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(54) **Lubricating oil composition**

(57) A lubricating oil composition containing a combination of oil of lubricating viscosity, one or more block copolymers of hydrogenated poly(monovinyl aromatic hydrocarbon) and poly(conjugated diene) as a viscosity

modifier, and one or more one or more optionally substituted bridged hydrocarbyl phenol condensates, or metal salts thereof, as a detergent.

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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 soot-handling performance, particularly in diesel 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 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 morphology of soot formed in such engines is such that the soot cannot be adequately dispersed by conventional high molecular weight dispersants, and that simply adding an increased amount of such dispersant does not adequately address the problem.

[0005] U.S. Published Patent Application No. 2007/0006855 suggests that soot-induced increases in lubricant viscosity associated with EGR-equipped diesel engines can be controlled by using certain phenylenediamine compounds. U.S. Patent Nos. 6,715, 473 and 6,886,919 suggest that by selecting certain additives, specifically certain viscosity modifiers, including diblock copolymers of poly(monovinyl aromatic hydrocarbon) and hydrogenated poly (conjugated diene), as well as dispersants and/or detergents, and/or controlling the level and basicity of dispersant nitrogen, the rapid increase in lubricant viscosity associated with the use of engines provided with EGR systems can be ameliorated. U.S. Patent No. 6,303,550 suggests that diblock copolymers of poly(monovinyl aromatic hydrocarbon) and hydrogenated poly (conjugated diene) in a number average molecular weight range of 8,000 to 30,000 display a certain degree of dispersing characteristics.

[0006] It would be advantageous to identify lubricating oil compositions that better perform in diesel engines, specifically diesel engines equipped with EGR systems, especially diesel engines equipped with condensed EGR systems, more particularly, lubricating oil compositions that ameliorate soot-induced viscosity increase during use of such engines.

SUMMARY OF THE INVENTION

[0007] In accordance with a first aspect of the present invention, there is provided a lubricating oil composition which provides improved performance, particularly in diesel engines provided with exhaust gas recirculation (EGR) systems, and more particularly in diesel engines equipped with condensed EGR systems, which lubricating oil comprises a major amount of oil of lubricating viscosity, and minor amounts of (a) a viscosity modifier comprising one or more block copolymers of hydrogenated poly(monovinyl aromatic hydrocarbon) and poly (conjugated diene) and (b) one or more detergents comprising one or more optionally substituted bridged hydrocarbyl phenol condensates, or metal salts thereof.

[0008] In accordance with a second aspect of the present invention, there is provided a method of reducing soot-induced viscosity increase in lubricating oils for engines, particularly in diesel engines provided with exhaust gas recirculation (EGR) systems, and more particularly in diesel engines equipped with condensed EGR systems, which method comprises the step of formulating the lubricating oil composition with a combination of the viscosity modifier and detergent of the first aspect, lubricating the crankcase of the engine with the formulated lubricating oil composition and operating

the engine.

[0009] In accordance with a third aspect of the present invention, there is provided the use of the combination of the viscosity modifier and the detergent of the first aspect to reduce the soot-induced viscosity increase of a lubricating composition for the lubrication of an engine, particularly in diesel engines provided with exhaust gas recirculation (EGR) systems, and more particularly in diesel engines equipped with condensed EGR systems during use.

[0010] Other and further objects, advantages and features of the present invention will be understood by reference to the following specification.

[0011] In the following specification, the term "hydrocarbyl", when referring to substituent groups attached to the remainder of a molecule, refers to groups that attach to the remainder of the molecule via a carbon atom, which are purely hydrocarbon or predominantly hydrocarbon in character within the context of this invention. Such groups include (i) purely hydrocarbon groups; that is aliphatic, alicyclic, aromatic, aliphatic- and alicyclic-substituted aromatic, aromatic-substituted aliphatic and alicyclic groups and the like, as well as cyclic groups wherein the ring is completed through another portion of the molecule (e.g., where any two indicated substituents together form an alicyclic group; (ii) substituted hydrocarbon groups; that is, groups containing non-hydrocarbyl substituents that do not alter the predominantly hydrocarbon character of the group, such as hydroxy, nitro, cyano, alkoxy and acyl; (iii) hetero groups, that is groups that, while predominantly hydrocarbon in character, contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Examples of such hetero atoms include nitrogen, oxygen and sulfur. In general, no more than three substituents or hetero atoms, such as no greater than one substituent or hetero atom, will be present for each 10 carbon atoms in the hydrocarbyl group.

