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(54) **Lubricating oil compositions**

(57) Soot induced kinematic viscosity increase of lubricating oil compositions for diesel engines can be ameliorated by combined use of derivatized high molecular weight olefin copolymers and high molecular weight nitrogen-containing dispersant.

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Description

[0001] The present invention relates to lubricating oil compositions. More specifically, the present invention is directed to lubricating oil compositions that provide improved lubricant performance in highly sooted environments, such as those present in heavy duty diesel (HDD) engines provided with exhaust gas recirculation (EGR) systems.

BACKGROUND OF THE INVENTION

[0002] Environmental concerns have led to continued efforts to reduce the NO_x emissions of compression ignited (diesel) internal combustion engines. The latest technology being used to reduce the NO_x emissions of diesel engines is known as exhaust gas recirculation or EGR. EGR reduces NO_x emissions by introducing non-combustible components (exhaust gas) into the incoming air-fuel charge introduced into the engine combustion chamber. This reduces peak flame temperature and NO_x generation. In addition to the simple dilution effect of the EGR, an even greater reduction in NO_x emission is achieved by cooling the exhaust gas before it is returned to the engine. The cooler intake charge allows better filling of the cylinder, and thus, improved power generation. In addition, because the EGR components have higher specific heat values than the incoming air and fuel mixture, the EGR gas further cools the combustion mixture leading to greater power generation and better fuel economy at a fixed NO_x generation level.

[0003] Diesel fuel contains sulfur. Even "low-sulfur" diesel fuel contains 300 to 400 ppm of sulfur. When the fuel is burned in the engine, this sulfur is converted to SO_x. In addition, one of the major by-products of the combustion of a hydrocarbon fuel is water vapor. Therefore, the exhaust stream contains some level of NO_x, SO_x and water vapor. In the past, the presence of these substances has not been problematic because the exhaust gases remained extremely hot, and these components were exhausted in a disassociated, gaseous state. However, when the engine is equipped with an EGR, and particularly when the exhaust gas is mixed with cooler intake air and recirculated through the engine, the water vapor can condense and react with the NO_x and SO_x components to form a mist of nitric and sulfuric acids in the EGR stream. This phenomenon is further exacerbated when the EGR stream is cooled before it is returned to the engine.

[0004] In the presence of these acids, it has been found that soot levels in lubricating oil compositions build rapidly, and that under said conditions, the kinematic viscosity (kv) of lubricating oil compositions increase to unacceptable levels, even in the presence of relatively small levels of soot (e.g., 3 wt. % soot). Because increased lubricant viscosity adversely affects performance, and can even cause engine failure, the use of an EGR system requires more frequent lubricant replacement. It has been found that the simple addition of an additional amount of dispersant does not adequately address the problem.

[0005] Therefore, it would be advantageous to identify lubricating oil compositions that better perform in HDD engines, particularly those equipped with EGR systems. Surprisingly, it has been found that by using, in combination, selected nitrogen-containing dispersants and high molecular weight functionalized olefinic polymers or copolymers, rapid increases in lubricant viscosity associated with high soot levels can be ameliorated.

SUMMARY OF THE INVENTION

[0006] In accordance with a first aspect of the invention, there is provided a lubricating oil composition comprising a major amount of at least one of a Group I, Group II and/or Group III mineral oil of lubricating viscosity; a minor amount of one or more high molecular weight polymers comprising olefin copolymers containing alkyl or aryl amine or amide groups, nitrogen-containing heterocyclic groups or ester linkages; and a minor amount of dispersant comprising one or more nitrogen-containing dispersants that are the reaction product of a polyalkenyl-substituted mono- or dicarboxylic acid, anhydride or ester and a polyamine; at least one nitrogen-containing dispersant having a polyalkenyl moiety with a number average molecular weight of at least about 1800, and from about 1.3 to 1.7 mono- or dicarboxylic acid producing moieties per polyalkenyl moiety; the one or more nitrogen-containing dispersants contributing at least 0.08 wt. % of nitrogen to the lubricating oil composition.

[0007] In accordance with a second aspect of the invention, there is provided a lubricating oil composition, as described in the first aspect, wherein the high molecular weight olefin copolymer comprises an ethylene-propylene copolymer grafted with maleic anhydride and derivatized with an aryl amine.

[0008] In accordance with a third aspect of the invention, there is provided a lubricating oil composition, as described in the first or second aspect, wherein the total amount of diaryl amine moieties in the lubricating oil composition is from about 0.5 to 5 mmols/kg, with greater than 50% of said diaryl amine moieties being introduced via molecules having a molecular weight of greater than about 5000.

[0009] In accordance with a fourth aspect of the invention, there is provided a lubricating oil composition, as described in the first, second or third aspect, wherein the lubricating oil composition further comprises from about 6 to about 50 mmols of phenate surfactant per kilogram of finished lubricating oil.

[0010] In accordance with a fifth aspect of the invention, there is provided a lubricating oil composition, as described in the first, second, third or fourth aspect, wherein said dispersant comprises from about 1.3 to about 1.6 mono- or dicarboxylic acid producing moieties per polyalkenyl moiety, and a boron content of less than about 20 ppm.

[0011] In accordance with a sixth aspect of the invention, there is provided a lubricating oil composition, as described in any of the first to fifth aspect, having a sulfated ash content of less than about 0.5 wt. %.

[0012] In accordance with a seventh aspect of the invention, there is provided a lubricating oil composition comprising a major amount of at least one of a Group I, Group II and/or Group III mineral oil of lubricating viscosity; a minor amount of one or more high molecular weight polymers comprising olefin copolymers containing alkyl or aryl amine or amide groups, nitrogen-containing heterocyclic groups or ester linkages; and a minor amount of dispersant comprising one or more nitrogen-containing dispersants that are the reaction product of a polyalkenyl-substituted mono- or dicarboxylic acid, anhydride or ester and a polyamine; at least one nitrogen-containing dispersant having a polyalkenyl moiety with a number average molecular weight of at least about 1800, and being derived from a polyalkene moiety having a molecular weight distribution (M_w/M_n) of from about 1.5 to about 2; said dispersants being chlorine-free.

[0013] In accordance with an eighth aspect of the invention, there is provided a lubricating oil composition, as in the seventh aspect, wherein said dispersant comprises from about 1.3 to about 1.6 mono- or di-carboxylic acid producing moieties per polyalkenyl moiety, and has a boron content of less than 20 ppm.

[0014] In accordance with a ninth aspect of the invention, there is provided a lubricating oil composition, as in the seventh or eighth aspect, having a sulfur content less than about 0.3 wt. %, a sulfated ash content of less than about 0.5 wt. %, and a chlorine content of less than about 50 ppm.

[0015] In accordance with a tenth aspect of the invention, there is provided a lubricating oil composition, as in any of the first to ninth aspect, wherein the functionalized, high molecular weight olefin molecule is derived from an amorphous ethylene-propylene copolymer, or a blend of an amorphous and a semi-crystalline ethylene-propylene copolymer with an SSI of from about 5 to about 30, produced by simultaneously shearing and functionalizing higher molecular weight ethylene-propylene copolymers, with maleic anhydride, in an extruder.

[0016] In accordance with an eleventh aspect of the invention, there is provided a method of operating a diesel engine provided with an exhaust gas recirculation system, which method comprises lubricating said engine with a lubricating oil composition of any of the first to tenth aspect.

[0017] Other and further objects, advantages and features of the present invention will be understood by reference to the following specification.

DETAILED DESCRIPTION OF THE INVENTION

[0018] The oils of lubricating viscosity useful in the practice of the invention 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 about 2 mm²/sec (centistokes) to about 40 mm²/sec, especially from about 3 mm²/sec to about 20 mm²/sec, most preferably from about 4 mm²/sec to about 10 mm²/sec, as measured at 100°C.

