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(54) Engine lubrication

(57) A trunk piston or cross-head diesel engine having a centrifuge system including a sealing medium is lubricated with a lubricant which, for the cross-head engine, is a system lubricant and which contains 0.04 to 5 mass %, expressed as active ingredient, of a combination of one or more linked aromatic compounds and one or more nitrogen containing ashless disperants, in a mass: mass ratio in the range of 1:3 to 9:1.

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Description

FIELD OF THE INVENTION

[0001] This invention concerns diesel engine lubrication, more specifically trunk piston diesel engine lubrication using trunk piston engine oil ('TPEO') and system lubrication of crosshead (also referred to as two-stroke or slow speed) diesel engines.

BACKGROUND OF THE INVENTION

[0002] Trunk piston diesel engines are used in marine, power generation and rail traction applications and typically have a rated speed of between 300 and 1000 rpm. In trunk piston diesel engines a single lubricant composition 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 a pumped circulation system. The cylinder liners are lubricated partially by splash lubrication and partially by oil from the circulation system which finds its way to the cylinder wall through holes in the piston skirt via the connecting rod and gudgeon pin. Crosshead diesel engines, on the other hand, are lubricated using two separate lubricants; the engine cylinders are lubricated using a marine diesel cylinder lubricant (or 'MDCL'), and the engine crankcase is lubricated using a separate lubricant referred to as a system oil.

[0003] Trunk piston diesel engines use a centrifuge system to remove contaminants, such as for example, soot or water, from the lubricating oil composition. Similar centrifuge systems are used to treat the system oil of some crosshead marine diesel engines. The centrifuge system relies on the use of a sealing medium that is heavier than the lubricating oil composition. The sealing medium is generally water. When the lubricating oil composition passes through the centrifuge system, it comes into contact with the water. The lubricating oil composition therefore needs to be capable of shedding the water and remaining stable in the presence of water. If the lubricating oil composition is unable to shed the water, the water builds up in the lubricating oil composition forming an emulsion, which leads to deposits building up in the centrifuge system and prevents the centrifuge system from working properly.

[0004] US-A1-2006/0189492 describes certain linked aromatic compounds that act as soot dispersants in lubricating oil compositions. It does not, however, describe their use in trunk piston or crosshead diesel engine lubrication or the need to be capable of shedding water.

SUMMARY OF THE INVENTION

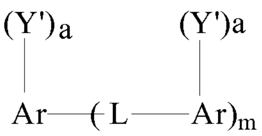
[0005] The present invention provides lubrication that improves soot handling and that is capable of shedding media used in centrifuge systems. The invention employs the above-mentioned linked aromatic compounds in combination with nitrogen-containing ashless dispersant in defined ratios.

[0006] In a first aspect, the invention comprises a trunk piston or cross-head diesel engine lubricating oil composition having a total base number of at least 15, such as at least 20, mg KOH/g, as determined by ASTM D2896, comprising:

(A) at least 40 mass % of an oil lubricating viscosity; and

(B) 0.04 to 5 mass %, expressed as active ingredient, of the lubricating oil composition, of a combination of:

(B1) at least one linked aromatic compound of the formula:



$$\overset{(Y')_a}{\overset{|}{\mathrm{Ar}}} - \left(\mathrm{L} - \overset{(Y')_a}{\overset{|}{\mathrm{Ar}}} \right)_m \qquad \text{(II)}$$

wherein:

each Ar independently represents an aromatic moiety having 0 to 3 substituents selected from the group consisting of alkyl, alkoxy, alkoxyalkyl, hydroxy, hydroxyalkyl, acyloxy, acyloxyalkyl, aryloxy, aryloxy alkyl, halo and combinations thereof;

each L is independently a linking moiety comprising a carbon-carbon single bond or a linking group;

each Y' is independently a moiety of the formula $Z(O(CR_2)_n)_yX$-, wherein X is selected from the group consisting of $(CR'_2)_z$, O and S; R and R' are each independently selected from H,C_1 to C_6 alkyl and aryl;

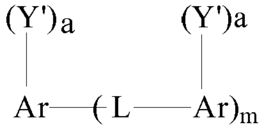
z is 1 to 10; n is 0 to 10 when X is $(CR'_2)_z$, and 2 to 10 when X is O or S; y is 1 to 30; Z is H, an acyl group, an

alkyl group or an aryl group;
each a is independently 0 to 3, with the proviso that at least one Ar moiety bears at least one group Y' in which Z is not H; and
m is 1 to 100; and
(B2) at least one nitrogen-containing dispersant, where the mass : mass ratio of (B1) to (B2) is in the range from 1:3 to 9:1, preferably in the range from 1:1 to 6:1, such as 3:1 1 to 6:1.

[0007] In a second aspect, a method of lubricating a trunk piston diesel engine, or cross-head diesel engine, having a centrifuge system including a sealing medium, the method comprising operation of the engine and lubrication of the trunk piston engine or system lubrication of the cross-head engine with a lubricating oil composition comprising:

(A) an oil of lubricating viscosity, in a major amount; and
(B) 0.04 to 5 mass %, expressed as active ingredient, of the lubricating oil composition, of a combination of:

(B1) at least one linked aromatic compound of the formula:



$$\underset{}{\overset{(Y')a}{Ar}} - (L - \overset{(Y')a}{Ar})_m \qquad (II)$$

wherein:
each Ar independently represents an aromatic moiety having 0 to 3 substituents selected from the group consisting of alkyl, alkoxy, alkoxyalkyl, hydroxy, hydroxyalkyl, acyloxy, acyloxyalkyl, aryloxy, aryloxy alkyl, halo and combinations thereof;
each L is independently a linking moiety comprising a carbon-carbon single bond or a linking group;
each Y' is independently a moiety of the formula $Z(O(CR_2)_n)_yX$-, wherein X is selected from the group consisting of $(CR'_2)_z$, O and S; R and R' are each independently selected from H,C_1 to C_6 alkyl and aryl; z is 1 to 10; n is 0 to 10 when X is $(CR'_2)_z$, and 2 to 10 when X is O or S; y is 1 to 30; Z is H, an acyl group, an alkyl group or an aryl group;
each a is independently 0 to 3, with the proviso that at least one Ar moiety bears at least one group Y' in which Z is not H; and
m is 1 to 100; and
(B2) at least one nitrogen-containing dispersant, where the mass : mass ratio of (B1) to (B2) is in the range from 1:3 to 9:1, preferably in the range from 1:1 to 6:1, such as 3:1 1 to 6:1.

[0008] In a third aspect, the invention comprises a method of enhancing the water-shedding properties, as measured by a centrifuge water shedding test, of a lubricating oil composition in the lubrication of a trunk piston engine, or the system lubrication of cross-head diesel engine, having a centrifuge system including a sealing medium, by employing a lubricating oil composition as defined in the first aspect of the invention when compared with a corresponding lubricating oil composition where (B) contains only (B2).

[0009] In this specification, the following words and expressions, if and when used, have the meanings ascribed below:

"active ingredient" 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 in excess of 50 mass % of a composition;
"minor amount" means less than 50 mass % of a composition;
"TBN" means total base number as measured by ASTM D2896.

[0010] Furthermore in this specification:

"phosphorus content" is as measured by ASTM D5185;
"sulphated ash content" is as measured by ASTM D874;

"sulphur content" is as measured by ASTM D2622;
"KV 100" means kinematic viscosity at 100°C as measured by ASTM D445.

[0011] 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.