[0012] The term "lower", as used herein in conjunction with terms such as hydrocarbyl, alkyl, alkenyl, alkoxy and the like is intended to refer to such groups containing a total of up to 7 carbon atoms.

[0013] "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.

[0014] The term "major amount" means in excess of 50 mass % of a composition; and the term "minor amount" means less than 50 mass % of a composition.

[0015] Further, it is intended that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

DETAILED DESCRIPTION OF THE INVENTION

[0016] 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.

[0017] Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil); liquid petroleum oils and hydrorefined, solvent-treated or acid-treated mineral oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale also serve as useful base oils.

[0018] Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); 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.

[0019] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, and the alkyl and aryl ethers of polyoxyalkylene polymers (e.g., methyl-polyiso-propylene glycol ether having a molecular weight of 1000 or diphenyl ether of poly-ethylene glycol having a molecular weight of 1000 to 1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C₃-C₈ fatty acid esters and C₁₃ Oxo acid diester of tetraethylene glycol.

[0020] Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of such esters includes dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate,

the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0021] Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol esters such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

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

[0023] Unrefined, refined and re-refined oils can be used in lubricants of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations; petroleum oil obtained directly from distillation; or ester oil obtained directly from an esterification and used without further treatment would be an unrefined oil. Refined oils are similar to unrefined oils except that the oil is further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art. Re-refined oils are obtained by processes similar to those used to provide refined oils but begin with oil that has already been used in service. Such re-refined oils are also known as reclaimed or reprocessed oils and are often subjected to additionally processing using techniques for removing spent additives and oil breakdown products.

[0024] The oil of lubricating viscosity may comprise a Group I, Group II, Group III, Group IV or Group V base stocks or base oil blends of the aforementioned base stocks. Preferably, the oil of lubricating viscosity is a Group II, Group III, Group IV or Group V base stock, or a mixture thereof, or a mixture of a Group I base stock and one or more a Group II, Group III, Group IV or Group V base stock. 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.

[0025] 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.

[0026] 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

[0027] Viscosity modifiers useful in the practice of the present invention comprise block copolymers of hydrogenated poly(monovinyl aromatic hydrocarbon) and poly (conjugated diene). Suitable vinyl aromatic hydrocarbon monomers from which the poly(monovinyl aromatic hydrocarbon) block(s) may be derived include those containing from 8 to about 16 carbon atoms such as aryl-substituted styrene, alkoxy-substituted styrene, vinyl naphthalene, alkyl-substituted vinyl naphthalenes and the like. The alkyl and alkoxy substituents may typically comprise from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms. The number of alkyl or alkoxy substituents per molecule, if present, may range from 1 to 3, and is preferably 1.

[0028] Suitable diene monomers from which the poly(conjugated diene block(s) may be derived include, those containing from 2 to about 16 carbon atoms, for example, from 8 to about 12 carbon atoms, such as 1,3-butadiene, isoprene, piperylene, methylpentadiene, phenylbutadiene, 3,4-dimethyl-1,3-hexadiene, 4,5-diethyl-1,3-octadiene, with 1,3-butadiene and isoprene being preferred.

[0029] The hydrogenated poly(monovinyl aromatic hydrocarbon)/poly(conjugated diene) block copolymers of the present invention preferably have a number average molecular weight ($\bar{M}_n$) ranging from 85,000 to 1,500,000, for example, from 85,000 to 900,000, or from 85,000 to 300,000, or from 350,000 to 900,000. When the amount of vinyl aromatic content of the copolymer ranges from 5 % and about 40 % by weight of the copolymer, the number average molecular weight typically ranges from 85,000 to 300,000. 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).

[0030] The hydrogenated poly(monovinyl aromatic hydrocarbon)/poly (conjugated diene) block copolymers of the present invention are represented by the formula: $A_z-(B-A)_y-B_x$ wherein A is a polymeric block derived predominantly from vinyl aromatic hydrocarbon monomer; B is a polymeric block derived predominantly from conjugated diene monomer; x and z are each independently a number equal to 0 or 1; and y is a whole number ranging from 1 to about 15.

[0031] As used herein in connection with polymer block composition, "predominantly" means that the specified monomer or monomer type that is the principle component in that polymer block is present in an amount of at least 85% by weight of the block.

[0032] The hydrogenated poly(monovinyl aromatic hydrocarbon)/poly (conjugated diene) block copolymers of the present invention may also include tapered blocks and be represented by the formula A-A/B-B wherein A is a polymeric block derived predominantly from vinyl aromatic hydrocarbon monomer; B is a polymeric block derived predominantly from conjugated diolefin monomer; and A/B is a tapered segment derived from both vinyl aromatic hydrocarbon monomer and conjugated diolefin monomer.