[0019] 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.

[0020] 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. 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 0.3%, by weight.

[0021] Preferably the volatility of the oil or oil blend, as measured by the NOACK 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 to 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.

[0022] 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 1 -

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

[0023] High molecular weight polymers useful in the practice of the present invention are olefin copolymers (OCPs) containing dispersing groups such as alkyl or aryl amine, or amide groups, nitrogen-containing heterocyclic groups or ester linkages. The olefin copolymers can comprise any combination of olefin monomers, but are most commonly ethylene and at least one other α -olefin. The at least one other α -olefin monomer is conventionally an α -olefin having 3 to 18 carbon atoms, and is most preferably propylene. As is well known, copolymers of ethylene and higher α -olefins, such as propylene, often include other polymerizable monomers. Typical of these other monomers are non-conjugated dienes such as the following, non-limiting examples:

- straight chain dienes such as 1,4-hexadiene and 1,6-octadiene;
- branched chain acyclic dienes such as 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene; 3,7-dimethyl-1,7-octadiene and mixed isomers of dihydro-myrcene and dihydroocimene;
- single ring alicyclic dienes such as 1,4-cyclohexadiene; 1,5-cyclooctadiene; and 1,5-cyclododecadiene;
- multi-ring alicyclic fused and bridged ring dienes such as tetrahydroindene; methyltetrahydroindene; dicyclopentadiene; bicyclo-(2,2,1)-hepta-2,5-diene; alkenyl, alkylidene, cycloalkenyl and cycloalkylidene norbornenes such as 5-methylene-2-norbornene (MNB), 5-ethylidene-2-norbornene (ENB), 5-propylene-2-norbornene, 5-isopropylidene-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene; 5-cyclohexylidene-2-norbornene.

[0024] Of the non-conjugated dienes typically used, dienes containing at least one of the double bonds in a strained ring are preferred. The most preferred diene is 5-ethylidene-2-norbornene (ENB). The amount of diene (wt. basis) in the copolymer can be from 0% to about 20%, with 0% to about 15% being preferred, and 0% to about 10% being most preferred. As already noted, the most preferred olefin copolymer is ethylene-propylene. The average ethylene content of the copolymer can be as low as 20% on a weight basis. The preferred minimum ethylene content is about 25%. A more preferred minimum is 30%. The maximum ethylene content can be as high as 90% on a weight basis; preferably the maximum ethylene content is 85%, most preferably about 80%. Preferably, the olefin copolymers contain from about 35 to 75 wt. % ethylene, more preferably from about 40 to about 70 wt. % of ethylene. Ethylene-propylene copolymers having an ethylene content of up to about 55 wt. % are considered amorphous; such copolymers having higher ethylene contents are referred to as semi-crystalline. Ethylene content of ethylene-propylene can generally be measured using the procedure of ASTM-D3900.

[0025] The molecular weight (number average) of the olefin copolymer can be as low as 2000, but the preferred minimum is 10,000. The more preferred minimum is 15,000, with the most preferred minimum number average molecular weight being 20,000. It is believed that the maximum number average molecular weight can be as high as 12,000,000. The preferred maximum is about 1,000,000, with the most preferred maximum being about 750,000. An especially preferred range of number average molecular weight for the olefin copolymers of the present invention is from about 50,000 to about 500,000.

[0026] Polymer molecular weight, specifically, \bar{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). Another useful method for determining molecular weight, particularly for lower molecular weight polymers, is vapor pressure osmometry (see, e.g., ASTM D3592).

[0027] Olefin copolymers can be rendered multifunctional by attaching a nitrogen-containing polar moiety (e.g., amine, amine-alcohol or amide) to the polymer backbone. The nitrogen-containing moieties are conventionally of the formula R-N-R'R", wherein R, R' and R" are independently alkyl, aryl or H. Also suitable are aromatic amines of the formula R'-R'-NH-R"-R, wherein R' and R" are aromatic groups and each are alkyl. The most common method for forming a multifunctional OCP viscosity modifier involves the free radical addition of the nitrogen-containing polar moiety to the polymer backbone. The nitrogen-containing polar moiety can be attached to the polymer using a double bond within the polymer (i.e., the double bond of the diene portion of an EPDM polymer, or by reacting the polymer with a compound providing a bridging group containing a double bond (e.g., maleic anhydride as described, for example, in U.S. Patent Nos. 3,316,177; 3,326,804; and carboxylic acids and ketones as described, for example, in U.S. Patent No. 4,068,056), and subsequently derivatizing the functionalized polymer with the nitrogen-containing polar moiety. A more complete list of nitrogen-containing compounds that can be reacted with the functionalized OCP is described *infra*, in the discussion of dispersants. Multifunctionalized OCPs and methods for forming such materials are known in the art and are available commercially (e.g., HITEC 5777 available from Ethyl Corporation and PA1160, a product of Dutch Staaten Minen).

[0028] Preferred are low ethylene olefin copolymers containing about 50 wt. % ethylene (amorphous) and having a number average molecular weight between 10,000 and 20,000 functionalized by grafting with maleic anhydride and aminated with arylphenyldiamine or other diaryl amine. In one preferred embodiment, the functionalized high molecular weight olefin polymer is derived from an amorphous ethylene-propylene copolymer or a blend of an amorphous and semi-crystalline ethylene-propylene copolymer having, or having on average, a Shear Stability Index, or "SSI" of from about 5 to about 30 (as determined according to ASTM D6278-98) produced via simultaneous shearing and functionalizing higher molecular weight ethylene-propylene copolymers with maleic anhydride in an extruder. Such methods are known and described, for example, in U.S. Patent No. 5,075,383. In a further preferred embodiment, the semi-crystalline ethylene-propylene copolymer is produced in a tubular reactor to have a tapered structure (ethylene-propylene distribution).

[0029] Lubricating oil compositions useful in the practice of the present invention contain the high molecular weight olefin copolymers (OCPs) containing dispersing groups in an amount of from about 0.10 to about 2 wt. %, based on polymer weight; more preferably from about 0.2 to about 1 wt. %, most preferably from about 0.3 to about 0.8 wt. %. Alternatively said components are present in an amount providing from about 0.0001 to about 0.02 wt. %, preferably from about 0.0002 to about 0.01 wt. %, most preferably from about 0.0003 to about 0.008 wt. % of nitrogen to the lubricating oil composition. Preferably, the total amount of diaryl amine moieties in the lubricating oil composition is from about 0.5 to 5 mmols/kg, with greater than 50% of the diaryl amine moieties being introduced into the lubricating oil composition via molecules having a number average molecular weight of greater than about 5000.

[0030] Dispersants useful in the context of the present invention include the range of nitrogen-containing, ashless (metal-free) dispersants known to be effective to reduce formation of deposits upon use in gasoline and diesel engines, when added to lubricating oils. The ashless, dispersants 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 have amine, amine-alcohol or amide 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.

[0031] The dispersant compositions of the present invention comprise at least one dispersant that is derived from polyalkenyl-substituted mono- or dicarboxylic acid, anhydride or ester, which dispersant has a polyalkenyl moiety with a number average molecular weight of at least about 1800 and from greater than about 1.3 to about 1.7, preferably from greater than about 1.3 to about 1.6, most preferably from greater than about 1.3 to about 1.5 functional groups (mono- or dicarboxylic acid producing moieties) per polyalkenyl moiety (a medium functionality dispersant). Functionality (F) can be determined according to the following formula:

$$F = (SAP \times M_n) / ((112,200 \times A.I.) - (SAP \times 98)) \quad (1)$$

wherein SAP is the saponification number (i.e., the number of milligrams of KOH consumed in the complete neutralization of the acid groups in one gram of the succinic-containing reaction product, as determined according to ASTM

D94); M_n is the number average molecular weight of the starting olefin polymer; and A.I. is the percent active ingredient of the succinic-containing reaction product (the remainder being unreacted olefin polymer, succinic anhydride and diluent).

