

Marine Engine Lubrication

FIELD OF THE INVENTION

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

BACKGROUND OF THE INVENTION

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

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

It is known in the art to include brightstock in MDCL’s and TPEO’s, brightstock being a high viscosity oil that is highly refined and dewaxed and that is produced from residual stocks or bottoms. It may, for example, have a kinematic viscosity at 100°C of greater than 25, usually greater than 30, 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} .

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

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

SUMMARY OF THE INVENTION

It is now found that the use of star polymers such as amorphous styrene-diene copolymer in an MDCL or a TPEO enables the above problem to be overcome.

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

- (A) additives, in respective minor amounts; and
- (B) a viscosity modifier in the form of a polymer comprising a core and a plurality of polymeric arms extending therefrom, in an amount in the range of 0.05 -6 mass%,

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

In further aspects the present invention comprises:-

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

absent or is substantially absent from the marine diesel cylinder lubricant or the trunk piston engine oil;

a method of lubricating a cross-head marine diesel engine comprising supplying the composition 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

a method of, or for, reducing the amount of brightstock in a two-stroke or four-stroke marine engine lubricating oil composition comprising an oil of lubricating viscosity in a major amount and (A) additives, in respective minor amounts; the method comprising the step of replacing, in part or in full, the brightstock with (B) a viscosity modifier in the form of a polymer comprising a core and a plurality of polymeric arms extending therefrom, in an amount in the range of 0.05 to 6 mass %.

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

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

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

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

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

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

Furthermore in this specification, if and when used:

“calcium content” is as measured by ASTM 4951;

“phosphorus content” is as measured by ASTM D5185;

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

“sulphur content” is as measured by ASTM D2622;

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

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

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

DETAILED DESCRIPTION OF THE INVENTION

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

OIL OF LUBRICATING VISCOSITY

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

such as 90 to 95. The lubricating oil may comprise greater than 60, typically greater than 70. mass % of the composition.

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

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

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

Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol).

Specific examples of such esters includes dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

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

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

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

Marine Diesel Cylinder Lubricant ("MDCL")

An MDCL may employ 10-35, preferably 13-30, most preferably 16-24, mass % of a concentrate or additive package, the remainder being base stock. It preferably includes at least 50, more preferably at least 60, even more preferably at least 70, mass % of oil of lubricating viscosity based on the total mass of MDCL.

Preferably, the MDCL has a compositional TBN (using ASTM D2896) of 40-100, such as 50-60.

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

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

Trunk Piston Engine Oil ("TPEO")

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

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

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

base stock

balance

balance

When a plurality of additives is employed it may be desirable, although not essential, to prepare one or more additive packages comprising the additives, whereby several additives can be added simultaneously to the base oil to form the lubricating oil composition. Dissolution of the additive package(s) into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The additive package(s) will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration, and/or to carry out the intended function, in the final formulation when the additive package(s) is/are combined with a predetermined amount of base lubricant. Thus, compounds in accordance with the present invention may be admixed with small amounts of base oil or other compatible solvents together with other desirable additives to form additive packages containing active ingredients.

More detailed description of additive components is given below.

Detergents

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

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

The detergent is preferably an alkali metal or alkaline earth metal additive such as an overbased oil-soluble or oil-dispersible calcium, magnesium, sodium or

barium salt of a surfactant selected from phenol, sulphonic acid, carboxylic acid, salicylic acid and naphthenic acid, wherein the overbasing is provided by an oil-insoluble salt of the metal, e.g. carbonate, basic carbonate, acetate, formate, hydroxide or oxalate, which is stabilised by the oil-soluble salt of the surfactant. The metal of the oil-soluble surfactant salt may be the same or different from that of the metal of the oil-insoluble salt. Preferably the metal, whether the metal of the oil-soluble or oil-insoluble salt, is calcium.

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

Anti-oxidants

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

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

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

The terms 'oil-soluble' or 'oil-dispersable' as used herein do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible or capable of being suspended in the oil in all proportions. These do mean, however, that they

are, for instance, soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

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

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

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

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

VISCOSITY MODIFIER

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

This invention employs 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 %.

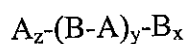
The viscosity modifier may comprise at least one star-shaped, at least partially hydrogenated, polymer derivable, at least in part, from the polymerisation of one or more conjugated diene monomers as defined hereinbefore. Suitably, the star-shaped polymer includes multiple arms extending from a central 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.

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.

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.

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.

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:



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.

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



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.