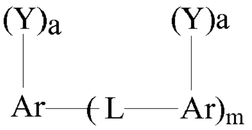
[0012] Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

DETAILED DESCRIPTION OF THE INVENTION

[0013] The features of the invention relating, where appropriate, to each and all aspects of the invention, will now be described in more detail as follows:

(B1) LINKED AROMATIC COMPOUND

[0014] US 2006/0189492 Al describes these compounds which can be prepared from compounds of formula (I) below.



$$\overset{(\mathrm{Y})a}{\overset{|}{\mathrm{Ar}}}-\!\left(\mathrm{L}-\overset{(\mathrm{Y})a}{\overset{|}{\mathrm{Ar}}}\right)_m$$

(I)

wherein each Ar independently represents an aromatic moiety having 0 to 3 substituents selected from the group consisting of alkyl, alkoxy, alkoxyalkyl, hydroxy, hydroxyalkyl, halo and combinations thereof; each L is independently a linking moiety comprising a carbon-carbon single bond or a linking group; each Y is independently a moiety of the formula $H(O(CR_2)_n)_yX$-, wherein X is selected from the group consisting of $(CR'_2)_z$, O and S; R and R' are each independently selected from H, C_1 to C_6 alkyl and aryl; z is 1 to 10; n is 0 to 10 when X is $(CR'_2)_z$, and 2 to 10 when X is O or S; and y is 1 to 30; each a is independently 0 to 3, with the proviso that at least one Ar moiety bears at least one group Y; and m is 1 to 100.

[0015] Aromatic moieties Ar of Formula (I) can be a mononuclear carbocyclic moiety (phenyl) or a polynuclear carbocyclic moiety. Polynuclear carbocyclic moieties may comprise two or more fused rings, each ring having 4 to 10 carbon atoms (e.g., naphthalene) or may be linked mononuclear aromatic moieties, such as biphenyl, or may comprise linked, fused rings (e.g., binaphthyl). Examples of suitable polynuclear carbocyclic aromatic moieties include naphthalene, anthracene, phenanthrene, cyclopentenophenanthrene, benzanthracene, dibenzanthracene, chrysene, pyrene, benzpyrene and coronene and dimer, trimer and higher polymers thereof. Ar can also represent a mono- or polynuclear heterocyclic moiety. Heterocyclic moieties Ar include those comprising one or more rings each containing 4 to 10 atoms, including one or more hetero atoms selected from N, O and S. Examples of suitable monocyclic heterocyclic aromatic moieties include pyrrole, furan, thiophene, imidazole, oxazole, thiazole, pyrazole, pyridine, pyrimidine and purine. Suitable polynuclear heterocyclic moieties Ar include, for example, quinoline, isoquinoline, carbazole, dipyridyl, cinnoline, phthalazine, quinazoline, quinoxaline and phenanthroline. Each aromatic moiety (Ar) may be independently selected such that all moieties Ar are the same or different. Polycyclic carbocyclic aromatic moieties are preferred. Most preferred are compounds of Formula I wherein each Ar is naphthalene. Each aromatic moiety Ar may independently be unsubstituted or substituted with 1 to 3 substituents selected from alkyl, alkoxy alkoxyalkyl, hydroxyl, hydroxyalkyl, halo, and combinations thereof. Preferably, each Ar is unsubstituted (except for group(s) Y and terminal groups).

[0016] Each linking group (L) may be the same or different, and can be a carbon to carbon single bond between the carbon atoms of adjacent moieties Ar, or a linking group. Suitable linking groups include alkylene linkages, ether linkages, diacyl linkages, ether-acyl linkages, amino linkages, amido linkages, carbamido linkages, urethane linkages, and sulfur linkage. Preferred linking groups are alkylene linkages such as $-CH_3CHC(CH_3)_2-$, or $C(CH_3)_2-$; diacyl linkages such as -COCO- or $-CO(CH_2)_4CO-$; and sulfur linkages, such as $-S_1-$ or $-S_x-$. More preferred linking groups are alkylene linkages, most preferably $-CH_2-$.

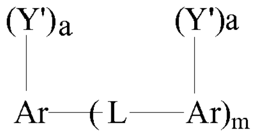
[0017] Preferably, Ar of Formula (I) represents naphthalene, and more preferably, Ar is derived from 2-(2-naphthyloxy)-ethanol. Preferably, each Ar is derived from 2-(2-naphthyloxy)-ethanol, and m is 2 to 25. Preferably, Y of Formula (I) is the group $H(O(CR_2)_2)_yO-$, wherein y is 1 to 6. More preferably, Ar is naphthalene, Y is $HOCH_2CH_2O-$ and L is $-CH_2-$.

[0018] Methods for forming compounds of Formula (I) should be apparent to those skilled in the art. A hydroxyl aromatic compound, such as naphthol can be reacted with an alkylene carbonate (e.g., ethylene carbonate) to provide a compound of the formula $AR-(Y)_a$. Preferably, the hydroxyl aromatic compound and alkylene carbonate are reacted in the presence of a base catalyst, such as aqueous sodium hydroxide, and at a temperature of from 25 to 300, preferably from 50 to 200,°C. During the reaction, water may be removed from the reaction mixture by azeotropic distillation or other conventional means. If separation of the resulting intermediate product is desired, upon completion of the reaction (indicated by the cessation of CO_2 evolution), the reaction product can be collected, and cooled to solidify. Alternatively, a hydroxyl aromatic compound, such as naphthol, can be reacted with an epoxide, such as ethylene oxide, propylene oxide, butylenes oxide or styrene oxide, under similar conditions to incorporate one or more oxy-alkylene groups.

[0019] To form a compound of Formula (I), the resulting intermediate compound Ar-$(Y)_a$ may be further reacted with a polyhalogenated (preferably dihalogenated) hydrocarbon (e.g., 1-4-dichlorobutane, 2,2-dichloropropane, etc.), or a di- or polyolefin (e.g., butadiene, isoprene, divinylbenzene, 1,4-hexadiene, 1,5-hexadiene, etc.) to yield a compound of Formula (I) having an alkylene linking groups. Reaction of moieties Ar-$(Y)_a$ and a ketone or aldehyde (e.g., formaldehyde, acetone, benzophenone, acetophenone, etc.) provides an alkylene-linked compound. An acyl-linked compound can be formed by reacting moieties Ar-$(Y)_a$ with a diacid or anhydride (e.g., oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, succinic anhydride, etc.). Sulfide, polysulfide, sulfinyl and sulfonyl linkages may be provided by reaction of the moieties Ar-$(Y)_a$ with a suitable difunctional sulfurizing agent (e.g., sulfur monochloride, sulfur dichloride, thionyl chloride ($SOCl_2$), sulfuryl chloride (SO_2Cl_2), etc.). To provide a compound of Formula (I) with an alkylene ether linkage, moieties Ar-$(Y)_a$ can be reacted with a divinylether. Compounds of Formula (I), wherein L is a direct carbon to carbon link, may be formed via oxidative coupling polymerization using a mixture of aluminum chloride and cuprous chloride, as described, for example, by P. Kovacic, et al., J. Polymer Science: Polymer Chem. Ed., 21, 457 (1983). Alternatively, such compounds may be formed by reacting moieties Ar-$(Y)_a$ and an alkali metal as described, for example, in "Catalytic Benzene Coupling on Caesium/Nanoporous Carbon Catalysts", M.G. Stevens, K.M. Sellers, S. Subramoney and H.C. Foley, Chemical Communications, 2679-2680 (1988).

[0020] To form the preferred compounds of Formula (I), having an alkylene linking group, more preferably a methylene linking group, base remaining in the Ar-$(Y)_a$ reaction mixture can be neutralized with acid, preferably with an excess of acid (e.g., a sulfonic acid) and reacted with an aldehyde, preferably formaldehyde, and preferably in the presence of residual acid, to provide an alkylene, preferably methylene bridged compound of Formula (I). The degree of polymerization of the compounds of Formula I range from 2 to 101 (corresponding to a value of m of from 1 to 100), preferably from 2 to 50, most preferably from 2 to 25.