[0032] Generally, each mono- or dicarboxylic acid-producing moiety will react with a nucleophilic group (amine, alcohol, amide or ester polar moieties) and the number of functional groups in the polyalkenyl-substituted carboxylic acylating agent will determine the number of nucleophilic groups in the finished dispersant.

[0033] The polyalkenyl moiety of the dispersant of the present invention has a number average molecular weight of at least 1800, preferably between 1800 and 3000, such as between 2000 and 2800, more preferably from about 2100 to 2500, and most preferably from about 2200 to about 2400. The molecular weight of a dispersant is generally expressed in terms of the molecular weight of the polyalkenyl moiety as the precise molecular weight range of the dispersant depends on numerous parameters including the type of polymer used to derive the dispersant, the number of functional groups, and the type of nucleophilic group employed.

[0034] The polyalkenyl moiety suitable for forming the dispersant used in the dispersant composition of the present invention preferably has a narrow molecular weight distribution (MWD), also referred to as polydispersity, as determined by the ratio of weight average molecular weight (M_w) to number average molecular weight (M_n). Polymers having a M_w/M_n of less than 2.2, preferably less than 2.0, are most desirable. Suitable polymers have a polydispersity of from about 1.5 to 2.0, preferably from about 1.6 to about 1.8.

[0035] Suitable hydrocarbons or polymers employed in the formation of the dispersants of the present invention include homopolymers, interpolymers or lower molecular weight hydrocarbons. One family of such 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. Preferably, such polymers 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, ethylene-propylene copolymers, ethylene-butene-1 copolymers, propylene-butene copolymers and the like, wherein the polymer contains at least some terminal and/or internal unsaturation. Preferred polymers are unsaturated copolymers of ethylene and propylene and ethylene and butene-1. The interpolymers of this invention may contain a minor amount, e.g. 0.5 to 5 mole % of a C_4 to C_{18} non-conjugated 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 0 to 80 %, and more preferably 0 to 60 %. When propylene and/or butene-1 are employed as comonomer(s) with ethylene, the ethylene content of such copolymers is most preferably between 15 and 50 %, although higher or lower ethylene contents may be present.

[0036] 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 monounsaturations, 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.

[0037] Another useful class of polymers is polymers prepared by cationic polymerization of isobutene, styrene, and the like. Common polymers from this class include polyisobutenes obtained by polymerization of a C_4 refinery stream having a butene content of about 35 to about 75% by wt., and an isobutene content of about 30 to about 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 feedstreams such as Raffinate II. These feedstocks are disclosed in the art such as in U.S. Patent No. 4,952,739. Polyisobutylene is a most preferred backbone of the present invention because it is readily available by cationic polymerization from butene streams (e.g., using $AlCl_3$ or BF_3 catalysts). Such

polyisobutylenes generally contain residual unsaturation in amounts of about one ethylenic double bond per polymer chain, positioned along the chain. A preferred embodiment utilizes polyisobutylene prepared from a pure isobutylene stream or a Raffinate I stream to prepare reactive isobutylene polymers with terminal vinylidene olefins. Preferably, these polymers, referred to as highly reactive polyisobutylene (HR-PIB), have a terminal vinylidene content of at least 65%, e.g., 70%, more preferably at least 80%, most preferably, at least 85%. The preparation of such polymers is described, for example, in U.S. Patent No. 4,152,499. HR-PIB is known and HR-PIB is commercially available under the tradenames Glissopal™ (from BASF) and Ultravis™ (from BP-Amoco).

[0038] Polyisobutylene polymers that may be employed are generally based on a hydrocarbon chain of from about 1800 to 3000. Methods for making polyisobutylene are known. Polyisobutylene can be functionalized by halogenation (e.g. chlorination), the thermal "ene" reaction, or by free radical grafting using a catalyst (e.g. peroxide), as described below.

[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 any of the three processes mentioned above or combinations thereof, in any sequence.

[0040] 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; 5,777,025; 5,891,953; as well as EP 0 382 450 B1; CA-1,335,895 and GB-A-1,440,219. The polymer or hydrocarbon may be functionalized, 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.

[0041] Selective functionalization can be accomplished by halogenating, e.g., chlorinating or brominating the unsaturated α -olefin polymer to about 1 to 8 wt. %, 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°C, preferably 110 to 160°C, e.g., 120 to 140°C, for about 0.5 to 10, preferably 1 to 7 hours. The halogenated polymer or hydrocarbon (hereinafter backbone) is then reacted with sufficient monounsaturated reactant capable of adding the required number of functional moieties to the backbone, e.g., monounsaturated carboxylic reactant, at 100 to 250°C, usually about 180°C to 235°C, for about 0.5 to 10, e.g., 3 to 8 hours, such that the product obtained will contain the desired number of moles of the monounsaturated carboxylic reactant per mole of the halogenated backbones. Alternatively, the backbone and the monounsaturated carboxylic reactant are mixed and heated while adding chlorine to the hot material.

[0042] While chlorination normally helps increase the reactivity of starting olefin polymers with monounsaturated functionalizing reactant, it is not necessary with some of the polymers or hydrocarbons contemplated for use in the present invention, particularly those preferred polymers or hydrocarbons which possess a high terminal bond content and reactivity. It is advantageous to reduce the chlorine content of lubricating oil compositions to as low a level as possible. Preferably, lubricating oil compositions of the present invention have a chlorine content of less than 50 ppm. Preferably, therefore, the backbone and the monounsaturated functionality reactant used to form the dispersant(s), e.g., carboxylic reactant, are contacted at elevated temperature to cause an initial thermal "ene" reaction to take place. Ene reactions are known.

[0043] The hydrocarbon or polymer backbone can be functionalized by random attachment of functional moieties along the polymer chains by a variety of methods. For example, the polymer, in solution or in solid form, may be grafted with the monounsaturated carboxylic reactant, as described above, in the presence of a free-radical initiator. When performed in solution, the grafting takes place at an elevated temperature in the range of about 100 to 260°C, preferably 120 to 240°C. Preferably, free-radical initiated grafting would be accomplished in a mineral lubricating oil solution containing, e.g., 1 to 50 wt.%, preferably 5 to 30 wt. % polymer based on the initial total oil solution.

[0044] The free-radical initiators that may be used are peroxides, hydroperoxides, and azo compounds, preferably those that have a boiling point greater than about 100°C and decompose thermally within the grafting temperature range to provide free-radicals. Representative of these free-radical initiators are azobutyronitrile, 2,5-dimethylhex-3-ene-2,5-bis-tertiary-butyl peroxide and dicumene peroxide. The initiator, when used, typically is used in an amount of between 0.005% and 1% by weight based on the weight of the reaction mixture solution. Typically, the aforesaid monounsaturated carboxylic reactant material and free-radical initiator are used in a weight ratio range of from about 1.0:1 to 30:1, preferably 3:1 to 6:1. The grafting is preferably carried out in an inert atmosphere, such as under nitrogen blanketing. The resulting grafted polymer is characterized by having carboxylic acid (or 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.