[0033] Preferably, the hydrogenated poly(monovinyl aromatic hydrocarbon)/poly (conjugated diene) block copolymers of the present invention are linear, di-block copolymers.

[0034] Hydrogenated poly(monovinyl aromatic hydrocarbon)/poly (conjugated diene) block copolymers are known in the art and are commercially available. Such block copolymers can be made by anionic polymerization with an alkali metal initiator such as sec-butyllithium, as described, for example, in U.S. Pat. Nos. 4,764,572; 3,231,635; 3,700,633; and 5,194,530.

[0035] The poly(conjugated diene) block(s) of the block copolymer may be, and are preferably selectively hydrogenated, typically to a degree such that the residual ethylenic unsaturation of the block is reduced to at most 20%, more preferably at most 5%, most preferably at most 2% of the unsaturation level before hydrogenation. The hydrogenation of these copolymers may be carried out using a variety of well established processes including hydrogenation in the presence of such catalysts as Raney Nickel, noble metals such as platinum and the like, soluble transition metal catalysts and titanium catalysts as described in U.S. Patent No. 5,299,464.

[0036] Sequential polymerization or reaction with divalent coupling agents can be used to form linear polymers. It is also known that a coupling agent can be formed in-situ by the polymerization of a monomer having two separately polymerizable vinyl groups such as divinylbenzene to provide star polymers having from about 6 to about 50 arms. Di- and multivalent coupling agents containing 2 to 8 functional groups, and methods of forming star polymers are well known and such materials are available commercially.

[0037] According to the present invention, the hydrogenated poly(monovinyl aromatic hydrocarbon)/poly (conjugated diene) block copolymers include different mixtures of the polymers described above. For example, copolymer can comprise one or more linear block copolymers having different molecular weights, different vinyl aromatic contents.

[0038] Preferably, the hydrogenated poly(monovinyl aromatic hydrocarbon)/poly (conjugated diene) block copolymers will be those in which the hydrogenated poly(monovinyl aromatic hydrocarbon) segment comprises at least about 20 wt.% of the copolymer.

[0039] "Shear Stability Index" ("SSI") refers to the ability of a polymer to resist degradation under service conditions. The higher the SSI, the less stable the polymer and the more susceptible it is to degradation. SSI is defined as the percentage of polymer-derived viscosity loss and is calculated according to ASTM D6278-98 using the following equation:

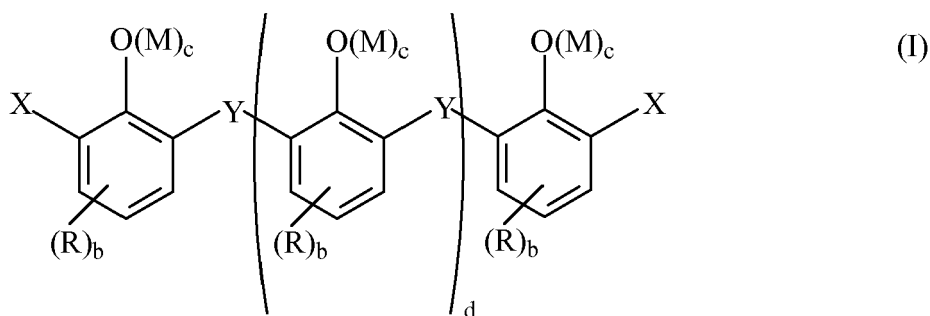
$$SSI = 100 \times \frac{kv_{fresh} - kv_{after}}{kv_{fresh} - kv_{oil}}$$

wherein kv_{fresh} is the kinematic viscosity of the polymer-containing solution before degradation and kv_{after} is the kinematic viscosity of the polymer-containing solution after degradation. Preferably, the hydrogenated poly(monovinyl aromatic hydrocarbon)/poly (conjugated diene) block copolymers used in the practice of the present invention have an SSI value of 2 % to 50 % after 90 cycles in the testing apparatus specified in the ASTM D6278-98 protocol with a diesel injector nozzle

[0040] Examples of commercially available hydrogenated poly(monovinyl aromatic hydrocarbon)/poly (conjugated diene) block copolymers useful in the practice of the invention include styrene/hydrogenated isoprene linear di-block copolymers Infineum SV140™, Infineum SV150™, Infineum SV155™ and Infineum SV160™, available from Infineum USA L.P. and Infineum UK Ltd.; Lubrizol® 7318 available from The Lubrizol Corporation; and Septon 1001™ and Septon 1020™, available from Septon Company of America (Kuraray Group). Another type of suitable di-block copolymer is styrene/1, 3-butadiene hydrogenated block copolymer, such as that sold under the tradename Glissoviscal by BASF.