[0021] The compounds of formula (II) can be formed by reacting a compound of formula (I) with at least one of an acylating agent, an alkylating agent and an arylating agent, and are represented by the formula:



$$\mathrm{Ar}\text{—}\left(\mathrm{L}\text{—}\mathrm{Ar}\right)_m \quad \text{each Ar bearing } (Y')_a \qquad \text{(II)}$$

wherein each Y' is independently a moiety of the formula $Z(O(CR_2)_n)_yX$-; Z is an acyl group, an alkyl group or an aryl group or H, and Ar, L, X, R, z, n and y are the same as defined in Formula (I), with the proviso that, at least one Ar moiety bears at least one substituent group Y' in which Z is not H; and m is 1 to 100.

[0022] Suitable acylating agents include hydrocarbyl carbonic acid, hydrocarbyl carbonic acid halides, hydrocarbyl sulfonic acid and hydrocarbyl sulfonic acid halides, hydrocarbyl phosphoric acid and hydrocarbyl phosphoric halides, hydrocarbyl isocyanates and hydrocarbyl succinic acylating agents. Preferred acylating agents are C_8 and higher hydrocarbyl isocyanates, such as dodecyl isocyanate and hexadodecyl isocyanate and C_8 or higher hydrocarbyl acylating agents, more preferably polybutenyl succinic acylating agents such as polybutenyl, or polyisobutenyl succinic anhydride (PIBSA). Preferably the hydrocarbyl succinic acylating agent will have a number average molecular weight ($\overline{M}_n$) of from 100 to 5000, preferably from 200 to 3000, more preferably from 450 to 2500. Preferred hydrocarbyl isocyanate acylating agent will have a number average molecular weight ($\overline{M}_n$) of from 100 to 5000, preferably from 200 to 3000, more preferably from 200 to 2000.

[0023] Acylating agents can be prepared by conventional methods known to those skilled in the art, such as chlorine-assisted, thermal and radical grafting methods. The acylating agents can be mono- or polyfunctional. Preferably, the acylating agents have a functionality of less than 1.3. Acylating agents are used in the manufacture of dispersants, and a more detailed description of methods for forming acylating agents is described in the description of suitable dispersants, presented *infra.*

[0024] Suitable alkylating agents include C_8 to C_{30} alkane alcohols, preferably C_8 to C_{18} alkane alcohols. Suitable arylating agents include C_8 to C_{30}, preferably C_8 to C_{18} alkane-substituted aryl mono- or polyhydroxide.

[0025] Molar amounts of the compound of Formula (I) and the acylating, alkylating and/or arylating agent can be adjusted such that all, or only a portion, such as 25% or more, 50% or more or 75% or more of groups Y are converted to groups Y'. In the case where the compound of Formula (I) has hydroxy and/or alkyl hydroxy substituents, and such compounds are reacted with an acylating group, it is possible that all or a portion of such hydroxy and/or alkylhydroxy substituents will be converted to acyloxy or acyloxy alkyl groups. In the case where the compound of Formula (I) has hydroxy and/or alkyl hydroxy substituents, and such compounds are reacted with an arylating group, it is possible that all or a portion of such hydroxy and/or alkylhydroxy substituents will be converted to aryloxy or aryloxy alkyl groups. Therefore, compounds of Formula (II) substituted with acyloxy, acyloxy alkyl, aryloxy and/or aryloxy alkyl groups are considered within the scope of the present invention. A salt form of compounds of Formula (II) in which Z is an acylating group, which salts result from neutralization with base (as may occur, for example, due to interaction with a metal detergent, either in an additive package or a formulated lubricant), is also considered to be within the scope of the invention.

[0026] Compounds of Formula (II) can be derived from the precursors of Formula (I) by reacting the precursors of Formula (I) with the acylating agent, preferably in the presence of a liquid acid catalyst, such as sulfonic acid, e.g., dodecyl benzene sulfonic acid, paratoluene sulfonic acid or polyphosphoric acid or a solid acid catalyst such as Amberlyst-15, Amberlyst-36, zeolites, mineral acid clay or tungsten polyphosphoric acid; at a temperature of from about 0 to 300, preferably from 50 to 250,°C. Under the above conditions, the preferred polybutenyl succinic acylating agents can form diesters, acid esters or lactone esters with the compound of Formula (I).

[0027] Compounds of Formula (II) can be derived from the precursors of Formula (I) by reacting the precursors of Formula (I) with the alkylating agent or arylating agent, preferably in the presence of triphenylphosphine and diethyl azodicarboxylate (DEAD), a liquid acid catalyst, such as sulfonic acid, e.g., dodecyl benzene sulfonic acid, paratoluene sulfonic acid or polyphosphoric acid or a solid acid catalyst such as Amberlyst-15, Amberlyst-36, zeolites, mineral acid clay or tungsten polyphosphoric acid; at a temperature of from 0 to 300, preferably from 50 to 250,°C.

(B2) ASHLESS DISPERSANT

[0028] Ashless dispersants useful in the compositions of the present invention comprise an oil-soluble polymeric long chain backbone having functional groups capable of associating with particles to be dispersed. Typically, such dispersants comprise amine, alcohol, amide or ester polar moieties attached to the polymer backbone, often via a bridging group. The ashless dispersant may be, for example, selected from oil-soluble salts, esters, amino-esters, amides, imides and oxazolines of long chain hydrocarbon-substituted mono- and polycarboxylic acids or anhydrides thereof; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having polyamine moieties attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine.

[0029] Preferably, the ashless dispersant is a "high molecular weight" dispersant having a number average molecular weight ($\overline{M}_n$) greater than or equal to 4,000, such as between 4,000 and 20,000. The precise molecular weight ranges will depend on the type of polymer used to form the dispersant, the number of functional groups present, and the type of polar functional group employed. For example, for a polyisobutylene-derivatized dispersant, a high molecular weight dispersant is one formed with a polymer backbone having a number average molecular weight of from 1680 to 5600. Typical commercially-available polyisobutylene-based dispersants contain polyisobutylene polymers having a number average molecular weight ranging from 900 to 2300, functionalized by maleic anhydride (MW = 98), and derivatized with polyamines having a molecular weight of from 100 to 350. Polymers of lower molecular weight may also be used to form high molecular weight dispersants by incorporating multiple polymer chains into the dispersant, which can be accomplished using methods that are known in the art.

[0030] Polymer molecular weight, specifically number average molecular weight ($\overline{M}_n$), can be determined by various known techniques. One convenient method is gel permeation chromatography (GPC), which additionally provides molecular weight distribution information (see W. W. Yau, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979). If the molecular weight of an amine-containing dispersant (e.g., PIBSA-polyamine or PIBSA-PAM) is being determined, the presence of the amine may cause the dispersant to be adsorbed by the column, leading to an inaccurate molecular weight determination. Persons familiar with the operation of GPC equipment understand that this problem may be eliminated by using a mixed solvent system, such as tetrahydrofuran (THF) mixed with a minor amount of pyridine, as opposed to pure THF. The problem may also be addressed by capping the amine with acetic anhydride and correcting the molecular weight based on the number of capping groups. Another useful method for determining molecular weight, particularly for lower molecular weight polymers, is vapor pressure osmometry (see, e.g., ASTM D3592).

[0031] The degree of polymerization D_p of a polymer is:

$$D_p = \sum_i \frac{\text{Mn x mol.\% monomer i}}{\text{100 x mol.wt monomer i}}$$

and thus for the copolymers of two monomers D_p may be calculated as follows:

$$D_p = \frac{\text{Mn x mol.\% monomer 1}}{\text{100 x mol.wt monomer 1}} + \frac{\text{Mn x mol.\% monomer 2}}{\text{100 x mol.wt monomer 2}}$$

[0032] Preferably, the degree of polymerization for the polymer backbones used in the invention is at least 30, typically from 30 to 165, more preferably 35 to 100.