[0045] 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 C₄ to C₁₀ dicarboxylic acid wherein (a) the carboxyl groups are vicinyl, (i.e., located on adjacent carbon atoms) and (b) at least one, preferably both, of said adjacent carbon atoms are part of said mono unsaturation; (ii) derivatives of (i) such as anhydrides or C₁ to C₅ alcohol derived mono- or diesters of (i); (iii) monounsaturated C₃ to C₁₀ monocarboxylic acid wherein the carbon-carbon double bond is conjugated with the carboxy group, i.e., of the structure -C=C-CO-; and (iv) derivatives of (iii) such as C₁ to C₅ alcohol derived mono- or diesters of (iii). Mixtures of monounsaturated carboxylic materials (i) - (iv) also may be used. Upon reaction with the backbone, the monounsaturated carboxylic reactant becomes saturated. Thus, for example, maleic anhydride becomes backbone-substituted succinic anhydride, and acrylic acid becomes backbone-substituted propionic acid. Exemplary of such monounsaturated carboxylic reactants are fumaric acid, itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, chloromaleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, and lower alkyl (e.g., C₁ to C₄ alkyl) acid esters of the foregoing, e.g., methyl maleate, ethyl fumarate, and methyl fumarate.

[0046] To provide the required functionality, the monounsaturated carboxylic reactant, preferably maleic anhydride, typically will be used in an amount ranging from about equimolar amount to about 100 wt. % excess, preferably 5 to 50 wt. % excess, based on the moles of polymer or hydrocarbon. Unreacted excess monounsaturated carboxylic reactant can be removed from the final dispersant product by, for example, stripping, usually under vacuum, if required.

[0047] The functionalized oil-soluble polymeric hydrocarbon backbone is then 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 about 2 to 60, such as 2 to 40 (e.g., 3 to 20) total carbon atoms having about 1 to 12, such as 3 to 12, preferably 3 to 9, most preferably from about 6 to about 7 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. Such polyamine mixtures, known as PAM, are commercially available. Particularly preferred polyamine mixtures are mixtures derived by distilling the light ends from PAM products. The resulting mixtures, known as "heavy" PAM, or HPAM, are also commercially available. The properties and attributes of both PAM and/or HPAM are described, for example, in U.S. Patent Nos. 4,938,881; 4,927,551; 5,230,714; 5,241,003; 5,565,128; 5,756,431; 5,792,730; and 5,854,186.

[0048] 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 amido-amines 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.

[0049] A preferred dispersant composition is one comprising at least one polyalkenyl succinimide, which is the reaction product of a polyalkenyl substituted succinic anhydride (e.g., PIBSA) and a polyamine (PAM) that has a coupling ratio of from about 0.65 to about 1.25, preferably from about 0.8 to about 1.1, most preferably from about 0.9 to about 1. In the context of this disclosure, "coupling ratio" may be defined as a ratio of succinyl groups in the PIBSA to primary amine groups in the polyamine reactant.

[0050] 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-cyclohexane-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.

[0051] Another class of high molecular weight ashless dispersants comprises Mannich base condensation products. Generally, these products are prepared by condensing about one mole of a long chain alkyl-substituted mono- or polyhydroxy benzene with about 1 to 2.5 moles of carbonyl compound(s) (e.g., formaldehyde and paraformaldehyde) and about 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*.

[0052] The dispersant(s) of the invention are preferably non-polymeric (e.g., are mono- or bis-succinimides). The dispersant(s) of the present invention can be borated by conventional means, as generally taught in U.S. Patent Nos. 3,087,936, 3,254,025 and 5,430,105. 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. Preferably, dispersants of the present invention are non-borated, or have a boron content of less than 20 ppm.

[0053] The dispersant or dispersants can be present in an amount sufficient to contribute at least 0.08 wt. % of nitrogen, preferably from about 0.10 to about 0.18 wt. %, more preferably from about 0.115 to about 0.16 wt. %, and most preferably from about 0.12 to about 0.14 wt. % of nitrogen to the lubricating oil composition.

[0054] Additional additives may be incorporated into the compositions of the invention to enable particular performance requirements to be met. Examples of additives which may be included in the lubricating oil compositions of the present invention are detergents, metal rust inhibitors, viscosity index improvers corrosion inhibitors, oxidation inhibitors, friction modifiers, anti-foaming agents, anti-wear agents and pour point depressants. Some are discussed in further detail below.

[0055] Metal-containing or ash-forming detergents function as both detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with a long hydrophobic tail. The polar head comprises a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as can be measured by ASTM D2896) of from 0 to 80. A large amount of a metal base may be incorporated by reacting excess metal compound (e.g., an oxide or hydroxide) with an acidic gas (e.g., carbon dioxide). The resulting overbased detergent comprises neutralized detergent as the outer layer of a metal base (e.g. carbonate) micelle. Such overbased detergents may have a TBN of 150 or greater, and typically will have a TBN of from 250 to 450 or more.

[0056] Detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals, e.g., barium, sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present in detergents used in a lubricant, and mixtures of calcium and/or magnesium with sodium. Particularly convenient metal detergents are neutral and overbased calcium sulfonates having TBN of from 20 to 450, neutral and overbased calcium phenates and sulfurized phenates having TBN of from 50 to 450 and neutral and overbased magnesium or calcium salicylates having a TBN of from 20 to 450. Combinations of detergents, whether overbased or neutral or both, may be used.

[0057] Sulfonates may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons. Examples included those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl or their halogen derivatives such as chlorobenzene, chlorotoluene and chloronaphthalene. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 70 carbon atoms. The alkaryl sulfonates usually contain from about 9 to about 80 or more carbon atoms, preferably from about 16 to about 60 carbon atoms per alkyl substituted aromatic moiety.

[0058] The oil soluble sulfonates or alkaryl sulfonic acids may be neutralized with oxides, hydroxides, alkoxides, carbonates, carboxylate, sulfides, hydrosulfides, nitrates, borates and ethers of the metal. The amount of metal compound is chosen having regard to the desired TBN of the final product but typically ranges from about 100 to 220 wt. % (preferably at least 125 wt. %) of that stoichiometrically required.

[0059] Metal salts of phenols and sulfurized phenols are prepared by reaction with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. Sulfurized phenols may be prepared by reacting a phenol with sulfur or a sulfur containing compound such as hydrogen sulfide, sulfur monohalide or sulfur dihalide, to form products which are generally mixtures of compounds in which 2 or more phenols are bridged by sulfur containing bridges.

[0060] Carboxylate detergents, e.g., salicylates, can be prepared by reacting an aromatic carboxylic acid with an

appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. The aromatic moiety of the aromatic carboxylic acid can contain heteroatoms, such as nitrogen and oxygen. Preferably, the moiety contains only carbon atoms; more preferably the moiety contains six or more carbon atoms; for example benzene is a preferred moiety. The aromatic carboxylic acid may contain one or more aromatic moieties, such as one or more benzene rings, either fused or connected via alkylene bridges. The carboxylic moiety may be attached directly or indirectly to the aromatic moiety. Preferably the carboxylic acid group is attached directly to a carbon atom on the aromatic moiety, such as a carbon atom on the benzene ring. More preferably, the aromatic moiety also contains a second functional group, such as a hydroxy group or a sulfonate group, which can be attached directly or indirectly to a carbon atom on the aromatic moiety.

[0061] Preferred examples of aromatic carboxylic acids are salicylic acids and sulfurized derivatives thereof, such as hydrocarbyl substituted salicylic acid and derivatives thereof. Processes for sulfurizing, for example a hydrocarbyl - substituted salicylic acid, are known to those skilled in the art. Salicylic acids are typically prepared by carboxylation, for example, by the Kolbe - Schmitt process, of phenoxides, and in that case, will generally be obtained, normally in a diluent, in admixture with uncarboxylated phenol.

[0062] Preferred substituents in oil - soluble salicylic acids are alkyl substituents. In alkyl - substituted salicylic acids, the alkyl groups advantageously contain 5 to 100, preferably 9 to 30, especially 14 to 20, carbon atoms. Where there is more than one alkyl group, the average number of carbon atoms in all of the alkyl groups is preferably at least 9 to ensure adequate oil solubility.