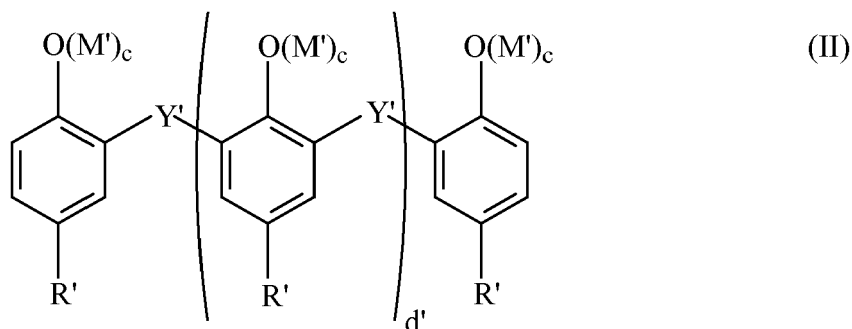
[0041] Lubricating oil compositions of the present invention can comprise from about 0.01 mass % to about 10 mass %, preferably from about 0.25 mass % to about 3 mass % of the hydrogenated poly(monovinyl aromatic hydrocarbon)/poly (conjugated diene) block copolymer viscosity modifier(s).

[0042] Detergents comprising bridged, optionally substituted phenol condensates and metal salts thereof, useful in the practice of the invention include detergents of general formula (I):



wherein d is 0 to 10, preferably 1 to 8, more preferably 2 to 6, and most preferably 3 to 5; Y is a divalent bridging group, particularly a hydrocarbyl group more preferably a hydrocarbyl group having from 1 to 4 carbon atoms, such as $-\text{CH}_2-$; or an ether group, preferably an ether group having from 1 to 4 carbon atoms, such as $-\text{CH}_2\text{OCH}_2-$; R is a hydrocarbyl group having from 4 to 30, preferably 8 to 18, and most preferably 9 to 15 carbon atoms, each b is independently 0, 1, 2 or 3, provided that at least aromatic group has an R substituent and that the total number of carbon atoms in all R groups is at least 7; each M is independently an alkali or alkaline earth metal ion; each c is 0 or 1, provided that, when c is 0, M is replaced with H ; and each X is independently H , $-\text{CHO}$ or CH_2OH .

[0043] In one embodiment of the invention, the optionally substituted bridged phenol condensates and metal salts thereof are simply bridged phenol condensates or metal salts thereof, represented by formula (II):

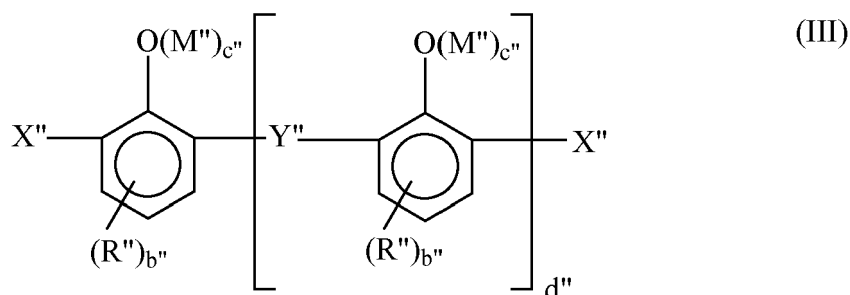


wherein d' is 0 to 10, preferably 1 to 8, more preferably 2 to 6, and most preferably 3 to 5; each Y' is a divalent bridging

group is a divalent bridging group, particularly a hydrocarbyl group more preferably a hydrocarbyl group having from 1 to 4 carbon atoms, such as $-\text{CH}_2-$; or an ether group, preferably an ether group having from 1 to 4 carbon atoms such as $-\text{CH}_2\text{OCH}_2-$; R' is a hydrocarbyl group having from 4 to 30, preferably 8 to 18, and most preferably 9 to 15 carbon atoms, each b' is independently 0, 1, 2 or 3, provided that at least aromatic group has an R' substituent and that the total number of carbon atoms in all R' groups is at least 7; each M' is independently an alkali or alkaline earth metal ion; and each c' is 0 or 1, provided that, when c' is 0, M' is replaced with H.