[0033] The preferred hydrocarbons or polymers employed in this invention include homopolymers, interpolymers or lower molecular weight hydrocarbons. One family of useful polymers comprise polymers of ethylene and/or at least one C_3 to C_{28} alpha-olefin having the formula $H_2C=CHR^1$, wherein R^1 is straight or branched chain alkyl radical comprising 1 to 26 carbon atoms and wherein the polymer contains carbon-to-carbon unsaturation, preferably a high degree of terminal ethenylidene unsaturation. One preferred class of such polymers employed in this invention comprise interpolymers of ethylene and at least one alpha-olefin of the above formula, wherein R^1 is alkyl of from 1 to 18 carbon atoms, and more preferably is alkyl of from 1 to 8 carbon atoms, and more preferably still of from 1 to 2 carbon atoms. Therefore, useful alpha-olefin monomers and comonomers include, for example, propylene, butene-1, hexene-1, octene-1, 4-methylpentene-1, decene-1, dodecene-1, tridecene-1, tetradecene-1, pentadecene-1, hexadecene-1, heptadecene-1, octadecene-1, nonadecene-1, and mixtures thereof (e.g., mixtures of propylene and butene-1, and the like). Exemplary of such polymers are propylene homopolymers, butene-1 homopolymers, propylene-butene copolymers, ethylene-propylene copolymers, ethylene-butene-1 copolymers and the like, wherein the polymer contains at least some terminal and/or internal unsaturation. Preferred polymers are unsaturated copolymers of ethylene and propylene and ethylene and butene-1. The interpolymers of this invention may contain a minor amount, e.g. 0.5 to 5 mole % of a C_4 to C_{18} nonconjugated diolefin comonomer. However, it is preferred that the polymers of this invention comprise only alpha-olefin homopolymers, interpolymers of alpha-olefin comonomers and interpolymers of ethylene and alpha-olefin comonomers. The molar ethylene content of the polymers employed in this invention is preferably in the range of 20 to 80, more preferably 30 to 70, %. When propylene and/or butene-1 are employed as comonomer(s) with ethylene, the ethylene content of such copolymers is most preferably between 45 and 65 %, although higher or lower ethylene contents may be present.

[0034] These polymers may be prepared by polymerizing alpha-olefin monomer, or mixtures of alpha-olefin monomers, or mixtures comprising ethylene and at least one C_3 to C_{28} alpha-olefin monomer, in the presence of a catalyst system comprising at least one metallocene (e.g., a cyclopentadienyl-transition metal compound) and an alumoxane compound. Using this process, a polymer in which 95% or more of the polymer chains possess terminal ethenylidene-type unsaturation can be provided. The percentage of polymer chains exhibiting terminal ethenylidene unsaturation may be determined by FTIR spectroscopic analysis, titration, or C^{13} NMR. Interpolymers of this latter type may be characterized by the formula POLY-$C(R^1)=CH_2$ wherein R^1 is C_1 to C_{26} alkyl, preferably C_1 to C_{18} alkyl, more preferably C_1 to C_8 alkyl, and most preferably C_1 to C_2 alkyl, (e.g., methyl or ethyl) and wherein POLY represents the polymer chain. The chain length of the R^1 alkyl group will vary depending on the comonomer(s) selected for use in the polymerization. A minor amount of the polymer chains can contain terminal ethenyl, i.e., vinyl, unsaturation, i.e. POLY-$CH=CH_2$, and a portion of the polymers can contain internal monounsaturation, e.g. POLY-$CH=CH(R^1)$, wherein R^1 is as defined above. These terminally unsaturated interpolymers may be prepared by known metallocene chemistry and may also be prepared as described in U.S. Patent Nos. 5,498,809; 5,663,130; 5,705,577; 5,814,715; 6,022,929 and 6,030,930.

[0035] Another useful class of polymers comprises polymers prepared by cationic polymerization of isobutene, styrene, and the like. Common polymers from this class include polyisobutenes obtained by polymerization of a C_4 refinery stream having a butene content of 35 to 75% by wt., and an isobutene content of 30 to 60% by wt., in the presence of a Lewis acid catalyst, such as aluminum trichloride or boron trifluoride. A preferred source of monomer for making poly-n-butenes is petroleum feed streams such as Raffinate II. These feedstocks are disclosed in the art such as in U.S. Patent No. 4,952,739. Polyisobutylene is a most preferred backbone of the present invention because it is readily available by cationic polymerization from butene streams (e.g., using $AlCl_3$ or BF_3 catalysts). Such polyisobutylenes generally contain residual unsaturation in amounts of one ethylenic double bond per polymer chain, positioned along the chain.

[0036] As noted above, the polyisobutylene polymers employed are generally based on a hydrocarbon chain of from 900 to 2,300. Methods for making polyisobutylene are known. Polyisobutylene can be functionalized by halogenation (e.g. chlorination), the thermal "ene" reaction, or by free radical grafting using a catalyst (e.g. peroxide), as described below.

[0037] Processes for reacting polymeric hydrocarbons with unsaturated carboxylic acids, anhydrides or esters and the preparation of derivatives from such compounds are disclosed in U.S. Patent Nos. 3,087,936; 3,172,892; 3,215,707; 3,231,587; 3,272,746; 3,275,554; 3,381,022; 3,442,808; 3,565,804; 3,912,764; 4,110,349; 4,234,435; and GB-A-1,440,219. The polymer or hydrocarbon may be functionalized, for example, with carboxylic acid producing moieties (preferably acid or anhydride) by reacting the polymer or hydrocarbon under conditions that result in the addition of functional moieties or agents, i.e., acid, anhydride, ester moieties, etc., onto the polymer or hydrocarbon chains primarily at sites of carbon-to-carbon unsaturation (also referred to as ethylenic or olefinic unsaturation) using the halogen assisted functionalization (e.g. chlorination) process or the thermal "ene" reaction.

[0038] When using the free radical grafting process employing a catalyst (e.g. peroxide), the functionalization is randomly effected along the polymer chain. Selective functionalization can be accomplished by halogenating, e.g., chlorinating or brominating the unsaturated α-olefin polymer to 1 to 8, preferably 3 to 7, wt. % chlorine, or bromine, based on the weight of polymer or hydrocarbon, by passing the chlorine or bromine through the polymer at a temperature of 60 to 250, preferably 110 to 160, e.g., 120 to 140,°C, for 0.5 to 10, preferably 1 to 7, hours. The halogenated polymer or hydrocarbon (hereinafter backbones) can then be reacted with sufficient monounsaturated reactant capable of adding functional moieties to the backbone, e.g., monounsaturated carboxylic reactant, at 100 to 250, usually 180 to 235,°C, for 0.5 to 10, e.g., 3 to 8, hours, such that the product obtained will contain the desired number of moles of the monounsaturated carboxylic reactant per mole of the halogenated backbones. Alternatively, the backbone and the monounsaturated carboxylic reactant can be mixed and heated while adding chlorine to the hot material.

[0039] The hydrocarbon or polymer backbone can be functionalized, e.g., with carboxylic acid producing moieties (preferably acid or anhydride moieties) selectively at sites of carbon-to-carbon unsaturation on the polymer or hydrocarbon chains, or randomly along chains using the three processes mentioned above, or combinations thereof, in any sequence.