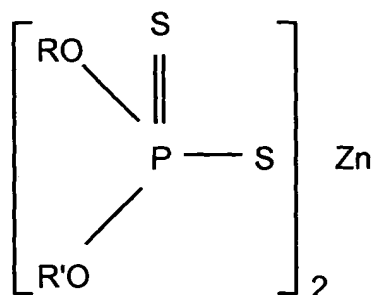
[0063] Detergents generally useful in the formulation of lubricating oil compositions also include "hybrid" detergents formed with mixed surfactant systems, e.g., phenate/salicylates, sulfonate/phenates, sulfonate/salicylates, sulfonates/phenates/salicylates, as described, for example, in pending U.S. Patent Application Nos. 09/180,435 and 09/180,436 and U.S. Patent Nos. 6,153,565 and 6,281,179.

[0064] Preferably, the detergent used will be a detergent system in which from about 60% to 100% of the total amount of detergent surfactant is phenate and/or salicylate. Phenate neutral and overbased detergents are preferred. Preferably, lubricating oil compositions useful in the present invention will contain no more than about 30 wt. %, preferably no more than about 20 wt. %, more preferably no more than 5 wt. % sulfonate detergent, based on the total weight of detergent. More preferably, the detergent system will provide the lubricating oil composition with from about 6 to about 50 mmols, more preferably from about 9 to about 40 mmols, most preferably from about 12 to about 30 mmols of neutral or overbased phenate detergent surfactant, and less than 1 mmol of salicylate detergent surfactant per kilogram of finished lubricant. Further preferably, the detergent system comprises sulfur-free detergent, particularly sulfur-free phenate detergent.

[0065] It is not unusual to add a detergent or other additive, to a lubricating oil, or additive concentrate, in a diluent, such that only a portion of the added weight represents an active ingredient (A.I.). For example, detergent may be added together with an equal weight of diluent in which case the "additive" is 50% A.I. detergent. As used herein, the term weight percent (wt. %), when applied to a detergent or other additive refers to the weight of active ingredient. Detergents conventionally comprise from about 0.5 to about 5 wt. %, preferably from about 0.8 to about 3.8 wt. %, most preferably from about 1.2 to about 3 wt. % of a lubricating oil composition formulated for use in a heavy duty diesel engine.

[0066] Dihydrocarbyl dithiophosphate metal salts are frequently used as antiwear and antioxidant agents. The metal may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. The zinc salts are most commonly used in lubricating oil in amounts of 0.1 to 10, preferably 0.2 to 2 wt. %, based upon the total weight of the lubricating oil composition. They may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with P_2S_5 and then neutralizing the formed DDPA with a zinc compound. For example, a dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the zinc salt, any basic or neutral zinc compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to the use of an excess of the basic zinc compound in the neutralization reaction.

[0067] The preferred zinc dihydrocarbyl dithiophosphates are oil soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



wherein R and R' may be the same or different hydrocarbonyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R' groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl. In order to obtain oil solubility, the total number of carbon atoms (i.e. R and R') in the dithiophosphoric acid will generally be about 5 or greater. The zinc dihydrocarbonyl dithiophosphate can therefore comprise zinc dialkyl dithiophosphates. The present invention may be particularly useful when used with lubricant compositions containing phosphorus levels of from about 0.02 to about 0.12 wt. %, preferably from about 0.03 to about 0.10 wt. %. More preferably, the phosphorous level of the lubricating oil composition will be less than about 0.08 wt. %, such as from about 0.05 to about 0.08 wt. %.

[0068] Oxidation inhibitors or antioxidants reduce the tendency of mineral oils to deteriorate in service. Oxidative deterioration can be evidenced by sludge in the lubricant, varnish-like deposits on the metal surfaces, and by viscosity growth. Such oxidation inhibitors include hindered phenols, alkaline earth metal salts of alkylphenolthioesters having preferably C₅ to C₁₂ alkyl side chains, calcium nonylphenol sulfide, oil soluble phenates and sulfurized phenates, phosphosulfurized or sulfurized hydrocarbons or esters, phosphorous esters, metal thiocarbamates, oil soluble copper compounds as described in U.S. Patent No. 4,867,890, and molybdenum-containing compounds.

[0069] Aromatic amines having at least two aromatic groups attached directly to the nitrogen constitute another class of compounds that is frequently used for antioxidancy. While these materials may be used in small amounts, preferred embodiments of the present invention are free of these compounds. They are preferably used in only small amounts, i.e., up to 0.4 wt. %, or more preferably avoided altogether other than such amount as may result as an impurity from another component of the composition.

[0070] Typical oil soluble aromatic amines having at least two aromatic groups attached directly to one amine nitrogen contain from 6 to 16 carbon atoms. The amines may contain more than two aromatic groups. Compounds having a total of at least three aromatic groups in which two aromatic groups are linked by a covalent bond or by an atom or group (e.g., an oxygen or sulfur atom, or a -CO-, -SO₂- or alkylene group) and two are directly attached to one amine nitrogen also considered aromatic amines having at least two aromatic groups attached directly to the nitrogen. The aromatic rings are typically substituted by one or more substituents selected from alkyl, cycloalkyl, alkoxy, aryloxy, acyl, acylamino, hydroxy, and nitro groups. The amount of any such oil soluble aromatic amines having at least two aromatic groups attached directly to one amine nitrogen should preferably not exceed 0.4 wt. % active ingredient.

[0071] Preferably, lubricating oil compositions in accordance with the present invention contain from about 0.05 to about 5 wt. %, preferably from about 0.10 to about 3 wt. %, most preferably from about 0.20 to about 1.5 wt. % of phenolic antioxidant, based on the total weight of the lubricating oil composition. Even more preferably, lubricating oil compositions in accordance with the present invention contain phenolic antioxidant in the amount set forth above, and comprise less than 0.1 wt. %, based on the total weight of the lubricating oil composition, aromatic amine antioxidant.

[0072] Friction modifiers and fuel economy agents that are compatible with the other ingredients of the final oil may also be included. Examples of such materials include glyceryl monoesters of higher fatty acids, for example, glyceryl mono-oleate; esters of long chain polycarboxylic acids with diols, for example, the butane diol ester of a dimerized unsaturated fatty acid; oxazoline compounds; and alkoxyated alkyl-substituted mono-amines, diamines and alkyl ether amines, for example, ethoxylated tallow amine and ethoxylated tallow ether amine. A preferred lubricating oil composition contains a dispersant composition of the present invention, base oil, and a nitrogen-containing friction modifier.

[0073] Other known friction modifiers comprise oil-soluble organo-molybdenum compounds. Such organo-molybdenum friction modifiers also provide antioxidant and antiwear credits to a lubricating oil composition. Examples of such oil soluble organo-molybdenum compounds include dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and the like, and mixtures thereof. Particularly preferred are molybdenum dithiocarbamates, dialkyl dithiophosphates, alkyl xanthates and alkylthioxanthates.

[0074] Additionally, the molybdenum compound may be an acidic molybdenum compound. These compounds will

react with a basic nitrogen compound as measured by ASTM test D-664 or D-2896 titration procedure and are typically hexavalent. Included are molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, and other alkaline metal molybdates and other molybdenum salts, e.g., hydrogen sodium molybdate, MoOCl_4 , MoO_2Br_2 , $\text{Mo}_2\text{O}_3\text{Cl}_6$, molybdenum trioxide or similar acidic molybdenum compounds.