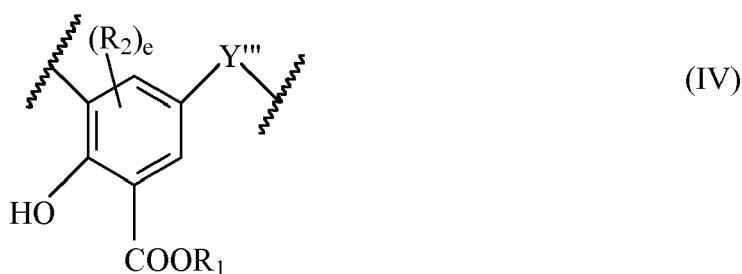
[0044] Preferred detergents of formula (II) are having a weight average molecular weight (M_w) of 1250 to 1680, as measured by MALDI-TOF (Matrix Assisted Laser Desorption Ionization- Time of Flight) mass spectrometry. Detergents of formula (II), and methods for forming same, are known; an ashless (metal-free) detergent of formula (II) is described, for example, in U.S. Published Patent Application No. 20050277559.

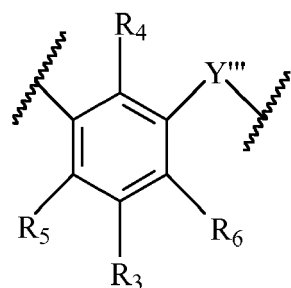
[0045] The optionally substituted bridged phenol condensates and metal salts thereof useful in the practice of the present invention also include hydrocarbyl-substituted saligenin detergents, represented by formula (III):



wherein each X'' is independently $-\text{CHO}$ or $-\text{CH}_2\text{OH}$; each Y'' is a divalent bridging group, particularly a hydrocarbyl group more preferably a hydrocarbyl group having from 1 to 4 carbon atoms, such as $-\text{CH}_2-$; or an ether group, preferably an ether group having from 1 to 4 carbon atoms such as $-\text{CH}_2\text{OCH}_2-$; provided that $-\text{CHO}$ groups comprise at least about 10 mole percent of the X'' and Y'' groups; each M'' is independently an alkali or alkaline earth metal ion; each R'' is independently a hydrocarbyl group containing 1 to about 60 carbon atoms; d'' is 1 to about 10; c'' is 0 or 1 provided that when c'' is 0 the M'' is replaced with H; and each b'' is independently 0, 1, 2, or 3; provided that at least one aromatic ring contains an R'' substituent and that the total number of carbon atoms in all R'' groups is at least 7; and further provided that if d'' is 1 or greater, then one of the X'' groups can be $-\text{H}$. Saligenin detergents of formula (III) and methods for forming same are known and described, for example, in U.S. Patent No. 7,462,583.

[0046] Also considered within the scope of the present invention are optionally substituted bridged phenol/salicylate condensates which are sometimes referred to as salixarate detergents and can be defined as detergents comprising one or more units of formula (IV) and/or formula (V):

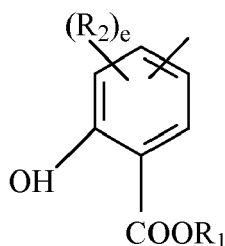




(V)

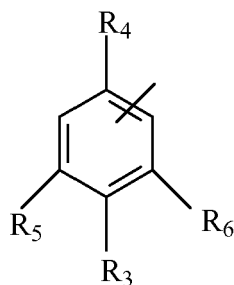
;

each end of the compound having a terminal group which is independently a unit of formula (VI) or formula (VII):



(VI)

or



(VII)

with the proviso that the salixarate must have at least one unit of formula (IV) or formula (VI) and one unit of either formula (V) or formula (VII); wherein in formulae (IV) through (VII), Y''' is a divalent bridging group, particularly a hydrocarbyl group more preferably a hydrocarbyl group having from 1 to 4 carbon atoms, such as -CH₂-; or an ether group, preferably an ether group having from 1 to 4 carbon atoms such as -CH₂OCH₂-; R₁ is hydrogen or a hydrocarbyl group; R₂ is hydrogen or a hydrocarbyl; e is 1 or 2; R₃ is hydrogen, a hydrocarbyl or a hetero-substituted hydrocarbyl group; either R₁ is hydroxyl and R₂ and R₄ are independently either hydrogen, hydrocarbyl or hetero-substituted hydrocarbyl, or R₂ and R₄ are hydroxyl and R₁ is either hydrogen, hydrocarbyl or hetero-substituted hydrocarbyl. Preferably such compounds have at least one unit of formula (IV) and at least two units of formula (V); more preferably, the ratio the number of units of units of formula (IV) to the number of units of formula (V) ranges from about 0.1:1 to about 2:1, more preferably 0.1:1 to 1:1, particularly 0.1:1 to 0.5:1. Y''' may optionally be sulfur in up to 50% of the units, such that the amount of sulfur incorporated in the molecule is up to 50 mole % of the Y groups. In one embodiment, the amount of sulfur is between 8 and 20 mole %, and in one embodiment the compound is sulfur-free.