[0040] The preferred monounsaturated reactants that are used to functionalize the backbone comprise mono- and dicarboxylic acid material, i.e., acid, anhydride, or acid ester material, including (i) monounsaturated C_4 to C_{10} dicarboxylic acid wherein (a) the carboxyl groups are vicinyl, (i.e., located on adjacent carbon atoms) and (b) at least one, preferably both, of said adjacent carbon atoms are part of said mono unsaturation; (ii) derivatives of (i) such as anhydrides or C_1 to C_5 alcohol derived mono- or diesters of (i); (iii) monounsaturated C_3 to C_{10} monocarboxylic acid wherein the carbon-carbon double bond is conjugated with the carboxy group, i.e., of the structure -C=C-CO-; and (iv) derivatives of (iii) such as C_1 to C_5 alcohol derived mono- or diesters of (iii). Mixtures of monounsaturated carboxylic materials (i) - (iv) also may be used. Upon reaction with the backbone, the monounsaturation of the monounsaturated carboxylic reactant becomes saturated. Thus, for example, maleic anhydride becomes backbone-substituted succinic anhydride, and acrylic acid becomes backbone-substituted propionic acid. Exemplary of such monounsaturated carboxylic reactants are fumaric acid, itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, chloromaleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, and lower alkyl (e.g., C_1 to C_4 alkyl) acid esters of the foregoing, e.g., methyl maleate, ethyl fumarate, and methyl fumarate. The monounsaturated carboxylic reactant, preferably maleic anhydride, typically will be used in an amount ranging from 0.01 to 20, preferably 0.5 to 10, wt. %, based on the weight of the polymer or hydrocarbon.

[0041] While chlorination normally helps increase the reactivity of starting olefin polymers with monounsaturated functionalizing reactant, it is not necessary with the polymers or hydrocarbons contemplated for use in the present invention, particularly those preferred polymers or hydrocarbons which possess a high terminal bond content and reactivity. Preferably, therefore, the backbone and the monounsaturated functionality reactant, e.g., carboxylic reactant, are contacted at elevated temperature to cause an initial thermal "ene" reaction to take place. Ene reactions are known.

[0042] The hydrocarbon or polymer backbone can be functionalized by random attachment of functional moieties along the polymer chains by a variety of methods. For example, the polymer, in solution or in solid form, may be grafted with the monounsaturated carboxylic reactant, as described above, in the presence of a free-radical initiator. When performed in solution, the grafting takes place at an elevated temperature in the range of 100 to 260, preferably 120 to 240,°C. Preferably, free-radical initiated grafting is accomplished in a mineral lubricating oil solution containing, for example, 1 to 50, preferably 5 to 30, wt. % polymer based on the initial total oil solution.

[0043] The free-radical initiators that may be used are peroxides, hydroperoxides, and azo compounds, preferably those that have a boiling point greater than 100°C and decompose thermally within the grafting temperature range to provide free-radicals. Representative of these free-radical initiators are azobutyronitrile, bis-tertiary-butyl peroxide and dicumene peroxide. The initiator, when used, typically is used in an amount of between 0.005 and 1% by weight based on the weight of the reaction mixture solution. Typically, the aforesaid monounsaturated carboxylic reactant material and free-radical initiator are used in a weight ratio range of from 1.0:1 1 to 30:1, preferably 3:1 to 6:1. The grafting is preferably carried out in an inert atmosphere, such as under nitrogen blanketing. The resulting grafted polymer is characterized by having carboxylic acid (or ester or anhydride) moieties randomly attached along the polymer chains, it being understood, of course, that some of the polymer chains remain ungrafted. The free radical grafting described above can be used for the other polymers and hydrocarbons of the present invention.

[0044] The functionalized oil-soluble polymeric hydrocarbon backbone may then be further derivatized with a nucleophilic reactant, such as an amine, amino-alcohol, alcohol, metal compound, or mixture thereof, to form a corresponding derivative. Useful amine compounds for derivatizing functionalized polymers comprise at least one amine and can comprise one or more additional amine or other reactive or polar groups. These amines may be hydrocarbyl amines or may be predominantly hydrocarbyl amines in which the hydrocarbyl group includes other groups, e.g., hydroxy groups, alkoxy groups, amide groups, nitriles, imidazoline groups, and the like. Particularly useful amine compounds include mono- and polyamines, e.g., polyalkene and polyoxyalkylene polyamines of 2 to 60, such as 2 to 40 (e.g., 3 to 20), total carbon atoms having 1 to 12, such as 3 to 12, preferably 3 to 9, nitrogen atoms per molecule. Mixtures of amine compounds may advantageously be used, such as those prepared by reaction of alkylene dihalide with ammonia. Preferred amines are aliphatic saturated amines, including, for example, 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; polyethylene amines such as diethylene triamine; triethylene tetramine; tetraethylene pentamine; and polypropyleneamines such as 1,2-propylene diamine; and di-(1,2-propylene)triamine.

[0045] Other useful amine compounds include: alicyclic diamines such as 1,4-di(aminomethyl) cyclohexane and heterocyclic nitrogen compounds such as imidazolines. Another useful class of amines is the polyamido and related amidoamines as disclosed in U.S. Patent Nos. 4,857,217; 4,956,107; 4,963,275; and 5,229,022. Also usable is tris(hydroxymethyl)amino methane (TAM) as described in U.S. Patent Nos. 4,102,798; 4,113,639; 4,116,876; and UK 989,409. Dendrimers, star-like amines, and comb-structured amines may also be used. Similarly, one may use condensed amines, as described in U.S. Patent No. 5,053,152. The functionalized polymer is reacted with the amine compound using conventional techniques as described, for example, in U.S. Patent Nos. 4,234,435 and 5,229,022, as well as in EP-A-208,560.

[0046] The functionalized, oil-soluble polymeric hydrocarbon backbones may also be derivatized with hydroxy compounds such as monohydric and polyhydric alcohols, or with aromatic compounds such as phenols and naphthols. Preferred polyhydric alcohols include alkylene glycols in which the alkylene radical contains from 2 to 8 carbon atoms. Other useful polyhydric alcohols include glycerol, mono-oleate of glycerol, monostearate of glycerol, monomethyl ether of glycerol, pentaerythritol, dipentaerythritol, and mixtures thereof. An ester dispersant may also be derived from unsaturated alcohols, such as allyl alcohol, cinnamyl alcohol, propargyl alcohol, 1-cyclohexene-3-ol, and oleyl alcohol. Still other classes of alcohols capable of yielding ashless dispersants comprise ether-alcohols, including oxy-alkylene and oxy-arylene. Such ether-alcohols are exemplified by ether-alcohols having up to 150 oxy-alkylene radicals in which the alkylene radical contains from 1 to 8 carbon atoms. The ester dispersants may be di-esters of succinic acids or acid-esters, i.e., partially esterified succinic acids, as well as partially esterified polyhydric alcohols or phenols, i.e., esters having free alcohols or phenolic hydroxy radicals. An ester dispersant may be prepared by any one of several known methods as described, for example, in U.S. Patent No. 3,381,022.

[0047] Preferred groups of dispersant include polyamine-derivatized poly α-olefin, dispersants, particularly ethylene/butene alpha-olefin and polyisobutylene-based dispersants. Particularly preferred are ashless dispersants derived from polyisobutylene substituted with succinic anhydride groups and reacted with polyethylene amines, e.g., polyethylene diamine, tetraethylene pentamine; or a polyoxyalkylene polyamine, e.g., polyoxypropylene diamine, trimethylolaminomethane; a hydroxy compound, e.g., pentaerythritol; and combinations thereof. One particularly preferred dispersant combination is a combination of (A) polyisobutylene substituted with succinic anhydride groups and reacted with (B) a hydroxy compound, e.g., pentaerythritol; (C) a polyoxyalkylene polyamine, e.g., polyoxypropylene diamine, or (D) a polyalkylene diamine, e.g., polyethylene diamine and tetraethylene pentamine using 0.3 to 2 moles of (B), (C) and/or (D) per mole of (A). Another preferred dispersant combination comprises a combination of (A) polyisobutenyl succinic anhydride with (B) a polyalkylene polyamine, e.g., tetraethylene pentamine, and (C) a polyhydric alcohol or polyhydroxy-substituted aliphatic primary amine, e.g., pentaerythritol or trismethylolaminomethane, as described in U.S. Patent No. 3,632,511.