[0075] Among the molybdenum compounds useful in the compositions of this invention are organo-molybdenum compounds of the formula



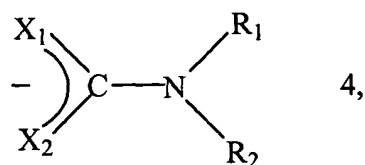
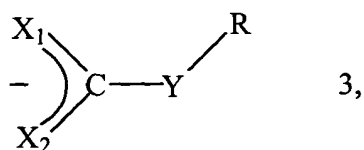
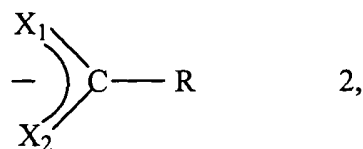
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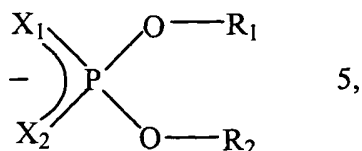
wherein R is an organo group selected from the group consisting of alkyl, aryl, aralkyl and alkoxyalkyl, generally of from 1 to 30 carbon atoms, and preferably 2 to 12 carbon atoms and most preferably alkyl of 2 to 12 carbon atoms. Especially preferred are the dialkyldithiocarbamates of molybdenum.

[0076] Another group of organo-molybdenum compounds useful in the lubricating compositions of this invention are trinuclear molybdenum compounds, especially those of the formula $\text{Mo}_3\text{S}_k\text{L}_n\text{Q}_z$ and mixtures thereof wherein the L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 through 7, Q is selected from the group of neutral electron donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. At least 21 total carbon atoms should be present among all the ligands' organo groups, such as at least 25, at least 30, or at least 35 carbon atoms.

[0077] The ligands are independently selected from the group of



and



and mixtures thereof, wherein X, X₁, X₂, and Y are independently selected from the group of oxygen and sulfur, and wherein R₁, R₂, and R are independently selected from hydrogen and organo groups that may be the same or different. Preferably, the organo groups are hydrocarbyl groups such as alkyl (e.g., in which the carbon atom attached to the remainder of the ligand is primary or secondary), aryl, substituted aryl and ether groups. More preferably, each ligand has the same hydrocarbyl group.

[0078] The term "hydrocarbyl" denotes a substituent having carbon atoms directly attached to the remainder of the ligand and is predominantly hydrocarbyl in character within the context of this invention. Such substituents include the following:

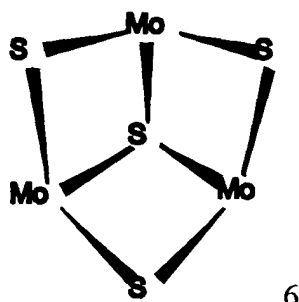
1. Hydrocarbon substituents, that is, aliphatic (for example alkyl or alkenyl), alicyclic (for example cycloalkyl or cycloalkenyl) substituents, aromatic-, aliphatic- and alicyclic-substituted aromatic nuclei and the like, as well as cyclic substituents wherein the ring is completed through another portion of the ligand (that is, any two indicated substituents may together form an alicyclic group).

2. Substituted hydrocarbon substituents, that is, those containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbyl character of the substituent. Those skilled in the art will be aware of suitable groups (e.g., halo, especially chloro and fluoro, amino, alkoxyl, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.).

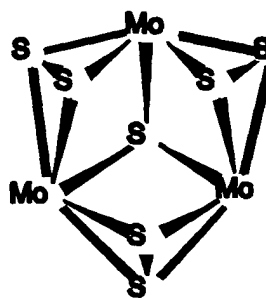
3. Hetero substituents, that is, substituents which, while predominantly hydrocarbon in character within the context of this invention, contain atoms other than carbon present in a chain or ring otherwise composed of carbon atoms.

[0079] Importantly, the organo groups of the ligands have a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil. For example, the number of carbon atoms in each group will generally range between about 1 to about 100, preferably from about 1 to about 30, and more preferably between about 4 to about 20. Preferred ligands include dialkyldithiophosphate, alkylxanthate, and dialkyldithiocarbamate, and of these dialkyldithiocarbamate is more preferred. Organic ligands containing two or more of the above functionalities are also capable of serving as ligands and binding to one or more of the cores. Those skilled in the art will realize that formation of the compounds of the present invention requires selection of ligands having the appropriate charge to balance the core's charge.

[0080] Compounds having the formula Mo₃S_kL_nQ_z have cationic cores surrounded by anionic ligands and are represented by structures such as



and



7,

and have net charges of +4. Consequently, in order to solubilize these cores the total charge among all the ligands must be -4. Four monoanionic ligands are preferred. Without wishing to be bound by any theory, it is believed that two or more trinuclear cores may be bound or interconnected by means of one or more ligands and the ligands may be multidentate. Such structures fall within the scope of this invention. This includes the case of a multidentate ligand having multiple connections to a single core. It is believed that oxygen and/or selenium may be substituted for sulfur in the core(s).

[0081] Oil-soluble or dispersible trinuclear molybdenum compounds can be prepared by reacting in the appropriate liquid(s)/solvent(s) a molybdenum source such as $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13} \cdot n(\text{H}_2\text{O})$, where n varies between 0 and 2 and includes non-stoichiometric values, with a suitable ligand source such as a tetralkylthiuram disulfide. Other oil-soluble or dispersible trinuclear molybdenum compounds can be formed during a reaction in the appropriate solvent(s) of a molybdenum source such as of $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13} \cdot n(\text{H}_2\text{O})$, a ligand source such as tetralkylthiuram disulfide, dialkyldithiocarbamate, or dialkyldithiophosphate, and a sulfur abstracting agent such cyanide ions, sulfite ions, or substituted phosphines. Alternatively, a trinuclear molybdenum-sulfur halide salt such as $[\text{M}']_2[\text{Mo}_3\text{S}_7\text{A}_6]$, where M' is a counter ion, and A is a halogen such as Cl, Br, or I, may be reacted with a ligand source such as a dialkyldithiocarbamate or dialkyldithiophosphate in the appropriate liquid(s)/solvent(s) to form an oil-soluble or dispersible trinuclear molybdenum compound. The appropriate liquid/solvent may be, for example, aqueous or organic.

[0082] A compound's oil solubility or dispersibility may be influenced by the number of carbon atoms in the ligand's organo groups. In the compounds of the present invention, at least 21 total carbon atoms should be present among all the ligand's organo groups. Preferably, the ligand source chosen has a sufficient number of carbon atoms in its organo groups to render the compound soluble or dispersible in the lubricating composition.

[0083] The terms "oil-soluble" or "dispersible" 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.

[0084] The molybdenum compound is preferably an organo-molybdenum compound. Moreover, the molybdenum compound is preferably selected from the group consisting of a molybdenum dithiocarbamate (MoDTC), molybdenum dithiophosphate, molybdenum dithiophosphinate, molybdenum xanthate, molybdenum thioxanthate, molybdenum sulfide and mixtures thereof. Most preferably, the molybdenum compound is present as molybdenum dithiocarbamate. The molybdenum compound may also be a trinuclear molybdenum compound.

[0085] The viscosity index of the base stock is increased, or improved, by incorporating therein certain polymeric materials that function as viscosity modifiers (VM) or viscosity index improvers (VII). Generally, polymeric materials useful as viscosity modifiers are those having number average molecular weights (M_n) of from about 5,000 to about 250,000, preferably from about 15,000 to about 200,000, more preferably from about 20,000 to about 150,000. These viscosity modifiers can be grafted with grafting materials such as, for example, maleic anhydride, and the grafted material can be reacted with, for example, amines, amides, nitrogen-containing heterocyclic compounds or alcohol, to form multifunctional viscosity modifiers (dispersant-viscosity modifiers). Certain of the high molecular weight olefin copolymers (OCPs) containing dispersing groups useful in the practice of the invention can be classified as dispersant-viscosity modifiers. In this instance, the high molecular weight olefin copolymers (OCPs) containing dispersing groups need not comprise the sole VM in the lubricating oil composition, and other VM, such as a hydrogenated styrene-isoprene block copolymer, or non-functionalized olefin copolymer VM may be used in combination therewith.