[0047] In a preferred embodiment, R₁ is a hydrocarbyl (e.g., alkyl) group of 1 to about 6 carbon atoms. R₂ is preferably a hydrocarbyl group of 1 to about 100 carbon atoms, such as 1 to about 30 carbon atoms, more preferably 1 to about 6 carbon atoms. R₃ is preferably a hydrocarbyl of 1 to about 100 carbon atoms, such as 1 to about 30 carbon atoms. R₃ may also be hetero-substituted. The hetero atoms or groups may be -O- or -NH-. In one embodiment, Y''' is CH₂; R₄

is hydroxyl; R_5 and R_6 are hydrogen; R_3 is a hydrocarbyl group of about 6 to about 60 carbon atoms, more preferably about 6 to about 18 carbon atoms; R_1 is hydrogen; R_2 is hydrogen; e is 1; the total number of units of formulae (IV) and (V) is least 5; and the number of units of formula (IV) is 1 or 2.

[0048] Salixarate detergents useful in the practice of the present invention also include metal salts of the above compounds. Salixarate detergents and methods for forming same are known and described, for example, in U.S. Patent No. 6,200,936.

[0049] The alkali and alkaline earth metals that are useful in the formation of metal salts of each of the above detergents include monovalent metals such as sodium, potassium, lithium or preferably, a divalent metal, particularly calcium or magnesium. The bridged phenol condensates useful in the practice of the present invention include the ashless (metal-free) compounds, as well as metal salts in which between 0 and 100 percent of the phenolic -OH groups are non-neutralized; the detergents can be non-neutralized, or partially or fully neutralized with one or more monovalent or divalent metal ions.

[0050] The fully neutralized salts of the above detergents 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 80mg KOH/g. 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 KOH/g or greater, and typically will have a TBN of from 250 to 450 KOH/g or more.

[0051] The optionally substituted bridged phenol condensate detergent(s) can be incorporated into lubricating oil compositions of the present invention in an amount ranging from 0.5 to 30, preferably from 2 to 20, more preferably from 2 to 15, mass %, based on the total mass of the lubricating oil composition.

[0052] Lubricating oil compositions of the present invention can also contain supplemental detergents other than the optionally substituted bridged phenol condensates described above. Supplemental 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 supplemental metal detergents are neutral and overbased calcium sulfonates having TBN of from 20 to 450 KOH/g, neutral and overbased calcium phenates and sulfurized phenates having TBN of from 50 to 450 KOH/g and neutral and overbased magnesium or calcium salicylates having a TBN of from 20 to 450 KOH/g. Combinations of detergents, whether overbased or neutral or both, may be used.

[0053] 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.

[0054] 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.

[0055] 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.

[0056] 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 hetero atoms, 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.

[0057] 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.

[0058] 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.

[0059] Supplemental detergents that may be used in the formulation of lubricating oil compositions of the present invention 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.

[0060] Where supplemental detergents are used in the formulation of lubricating oil compositions of the present invention, the molar amount of detergent soap introduced by the supplemental detergent(s) should be no greater than 80 %, such as no greater than 70 %, more preferably no greater than 60 %, such as no greater than 50 %, most preferably no greater than 40 %, such as no greater than 30 % or no greater than 20 %, of the total molar amount of detergent soap present in the lubricating oil composition.

[0061] Similarly, lubricating oil compositions of the present invention can also contain supplemental viscosity modifiers other than the hydrogenated poly(monovinyl aromatic hydrocarbon)/poly (conjugated diene) block copolymers described above. Supplemental viscosity modifiers that may be used include viscosity modifiers derived from 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, as well as the partially hydrogenated homopolymers of butadiene and isoprene.