[0048] Another class of ashless dispersants comprises Mannich base condensation products. Generally, these products are prepared by condensing about one mole of an alkyl-substituted mono- or polyhydroxy benzene with 1 to 2.5 moles of carbonyl compound(s) (e.g., formaldehyde and paraformaldehyde) and 0.5 to 2 moles of polyalkylene polyamine, as disclosed, for example, in U.S. Patent No. 3,442,808. Such Mannich base condensation products may include a polymer product of a metallocene catalyzed polymerization as a substituent on the benzene group, or may be reacted with a compound containing such a polymer substituted on a succinic anhydride in a manner similar to that described in U.S. Patent No. 3,442,808. Examples of functionalized and/or derivatized olefin polymers synthesized using metallocene catalyst systems are described in the publications identified *supra.*

[0049] The dispersant can be further post treated by a variety of conventional post treatments such as boration, as generally taught in U.S. Patent Nos. 3,087,936 and 3,254,025. Boration of the dispersant is readily accomplished by treating an acyl nitrogen-containing dispersant with a boron compound such as boron oxide, boron halide boron acids, and esters of boron acids, in an amount sufficient to provide from 0.1 to 20 atomic proportions of boron for each mole of acylated nitrogen composition. Useful dispersants contain from 0.05 to 2.0, e.g., from 0.05 to 0.7, mass % boron. The boron, which appears in the product as dehydrated boric acid polymers (primarily $(HBO_2)_3$), is believed to attach to the dispersant imides and diimides as amine salts, e.g., the metaborate salt of the diimide. Boration can be carried out by adding from 0.5 to 4, e.g., from 1 to 3, mass % (based on the mass of acyl nitrogen compound) of a boron compound, preferably boric acid, usually as a slurry, to the acyl nitrogen compound and heating with stirring at from 135 to 190, e.g., 140 to 170,°C, for from 1 to 5 hours, followed by nitrogen stripping. Alternatively, the boron treatment can be conducted by adding boric acid to a hot reaction mixture of the dicarboxylic acid material and amine, while removing water. Other post-reaction processes commonly known in the art can also be applied.

[0050] The dispersant may also be further post treated by reaction with a so-called "capping agent". Conventionally, nitrogen-containing dispersants have been "capped" to reduce the adverse effect such dispersants have on the fluoroelastomer engine seals. Numerous capping agents and methods are known. Of the known "capping agents", those that convert basic dispersant amino groups to non-basic moieties (e.g., amido or imido groups) are most suitable. The reaction of a nitrogen-containing dispersant and alkyl acetoacetate (e.g., ethyl acetoacetate (EAA)) is described, for example, in U.S. Patent Nos. 4,839,071; 4,839,072 and 4,579,675. The reaction of a nitrogen-containing dispersant and formic acid is described, for example, in U.S. Patent No. 3,185,704. The reaction product of a nitrogen-containing dispersant and other suitable capping agents are described in U.S. Patent Nos. 4,663,064 (glycolic acid); 4,612,132; 5,334,321; 5,356,552; 5,716,912; 5,849,676; 5,861,363 (alkyl and alkylene carbonates, e.g., ethylene carbonate); 5,328,622 (mono-epoxide); 5,026,495; 5,085,788; 5,259,906; 5,407,591 (poly (e.g., bis)-epoxides) and 4,686,054 (maleic anhydride or succinic anhydride). The foregoing list is not exhaustive and other methods of capping nitrogen-containing dispersants are known to those skilled in the art.

OIL OF LUBRICATING VISCOSITY (A)

[0051] Oils of lubricating viscosity useful in the context of the present invention may be selected from natural lubricating oils, synthetic lubricating oils and mixtures thereof. The lubricating oil may range in viscosity from light distillate mineral oils to heavy lubricating oils such as gasoline engine oils, mineral lubricating oils and heavy duty diesel oils. Generally, the viscosity of the oil ranges from 2 to 40, especially from 4 to 20, centistokes as measured at 100°C.

[0052] 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.

[0053] 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)); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and derivative, analogs and homologs thereof. Also useful are synthetic oils derived from a gas to liquid process from Fischer-Tropsch synthesized hydrocarbons, which are commonly referred to as gas to liquid, or "GTL" base oils.

[0054] 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 oftetraethylene glycol.

[0055] 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, sebasic 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.

[0056] 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.

[0057] Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxysilicone oils and silicate oils comprise another useful class of synthetic lubricants; such oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methyl-2-ethylhexyl)silicate, tetra-(p-tert-butyl-phenyl) silicate, hexa-(4-methyl-2-ethylhexyl) disiloxane, poly(methyl)siloxanes and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorous-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

[0058] The oil of lubricating viscosity may comprise a Group I, Group II or Group III, base stock or base oil blends of the aforementioned base stocks. Preferably, the oil of lubricating viscosity is a Group II or Group III base stock, or a mixture thereof, or a mixture of a Group I base stock and one or more a Group II and Group III. Preferably, a major amount of the oil of lubricating viscosity is a Group II, Group III, Group IV or Group V base stock, or a mixture thereof. The base stock, or base stock blend, preferably has a saturate content of at least 65, more preferably at least 75, such as at least 85, %. Most preferably, the base stock, or base stock blend, has a saturate content of greater than 90%. Preferably, the oil or oil blend will have a sulfur content of less than 1, preferably less than 0.6, most preferably less than 0.4,% by weight.

[0059] Preferably the volatility of the oil or oil blend, as measured by the Noack volatility test (ASTM D5880), is less than or equal to 30%, preferably less than or equal to 25%, more preferably less than or equal to 20%, most preferably less than or equal 16%. Preferably, the viscosity index (VI) of the oil or oil blend is at least 85, preferably at least 100, most preferably from about 105 to 140.

[0060] Definitions for the base stocks and base oils in this invention are the same as those found in the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998. Said publication categorizes base stocks as follows:

a) Group I base stocks contain less than 90 percent saturates and/or greater than 0.03 percent sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table 1.
b) Group II base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table 1.
c) Group III base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have a viscosity index greater than or equal to 120 using the test methods specified in Table 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.

Table I - Analytical Methods for Base Stock

Property	Test Method
Saturates	ASTM D 2007
Viscosity Index	ASTM D 2270
Sulfur	ASTM D 2622
	ASTM D 4294
	ASTM D 4927
	ASTM D 3120

(B) ADDITIVE COMBINATION

[0061] As stated, the mass: mass ratio of (B1) to (B2) is in the range from 1:3 to 9:1. Preferably it is in the range of 1: 1 to 6:1 1 more preferably in the range of 3:1 1 to 6:1. The respective masses are in terms of active ingredient.

[0062] The ratio of (B1) to (B2) may be expressed as the mass % of (B1), as active ingredient, to the mass % of nitrogen in (B2). For example, in these terms, it may be 30:1 to 750:1, such as 80:1 to 500:1, for example 250:1 to 500: 1; preferably, it is 40:1 to 80:1.

[0063] Also, as stated, additive combination (B) constitutes from 0.04 to 5 mass % of the lubricating oil composition. Preferably, it constitutes from 0.2 to 2.5, more preferably from 0.4 to 2, mass %.

[0064] Also, the concentration of (B2) in the lubricating oil composition, expressed as the mass % of nitrogen, may be less than 0.03, such as less than 0.02, for example in the range of 0.002 to 0.01, such as in the range of 0.004 to 0.005 or to 0.01, mass %.