[0086] Representative examples of suitable viscosity modifiers other than the high molecular weight olefin copolymers (OCPs) containing dispersing groups of the invention are polyisobutylene, copolymers of ethylene and propylene, polymethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, interpolymers of styrene and acrylic esters, and partially hydrogenated copolymers of styrene/ isoprene, styrene/buta-

diene, and isoprene/butadiene, as well as the partially hydrogenated homopolymers of butadiene and isoprene.

[0087] Pour point depressants (PPD), otherwise known as lube oil flow improvers (LOFIs) lower the temperature. Compared to VM, LOFIs generally have a lower number average molecular weight. Such additives are well known. Typical additives that improve the low temperature fluidity of the fluid are C₈ to C₁₈ dialkyl fumarate/vinyl acetate copolymers, and polymethacrylates. Like VM, LOFIs can be grafted with grafting materials such as, for example, maleic anhydride, and the grafted material can be reacted with, for example, amines, amides, nitrogen-containing heterocyclic compounds or alcohol, to form multifunctional additives.

[0088] Foam control can be provided by an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

[0089] Some of the above-mentioned additives can provide a multiplicity of effects; thus for example, a single additive may act as a dispersant-oxidation inhibitor. This approach is well known and need not be further elaborated herein.

[0090] In the present invention it may be necessary to include an additive which maintains the stability of the viscosity of the blend. Thus, although polar group-containing additives achieve a suitably low viscosity in the pre-blending stage it has been observed that some compositions increase in viscosity when stored for prolonged periods. Additives which are effective in controlling this viscosity increase include the long chain hydrocarbons functionalized by reaction with mono- or dicarboxylic acids or anhydrides which are used in the preparation of the ashless dispersants as hereinbefore disclosed.

[0091] When lubricating compositions contain one or more of the above-mentioned additives, each additive is typically blended into the base oil in an amount that enables the additive to provide its desired function. Representative effective amounts of such additives, when used in crankcase lubricants, are listed below. All the values listed are stated as mass percent active ingredient.

ADDITIVE	MASS % (Broad)	MASS % (Preferred)
Metal Detergents	0.1 - 15	0.2 - 9
Corrosion Inhibitor	0 - 5	0 - 1.5
Metal Dihydrocarbyl Dithiophosphate	0.1 - 6	0.1 - 4
Antioxidant	0 - 5	0.01 - 2
Pour Point Depressant	0.01 - 5	0.01 - 1.5
Antifoaming Agent	0 - 5	0.001 - 0.15
Supplemental Antiwear Agents	0 - 1.0	0 - 0.5
Friction Modifier	0 - 5	0 - 1.5
Viscosity Modifier	0.01 - 10	0.25 - 3
Basestock	Balance	Balance

[0092] Fully formulated lubricating oil compositions of the present invention preferably have a sulfur content of less than about 0.3 wt. %, preferably less than about 0.25 wt. % more preferably less than about 0.20 wt. %, most preferably less than about 0.15 wt. %. Preferably, the Noack volatility of the fully formulated lubricating oil composition (oil of lubricating viscosity plus all additives) will be no greater than 12, such as no greater than 10, preferably no greater than 8. Fully formulated lubricating oil compositions of the present invention preferably have a sulfated ash (SASH) content of less than about 0.5 wt. %.

[0093] It may be desirable, although not essential to prepare one or more additive concentrates comprising additives (concentrates sometimes being referred to as additive packages) whereby several additives can be added simultaneously to the oil to form the lubricating oil composition.

[0094] The final composition may employ from 5 to 25 mass %, preferably 5 to 18 mass %, typically 10 to 15 mass % of the concentrate, the remainder being oil of lubricating viscosity.

[0095] This invention will be further understood by reference to the following examples, wherein all parts are parts by weight, unless otherwise noted and which include preferred embodiments of the invention.

EXAMPLES

[0096] The most recent and stringent industry standard test for evaluating the ability of diesel engine oils to control soot-induced viscosity increase, is conducted in a T-11, EGR-equipped diesel engine, and is commonly referred to as the "Mack T-11" test (ASTM designation number not yet assigned). The Mack T-11 test determines the used oil soot

load at which the difference between used oil KV-100 (kinematic viscosity at 100°C, reported in cSt.) and KV-100 of a sheared fresh oil sample exceeds 12. To pass, a lubricating oil composition must score at least 6 (6% soot load). Higher numbers indicate better results (more soot handling capability).

[0097] To demonstrate the advantages of the present invention, a comparison was made between the T-11 performance of lubricating oil compositions formulated with Group II base oil, a base DI (detergent-inhibitor) package and modified versions thereof.

[0098] The base DI package was a commercial heavy duty diesel (HDD) package containing dispersant, a detergent blend, a hindered phenol (HP) antioxidant (AO), antiwear agent (ZDDP) and an olefin copolymer viscosity modifier. The dispersant employed ("Disp. 1") was a high molecular weight PIBSA-PAM-type dispersant (about 2200 M_n PIB) having a functionality of about 1.4 and a nitrogen content of about 1.2 wt.%. This "base lubricant" provided a calculated (based on bench test results) Mack T-11 score of 3.6.

[0099] "Disp. 2" is a commercial low molecular weight PIBSA-PAM-type dispersant (about 1000 M_n PIB) and a nitrogen content of about 1.6 wt. %. HITEC 5777 (H5777), a commercial product available from Ethyl Corporation, is a multifunctional dispersant viscosity modifier (DVM), which is prepared by functionalizing a high molecular weight ethylene-propylene copolymer with maleic anhydride, and derivatizing the resulting functionalized copolymer with aryl-phenylamine. "DPA", or dialkyl-diphenylamine, is a low molecular weight compound conventionally used in lubricating oil compositions as an antioxidant (AO). Using the above-components, lubricating oil compositions representing variations of the base lubricant were prepared as shown and subjected to Mack T-11 testing. Both calculated and actual Mack T-11 test results are provided.

Table 1

Ex.	Disp. (wt. %)	Disp. N (ppm)	DVM/Amount	DVM N (ppm)	AO	AO N (ppm)	Total N (ppm)	Mack T-11 (Predicted)	Mack T-11 (Measured)
Base	Disp. 1	876	---	---	HP	---	876	3.6	---
Comp. 1	Disp. 1	1679	---	---	HP	---	1679	5.1	5.2
Comp. 2	Disp. 2	1420	---	---	HP	---	1420	2.6	2.6
Comp. 3	Disp. 1	876	---	---	DPA	140	1016	3.1	---
Inv. 1	Disp. 1	876	H5777 /0.9	38	DPA	140	1054	6.9	6.8

[0100] A comparison between the results achieved with the base lubricant and Comp. 1 demonstrates that increased nitrogen content improves Mack T-11 performance to a certain extent. Testing of Comp. 2 shows that the use of a low molecular weight dispersant, at higher nitrogen content, causes a debit in Mack T-11 performance, as does the introduction of low molecular weight DPA (Comp. 3). As shown by the results achieved with Inv. 1, the combination of a high molecular weight dispersant and a small amount of an aminated, high molecular weight olefin copolymer provides an improvement in soot handling performance far greater than would be forecast based on compositional nitrogen content. The Mack T-11 results demonstrate that compositions of the invention achieve Mack T-11 results exceeding those of compositions containing approximately double the amount of dispersant nitrogen (Comp 1), even in the presence the performance debit-causing low molecular weight DPA antioxidant.

