piston marine diesel engine comprising supplying a composition of any one of claims 1-7 or 9 to the engine.

13. The composition, use or method of any one of claims 1-12, wherein the oil of lubricating viscosity contains 50% or more, such as substantially all, of a basestock that contains greater than or equal to 90% saturates and less than

or equal to 0.03% sulphur.

14. The composition, use or method of any one of claims 1-12, wherein the oil of lubricating viscosity contains 50% or more, such as substantially all, of a basestock that contains less than 90 percent saturates and/or greater than 0.03 % sulphur.

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EUROPEAN SEARCH REPORT

Application Number
EP 14 15 7359

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The present search report has been drawn up for all claims

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Place of search	Date of completion of the search	Examiner
Munich	16 June 2014	Bork, Ana-Maria

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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