CO-ADDITIVES

[0065] The lubricating oil composition, to be useful in a trunk piston or cross-head diesel engine, will contain at least one overbased metal detergent to provide the required TBN. Such detergents are well-known and established in the art and examples include alkali metal or alkaline earth metal additives such as overbased oil-soluble or oil-dispersible calcium, magnesium, sodium or barium salts of a surfactants selected from phenol, sulphonic acid, carboxylic acid, salicylic acid and naphthenic acid, wherein the overbasing is provided by oil-insoluble salts 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 salt or oil-insoluble salt, is calcium.

[0066] The TBN of the detergent may be low, i.e. less than 50, medium, i.e. 50-150, or high, i.e. over 150. Preferably the TBN is medium or high, i.e. more than 50. 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.

[0067] Surfactants for the surfactant system of the overbased detergent preferably contain at least one hydrocarbyl group, for example, as a substituent on an aromatic ring. The term "hydrocarbyl" as used herein means that the group concerned is primarily composed of hydrogen and carbon atoms and is bonded to the remainder of the molecule via a carbon atom but does not exclude the presence of other atoms or groups in a proportion insufficient to detract from the substantially hydrocarbon characteristics of the group. Advantageously, hydrocarbyl groups in surfactants for use in accordance with the invention are aliphatic groups, preferably alkyl or alkylene groups, especially alkyl groups, which may be linear or branched. The total number of carbon atoms in the surfactants should be at least sufficient to impart the desired oil-solubility.

[0068] Other co-additives that may be used include for example:

> Anti-wear additives such as metal (e.g. Zn) salts of dihydrocarbyl dithiophosphates (e.g. in an amount of from 0.10 to 3.0 mass % of the lubricating oil composition); anti-oxidants, or oxidation inhibitors, for example in the form of aromatic amines or hindered phenols (e.g. in an amount of up to 3 mass % of the lubricating oil composition);
> Other additives such as pour point depressants, anti-foamants, metal rust inhibitors, pour point depressants and/or demulsifiers may be provided, if necessary.

[0069] 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.

[0070] 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.

[0071] 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.

[0072] 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.

EXAMPLES

[0073] This invention will now be described in the following examples which are not intended to limit the scope of the claims hereof.

SYNTHESIS

Synthesis Example 1

Preparation of a compound of Formula (II):

Step 1 - Preparation of 2-(2-naphthyloxy) ethanol

[0074] A two-liter resin kettle equipped with mechanical stirrer, condenser/Dean-Stark trap, and inlets for nitrogen, was charged with 2-naphthol (600 g, 4.16 moles), ethylene carbonate (372 g, 4.22 moles) and xylene (200 g), and the mixture was heated to 90°C under nitrogen. Aqueous sodium hydroxide (50 mass %, 3.0 g) was added and water was removed by azeotropic distillation at 165°C. The reaction mixture was kept at 165°C for 2 hours. CO_2 evolved as the reaction progressed and the reaction was determined to be near completion when the evolution of CO_2 ceased. The product was collected and solidified while cooling to room temperature. The completion of reaction was confirmed by FT-IR and HPLC. The structure of the 2-(2-naphthyloxy) ethanol product was confirmed by 1H and ^{13}C-NMR.

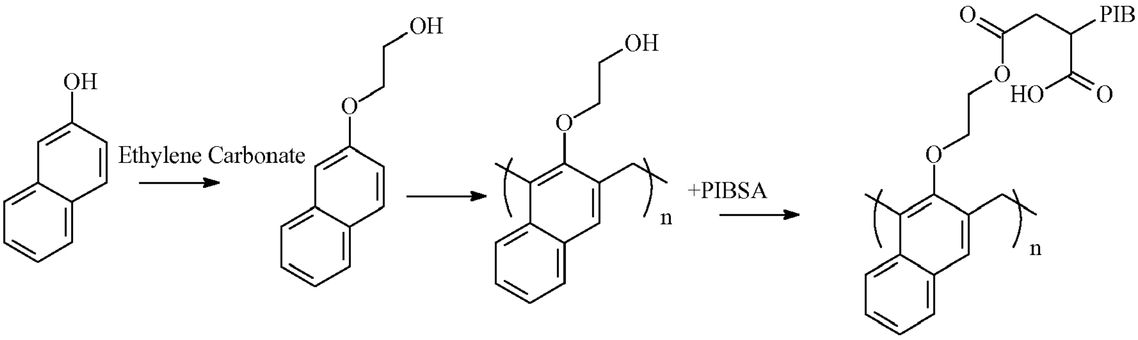
Step 2 - Oligomerization of 2-(2-naphthyloxy) ethanol

[0075] A two-liter resin kettle equipped with mechanical stirrer, condenser/Dean-Stark trap, and inlets for nitrogen, was charged with 2-(2-naphthyloxy) ethanol from Step 1, toluene (200 g), SA 117 (60.0 g), and the mixture was heated to 70°C under nitrogen. Para-formaldehyde was added over 15 min at 70 -80°C, and heated to 90°C and the reaction mixture was kept at that temperature for 30 min to 1 hour. The temperature was gradually increased to 110°C to 120°C over 2-3 hours and water (75-83 ml) was removed by azeotropic distillation. The polymer was collected and solidified while cooling to room temperature. $\overline{M}_n$ was determined by GPC using polystyrene standard corrected with the elution volume of 2-(2-naphthyloxy) ethanol as internal standard. THF was used as eluent. ($\overline{M}_n$ of 1000 dalton). ^{1}H and ^{13}C NMR confirmed the structure. FDMS and MALDI-TOF indicates the product contains mixture of methylene-linked 2-(2-naphthyloxy) ethanol oligomer of Formula (I) containing from 2 to 24 2-(2-naphthyloxy) ethanol units (m is 1 to 23).

Step 3 - Reaction of methylene-linked 2-(2-naphthyloxy) ethanol oligomer and an acylating agent (PIBSA)

[0076] A five-liter resin kettle equipped with mechanical stirrer, condenser/Dean-Stark trap, inlets for nitrogen, and additional funnel was charged with poly (2-(2-naphthyloxy) ethanol)-co-formaldehyde) from Step 2, toluene (200 g), and the mixture is heated to 120 °C under nitrogen. Polyisobutenyl succinic anhydride (PIBSA $\overline{M}_n$ of 450, 2,500 g) was added portion wise (-250 g at 30 min intervals) and the temperature was maintained at 120 °C for 2 hours followed by heating to 140 °C under nitrogen purge for an additional 2 hours to strip off all solvents to a constant weight. Base oil (AMEXOM 100 N, 1100 g) was added, and the product was collected at room temperature. GPC and FT-IR confirmed the desired structure.

[0077] The reaction scheme representing the above synthesis is shown below:



TESTING AND RESULTS

[0078] The following examples use a centrifuge water shedding test which evaluates the ability of an oil to shed water from a prepared test mixture of oil and water. The test uses an Alfa Laval MAB103B 2.0 centrifuge coupled to a Watson Marlow peristaltic pump. The centrifuge is sealed with 800 ml of water. A measurement is made of the amount of deposits formed in the centrifuge during the test. Premeasured amounts of water and the test oil are mixed together and then passed through the centrifuge at a rate of 2 litres/min. The test is run for an hour and a half, allowing the mixture to pass through the centrifuge about 10 times. The centrifuge is weighed before and after the test. A poor trunk piston diesel engine lubricant will produce a larger amount of deposits in the centrifuge system.

[0079] A set of lubricant formulations was tested as set forth in the table below. Reference Examples A, B and C are for comparison purposes. Example 1 is an example of the invention. The key to the table is as follows:

PIBSA/PAM: a polyisobutenyl succinic anhydride/polyamine dispersant.
PmNE: the final product of Synthesis Example 1 above.