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.

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.

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.

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.

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.

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.

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.

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 (M_w/M_n), such as a molecular weight distribution of less than about 1.2

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 monolithium 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.

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.

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.

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.

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.

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-

$(\text{CH}=\text{CH}_2)_x$ 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.

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.

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.

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.

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.

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 ($\text{Al}(\text{Et}_3)$) 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 acetonylacetate, 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.

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.

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.

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.

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.

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.

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.

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.

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.

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 Cross-linking 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.

EXAMPLES

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

MDCL's

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

TPEO's

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

TESTING & RESULTS

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

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

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

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

<u>Table 1</u>					
<u>TPEO</u>	<u>Additive</u>	<u>Base oil</u>	<u>Brightstock</u>	<u>Star Polymer</u>	<u>Result</u> (wear vol m ³)
Control	16	84	-	-	5,584
Reference	16	75.5	8.5	-	8,279
1	16	82.98	-	1.02	2,170
<u>MDCL</u>					
Control	20.89	79.11	-	-	33,960
Reference	20.89	58.89	20.22	-	3,940
2	20.89	76.68	-	2.43	13,291

The above results show amorphous styrene-diene isoprene star polymer advantageously reduces the wear scar volume as compared with the control and reference for TPEO oils. For MDCL it is clearly advantageous to include the star polymer versus using no brightstock at all.

CLAIMS:

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

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

2. The composition as claimed in claim 1, wherein the arms of the polymer comprise a hydrogenated isoprene-butadiene copolymer, a hydrogenated styrene-isoprene-butadiene copolymer, a hydrogenated isoprene-styrene copolymer or a hydrogenated butadiene-styrene copolymer.
3. The composition as claimed in claim 1 or claim 2, wherein the polymeric arms comprise a linear diblock copolymer.
4. The composition as claimed in any one of claims 1-3, wherein the polymer has a number average molecular weight of 10,000-700,000, such as 30,000-500,000.
5. The composition as claimed in any one of claims 1-4 in the form of a marine diesel cylinder lubricant.

6. The composition as claimed in any one of claims 1-4 in the form of a trunk piston engine oil.
7. The use of a viscosity modifier (B) as defined in any one of claims 1-4 to improve the anti-wear properties of a marine diesel cylinder lubricant or a trunk piston engine oil which includes less than 0.5 mass%, preferably less than 0.1 mass%, of brightstock; the two-stroke marine engine lubricating oil composition having a TBN of 40 to 100 using ASTM D2896, or the four-stroke marine engine lubricating oil composition having a TBN of 25 to 60 using ASTM D2896.
8. The use as claimed in claim 7, wherein the marine diesel cylinder lubricant or the trunk piston engine oil is substantially free from brightstock.
9. Use of a viscosity modifier (B) as defined in any one of claims 1-4 as a replacement, in part or in full, for brightstock in a marine diesel cylinder lubricant or a trunk piston engine oil so that the marine diesel cylinder lubricant or the trunk piston engine oil includes less than 0.5 mass%, preferably less than 0.1 mass%, of brightstock.
10. A method of lubricating a cross-head marine diesel engine comprising supplying a composition as claimed in any of claims 1-5 to the piston/cylinder assembly of the engine.
11. A method of lubricating a trunk piston marine diesel engine comprising supplying a composition as claimed in any of claims 1-4 or 6 to the engine.
12. A method of reducing the amount of brightstock in a two-stroke or four-stroke marine engine lubricating oil composition comprising an oil of lubricating viscosity in a major amount and (A) additives, in respective minor amounts; the method comprising the step of replacing, in part or in full, the brightstock with (B) a viscosity modifier in the form of a polymer comprising a core and a

plurality of polymeric arms extending therefrom, in an amount in the range of 0.05 to 6 mass %.

13. The method as claimed in claim 12, wherein (B) substantially replaces the brightstock so that the composition includes less than 0.5 mass%, preferably less than 0.1 mass%, of brightstock; preferably so that the composition is completely or substantially free from brightstock.
14. The method as claimed in claims 12 or 13, wherein the composition includes less than 0.5 mass%, preferably less than 0.1 mass%, of brightstock; preferably the composition is completely or substantially free from brightstock.
15. The method as claimed in any one of claims 12, 13 or 14, wherein the two-stroke marine engine lubricating oil composition has a TBN of 40 to 100 using ASTM D2896, or the four-stroke marine engine lubricating oil composition has a TBN of 25 to 60 using ASTM D2896.