[0062] A dispersant - viscosity index improver functions as both a viscosity index improver and as a dispersant and may also be included in lubricating oil compositions of the present invention. Examples of dispersant - viscosity index improvers include reaction products of amines, for example polyamines, with a hydrocarbyl-substituted mono- or dicarboxylic acid in which the hydrocarbyl substituent comprises a chain of sufficient length to impart viscosity index improving properties to the compounds. In general, the viscosity index improver dispersant may be, for example, a polymer of a C₄ to C₂₄ unsaturated ester of vinyl alcohol or a C₃ to C₁₀ unsaturated monocarboxylic acid or a C₄ to C₁₀ di-carboxylic acid with an unsaturated nitrogen-containing monomer having 4 to 20 carbon atoms; a polymer of a C₂ to C₂₀ olefin with an unsaturated C₃ to C₁₀ mono- or di-carboxylic acid neutralized with an amine, hydroxyl amine or an alcohol; or a polymer of ethylene with a C₃ to C₂₀ olefin further reacted either by grafting a C₄ to C₂₀ unsaturated nitrogen-containing monomer thereon or by grafting an unsaturated acid onto the polymer backbone and then reacting carboxylic acid groups of the grafted acid with an amine, hydroxy amine or alcohol.

[0063] Where supplemental viscosity modifiers and/or dispersant - viscosity modifiers are employed, said supplemental viscosity modifier(s) and dispersant - viscosity modifier(s) should provide no greater than 80 %, such as no greater than 70 %, more preferably no greater than 60 %, such as no greater than 50 %, most preferably no greater than 40 %, such as no greater than 30 % or no greater than 20 %, of the total mass % of viscosity modifier present in the lubricating oil composition.

[0064] Additional additives that may be incorporated in the compositions of the invention to enable them to meet particular requirements include dispersants, corrosion inhibitors, oxidation inhibitors, friction modifiers, other dispersants, antifoaming agents, anti-wear agents and pour point depressants. Some are discussed in further detail below.

[0065] Ashless dispersants effectively reduce formation of deposits upon use in gasoline and diesel engines, when added to lubricating oils. Ashless dispersants useful in the compositions of the present invention comprises 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. The most common dispersant in use is the well known succinimide dispersant, which is a condensation product of a hydrocarbyl-substituted succinic anhydride and a poly(alkyleneamine). Both mono-succinimide and bis-succinimide dispersants (and mixtures thereof) are well known.

[0066] Preferably, the ashless dispersant is a "high molecular weight" dispersant having a number average molecular weight ($\bar{M}_n$) 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 about 1680 to about 5600. Typical commercially available polyisobutylene-based dispersants contain polyisobutylene polymers having a number average molecular weight ranging from about 900 to about 2300, functionalized by maleic anhydride (MW = 98), and derivatized with polyamines having a molecular weight of from about 100 to about 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.

[0067] Preferred groups of dispersant include polyamine-derivatized poly α -olefin, dispersants, particularly ethylene/butene α -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 about 0.3 to about 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 trimethylolaminomethane, as described in U.S. Patent No. 3,632,511.

[0068] 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 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*.

[0069] 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 about 0.1 to about 20 atomic proportions of boron for each mole of acylated nitrogen composition. Useful dispersants contain from about 0.05 to about 2.0 mass %, e.g., from about 0.05 to about 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 about 0.5 to 4 mass %, e.g., from about 1 to about 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 about 135°C to about 190°C, e.g., 140°C to 170°C, for from about 1 to about 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.

[0070] 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 fluor-elastomer 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.

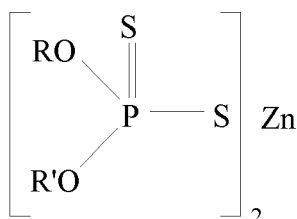
[0071] Preferably, the dispersant is a thermally maleated dispersant formed by reacting a polyalkenyl-substituted mono- or dicarboxylic acid, anhydride or ester; and a polyamine, having from greater than about 1.3 to less than about 1.7 mono- or di- carboxylic acid producing moieties per polyalkenyl moiety and wherein said polyalkenyl moiety has a molecular weight distribution (M_w/M_n) of from 1.5 to 2.0 and a number average molecular weight (M_n) of from about 1800 to about 3000. Such preferred dispersants are described, for example, in U.S. Patent Nos. 6,734,148 and 6,743,757.

[0072] For adequate piston deposit control, a nitrogen-containing dispersant can be added in an amount providing the lubricating oil composition with from about 0.03 mass % to about 0.15 mass %, preferably from about 0.07 to about

0.12 mass % of nitrogen.

[0073] 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.

[0074] 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 hydrocarbyl 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, butyl-phenyl, 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 dihydrocarbyl 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 mass %, such as from about 0.03 to about 0.10 mass %, or from about 0.05 to about 0.08 mass %, based on the total mass of the composition. In one preferred embodiment, lubricating oil compositions of the present invention contain zinc dialkyl dithiophosphate derived predominantly (e.g., over 50 mol. %, such as over 60 mol. %) from secondary alcohols.