[0080] Each formulation comprised a Group II base oil and a Group 1 bright stock, a zinc dihydrocarbyl dithiophosphate antiwear additive, and a detergent system in the form of a 225 TBN calcium salicylate and a 350 TBN calcium salicylate in the ratio (mass : mass) of 1.419:1. Additionally, each formulation contained one or both of a PIBSA/PAM and the PmNE in the amounts (mass %) given in the table below; otherwise the formulations are equivalent.

EXAMPLE	PmNE (active ingredient)	PIBSA/PAM (mass % N)	TOTAL MASS OF DEPOSITS MEASURED (g)
Reference A		0.012*	140
Reference B	0.4	-	72
Reference C	-	0.00426**	35
1	0.32	0.00426**	45
* corresponds to 0.6 mass % active ingredient ** corresponds to 0.1 mass % active ingredient			

[0081] Reference Example C contains a low total proportion of dispersant and therefore exhibits a good water shedding result as demonstrated by the low mass of deposits. Reference Example C, however, would exhibit poor soot handling properties because of its low total proportion of dispersant.

[0082] Reference Examples A and B, respectively containing PIBSA/PAM and PmNE as sole dispersants and, for Reference Example A, in a higher proportion than in Reference Example C, exhibit poor water shedding properties.

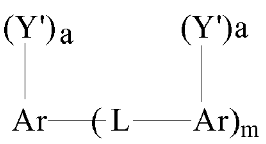
[0083] Example 1, of the invention, contains both PIBSA/PAM and PmNE and exhibits much better water shedding performance than Reference Examples A and B at the same total dispersant treat rate. Also, because of its higher total dispersant treat rate, Example 1 would exhibit much better soot handling properties than Reference Example C.

Claims

1. A trunk piston or cross-head diesel engine lubricating oil composition having a total base number of at least 15 mg KOH/g, as determined by ASTM D2896, comprising:

   (A) at least 40 mass % of an oil lubricating viscosity; and
   (B) from 0.04 to 5 mass %, expressed as active ingredient, of the lubricating oil of a combination of:

   (B1) at least one linked aromatic compound of the formula:



$$\overset{(Y')_a}{\mathrm{Ar}}\!-\!\left(\mathrm{L}-\overset{(Y')_a}{\mathrm{Ar}}\right)_m \qquad \text{(II)}$$

   wherein:
   each Ar independently represents an aromatic moiety having 0 to 3 substituents selected from the group consisting of alkyl, alkoxy, alkoxyalkyl, hydroxy, hydroxyalkyl, acyloxy, acyloxyalkyl, aryloxy, aryloxy alkyl, halo and combinations thereof;
   each L is independently a linking moiety comprising a carbon-carbon single bond or a linking group;
   each Y' is independently a moiety of the formula $Z(O(CR_2)_n)_yX$-, wherein X is selected from the group consisting of $(CR'_2)_z$, O and S; R and R' are each independently selected from H,C_1 to C_6 alkyl and aryl; z is 1 to 10; n is 0 to 10 when X is $(CR'_2)_z$, and 2 to 10 when X is O or S; y is 1 to 30; Z is H, an acyl group, an alkyl group or an aryl group; each a is independently 0 to 3, with the proviso that at least one Ar moiety bears at least one group Y' in which Z is not H; and
   m is 1 to 100, and
   (B2) at least one nitrogen-containing dispersant, where the mass: mass ratio of (B1) to (B2) is in the range from 1:3 to 9:1.

2. The trunk piston or cross-head diesel engine lubricating oil composition as claimed in claim 1, wherein said mass: mass ratio of (B1) to (B2) is in the range of from 1:1 to 6:1, preferably 3:1 to 6:1.

3. The trunk piston or cross-head diesel engine lubricating oil composition as claimed in claims 1 or 2, wherein Y' is $Z(O(CR_2)_2)_yO$-, Z is an acyl group and y is 1 to 6.

4. The trunk piston or cross-head diesel engine lubricating oil composition as claimed in any one of the preceding claims, wherein Ar is naphthalene, Y' is $ZOCH_2CH_2O$-, Z is an acyl group and L is CH_2.

5. The trunk piston or cross-head diesel engine lubricating oil composition as claimed in any one of the preceding claims, wherein Ar is derived from 2-(2-naphthyloxy)-ethanol and m is 2 to 25.

6. The trunk piston or cross-head diesel engine lubricating oil composition as claimed in any one of the preceding claims, wherein Z is derived from a polyalkyl or polyalkenyl succinic acylating agent having $\overline{M}_n$ of from about 100 to about 5000.

7. The trunk piston or cross-head diesel engine lubricating oil composition as claimed in one of the preceding claims, wherein Z is derived from hydrocarbyl isocyanate.

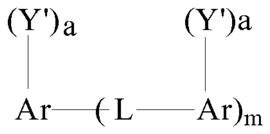
8. The trunk piston or cross-head diesel engine lubricating oil composition as claimed in one of the preceding claims, wherein the nitrogen-containing dispersant is a polybutenyl polyalkyleneamine succinimide derived from polybutene having an $\overline{M}_n$ of from 900 to 2500.

9. The trunk piston or cross-head diesel engine lubricating oil composition as claimed in one of the preceding claims, wherein the lubricating oil composition comprises one or more overbased calcium salicylate detergent additives and has a total base number of at least 15 mg KOH/g, as determined by ASTM D2896.

10. A method of lubricating a trunk piston or cross-head diesel engine having a centrifuge system including a sealing medium, comprising operation of the engine and lubrication of the trunk piston engine or system lubrication of the cross-head engine with a lubricating oil composition comprising, or made by admixing:

(A) an oil of lubricating viscosity, in a major amount; and
(B) from 0.04 to 5 mass %, expressed as active ingredient, of the lubricating oil of a combination of:

(B1) at least one linked aromatic compound of the formula:



$$\overset{(Y')a}{\mathrm{Ar}}-\!\left(\mathrm{L}-\overset{(Y')a}{\mathrm{Ar}}\right)_m \qquad \mathrm{(II)}$$

wherein:
each Ar independently represents an aromatic moiety having 0 to 3 substituents selected from the group consisting of alkyl, alkoxy, alkoxyalkyl, hydroxy, hydroxyalkyl, acyloxy, acyloxyalkyl, aryloxy, aryloxy alkyl, halo and combinations thereof;
each L is independently a linking moiety comprising a carbon-carbon single bond or a linking group;
each Y' is independently a moiety of the formula $Z(O(CR_2)_n)_yX$-, wherein X is selected from the group consisting of $(CR'_2)_z$, O and S; R and R' are each independently selected from H,C_1 to C_6 alkyl and aryl; z is 1 to 10; n is 0 to 10 when X is $(CR'_2)_z$, and 2 to 10 when X is O or S; y is 1 to 30; Z is H, an acyl group, an alkyl group or an aryl group; each a is independently 0 to 3, with the proviso that at least one Ar moiety bears at least one group Y' in which Z is not H; and
m is 1 to 100, and
(B2) at least one nitrogen-containing dispersant, where the mass : mass ratio of (B1) to (B2) is in the range from 1:3 to 9:1.

11. The method as claimed in claim 10, wherein the sealing medium is water.

12. A method of enhancing the water-shedding properties, as measured by a centrifuge water shedding test, of a lubricating oil composition in the lubrication of a trunk piston engine or the system lubrication of cross-head diesel engine by employing a lubricating oil composition as defined in any one of claims 1 to 9, when compared with a corresponding lubricating oil composition where (B) contains only (B2).

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EUROPEAN SEARCH REPORT

Application Number
EP 09 15 1448

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	20 April 2009	Greß, Tobias

CATEGORY OF CITED DOCUMENTS

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EUROPEAN SEARCH REPORT

Application Number
EP 09 15 1448

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