[0101] As a bench test, a Haake Rheometer can be used to simulate the soot viscosity performance in the Mack T-11 test using carbon black as a soot surrogate. This test method uses a rheometer in a controlled shear rate mode of operation to determine the rotational viscosity of heavy duty diesel oils at 100°C at different levels of carbon black. A fresh oil sample is heated at 90°C for 30 minutes and then added slowly to the corresponding amount of carbon black (e.g., 99.00 g of fresh oil plus 1.00 gram carbon black for a 1% carbon black test). The mixture is heated at 90°C and blended overnight (16 hours). The blend is then heated to 100°C and blended for 30 minutes before testing.

[0102] Lubricating oil samples, prepared with a Group I base oil and a base DI package identical but for the dispersant employed, were tested in a Haake Rheometer according to the above procedure, at a carbon black level of 4.76 wt. % and a shear rate of 0.45 sec⁻¹. The samples all contained PIBSA-PAM-type dispersants of varying functionalities and molecular weight distributions; the amount of dispersant in each sample was adjusted to provide comparable dispersant nitrogen levels. Dispersants having a MWD of 1.8 were based on HR-PIB while those having a MWD of 2.1 were derived from conventional PIB. The measured rotational viscosities of the samples are set forth in Table 2:

Table 2

Sample	Polymer MWD	Dispersant Functionality	Sample Nitrogen Content (gN/100g)	Rot. Viscosity (Pa.s)
A	1.8	1.4	0.050	2.476
B	1.8	1.4	0.025	5.546
C	2.1	1	0.050	3.470
D	2.1	1	0.025	6.105

[0103] The data of Table 2 demonstrate that, when used at comparable nitrogen levels, dispersants having a higher level of functionality and narrow molecular weight distribution provide an improved ability to maintain soot dispersal in the oil.

[0104] Using the above-described procedure, samples containing borated dispersants were then compared to otherwise identical samples containing non-borated dispersants. All dispersants were PIBSA-PAM-type dispersants having a polymer number average molecular weight of about 2200 and a functionality of 1.4. Dispersants based on both HR-PIB (MWD of 1.8) and conventional PIB (MWD of 2.1) were tested. The results are provided in Table 3:

Table 3

Sample	Polymer MWD	Sample Nitrogen Content (gN/100g)	Dispersant Boron Content (wt. %)	Rot. Viscosity (Pa.s)
E	1.8	0.050	0.00	5.02
F	1.8	0.050	0.27	7.35
G	2.1	0.050	0.00	4.00
H	2.1	0.050	0.13	6.30
I	1.8	0.025	0.00	6.06
J	1.8	0.025	0.27	7.19
K	2.1	0.025	0.00	7.42
L	2.1	0.025	0.13	9.02

[0105] The above data demonstrate that the presence of significant amounts of boron adversely affect the resulting

performance of the dispersant. A comparison between the samples containing the HR-PIB-based dispersant and the corresponding samples containing the dispersant produced from conventional PIB further illustrates the advantages of using a dispersant based on a polymer having a narrow molecular weight distribution.

[0106] The disclosures of all patents, articles and other materials described herein are hereby incorporated, in their entirety, into this specification by reference. All amounts are expressed on an active ingredient (AI) basis, unless otherwise indicated. Compositions described as "comprising" a plurality of defined components are to be construed as including compositions formed by mixing the defined plurality of defined components. Principles, preferred embodiments and modes of operation of the present invention have been described in the foregoing specification. What applicants submit is their invention, however, is not to be construed as limited to the particular embodiments disclosed, since the disclosed embodiments are regarded as illustrative rather than limiting. Changes may be made by those skilled in the art without departing from the spirit of the invention.

Claims

1. A lubricating oil composition comprising a major amount of at least one of a Group I, Group II Group III mineral oil of lubricating viscosity, or a mixture thereof; a minor amount of one or more high molecular weight polymers comprising olefin copolymers containing at least one moiety selected from alkyl amine, alkyl amide, aryl amine or aryl amide groups, nitrogen-containing heterocyclic groups or ester linkages; and a minor amount of dispersant comprising one or more nitrogen-containing dispersants that are the reaction product of a polyalkenyl-substituted mono- or dicarboxylic acid, anhydride or ester and a polyamine; at least one of the nitrogen-containing dispersants having a polyalkenyl moiety with a number average molecular weight of at least 1800, and from 1.3 to 1.7 mono- or dicarboxylic acid producing moieties per polyalkenyl moiety the dispersant contributing at least 0.08 wt. % of nitrogen to the lubricating oil composition.
2. A lubricating oil composition comprising a major amount of at least one of a Group I, Group II and/or Group III mineral oil of lubricating viscosity, or a mixture thereof; a minor amount of one or more high molecular weight polymers comprising olefin copolymers containing at least one moiety selected from alkyl amine, alkyl amide, aryl amine or aryl amide groups, nitrogen-containing heterocyclic groups or ester linkages; and a minor amount of dispersant comprising one or more nitrogen-containing dispersants that are the reaction product of a polyalkenyl-substituted mono- or dicarboxylic acid, anhydride or ester and a polyamine; at least one of the nitrogen-containing dispersants having a polyalkenyl moiety with a number average molecular weight of at least 1800, and being derived from a polyalkene moiety having a molecular weight distribution (M_w/M_n) of from about 1.5 to about 2; said dispersant being essentially chlorine-free.
3. A lubricating oil composition according to claim 1 or 2, wherein said polyalkenyl moiety with a number average molecular weight of from 1800 to 3000.
4. A lubricating oil composition according to claim 1, 2 or 3, wherein the high molecular weight olefin copolymer comprises an ethylene-propylene copolymer grafted with maleic anhydride and derivatized with an aryl amine.
5. A lubricating oil composition according to any one of the preceding claims, wherein the total amount of diaryl amine moieties in the lubricating oil composition is from 0.5 to 5 mmols/kg, and greater than 50% of said diaryl amine moieties are derived from molecules having a number average molecular weight of greater than 5000.
6. A lubricating oil composition according to any one of the preceding claims, which further comprises from 6 to 50 mmols of phenate surfactant per kilogram of finished lubricating oil.
7. A lubricating oil composition according to any one of the preceding claims, wherein said dispersant comprises from 1.3 to 1.6 mono- or di-carboxylic acid producing moieties per polyalkenyl moiety, and has a boron content of less than 20 ppm.
8. A lubricating oil composition according to any one of the preceding claims, having a sulfated ash content of less than 0.5 wt. %.
9. A lubricating oil composition according to claim 2, wherein said dispersant contributes at least 0.08 wt. % of nitrogen to the lubricating oil composition.

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10. A lubricating oil composition of claim 2, having a sulfur content less than about 0.3 wt. %, a sulfated ash content of less than about 0.5 wt. %, and a chlorine content of less than about 50 ppm.

5 11. A lubricating oil composition according to any one of the preceding claims, wherein the functionalized, high molecular weight olefin molecule is derived from an amorphous ethylene-propylene copolymer, or a blend of an amorphous and a semi-crystalline ethylene-propylene copolymer with an SSI of from 5 to 30, produced by simultaneously shearing and functionalizing higher molecular weight ethylene-propylene copolymers, with maleic anhydride, in an extruder.

10 12. A lubricating oil composition of claim 11, wherein said semi-crystalline ethylene-propylene copolymer has a tapered structure and is produced in a tubular reactor.

15 13. A method of operating a diesel engine, which method comprises the step of lubricating said engine with a lubricating oil composition of any one of the preceding claims.

20 14. A method according to claim 13, wherein said diesel engine is provided with an exhaust gas recirculation system.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 04 25 6985

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