[0075] 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 C_5 to C_{12} alkyl side chains, calcium nonylphenol sulfide, oil soluble phenates and sulfurized phenates, phosphosulfurized or sulfurized hydrocarbons, phosphorous esters, metal thiocarbamates, oil soluble copper compounds as described in U.S. Patent No. 4,867,890, and molybdenum-containing compounds.

[0076] 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 $-CO-$, $-SO_2-$ 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.

[0077] Multiple antioxidants are commonly employed in combination. In one preferred embodiment, lubricating oil compositions of the present invention contain from about 0.1 to about 1.2 mass % of aminic antioxidant and from about 0.1 to about 3 mass % of phenolic antioxidant. In another preferred embodiment, lubricating oil compositions of the present invention contain from about 0.1 to about 1.2 mass % of aminic antioxidant, from about 0.1 to about 3 mass % of phenolic antioxidant and a molybdenum compound in an amount providing the lubricating oil composition from about 10 to about 1000 ppm of molybdenum.

[0078] 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.

[0079] 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, dialkyldithiophosphates, alkyl xanthates and alkylthioxanthates.

[0080] 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.

[0081] Among the molybdenum compounds useful in the compositions of this invention are organo-molybdenum compounds of the formulae:



and



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.

[0082] 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 ligand organo groups, such as at least 25, at least 30, or at least 35 carbon atoms.

[0083] Pour point depressants, otherwise known as lube oil flow improvers (LOFI), lower the minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Typical of those additives that improve the low temperature fluidity of the fluid are C_8 to C_{18} dialkyl fumarate/vinyl acetate copolymers, and polymethacrylates. Foam control can be provided by an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

[0084] 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.

[0085] In the present invention it may also be preferable 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.

[0086] 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.

[0087] 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. 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.

[0088] Fully formulated lubricating oil compositions of the present invention preferably have a TBN of at least 8.5, preferably at least 9, such as from about 8.5 to about 13, preferably from about 9 to about 13, and more preferably from about 9 to about 11 mg KOH/g (ASTM D2896).

[0089] Fully formulated lubricating oil compositions of the present invention preferably have a sulfated ash (SASH) content (ASTM D-874) of about 1.1 mass % or less, preferably about 1.0 mass % or less, more preferably about 0.8 mass % or less.

[0090] Fully formulated lubricating oil compositions of the present invention further preferably have a sulfur content of less than about 0.4 mass %, more less than about 0.35 mass % more preferably less than about 0.03 mass %, such as less than about 0.15 mass %. Preferably, the Noack volatility (ASTM D5880) of the fully formulated lubricating oil

composition (oil of lubricating viscosity plus all additives and additive diluent) will be no greater than 13, such as no greater than 12, preferably no greater than 10. Fully formulated lubricating oil compositions of the present invention preferably have no greater than 1200 ppm of phosphorus, such as no greater than 1000 ppm of phosphorus, or no greater than 800 ppm of phosphorus.

[0091] All weight (and mass) percents expressed herein (unless otherwise indicated) are based on active ingredient (A.I.) content of the additive, and/or additive-package, exclusive of any associated diluent. However, detergents, including the detergents of the present invention, are conventionally formed in diluent oil, which is not removed from the product, and the TBN of a detergent is conventionally provided for the active detergent in the associated diluent oil. Therefore, weight (and mass) percents, when referring to detergents are (unless otherwise indicated) total weight (or mass) percent of active ingredient and associated diluent oil.

[0092] This invention will be further understood by reference to the following examples, wherein all parts are parts by weight (or mass), unless otherwise noted.

EXAMPLES

[0093] The present invention is illustrated by the following, non-limiting examples. Examples 1-4 are lubricant compositions made from the components shown in Table 1 using techniques which are well known in the art. The base stock ratio was constant in all of the exemplified compositions.

[0094] Examples 3 and 4 contained an ashless (non-metallized) methylene bridged alkyl phenol having a weight average molecular weight ranging from 1100 to 1700. The ashless methylene bridged alkyl phenol was prepared by adding dodecylphenol, sulphonic acid (catalyst), paraformaldehyde, water and heptane to a 5 L baffled reactor provided with a stirrer (200 rpm), nitrogen blanket (600 ml/min), condenser, Dean and Stark trap, a temperature controlling system, and Cardice/Acetone trap vacuum system. The reaction components were heated from ambient to 80°C over 30 minutes, then heated further from 80°C to 100°C over 2 hours, during which time water was removed by azeotropic distillation. The residual heptane and dodecyl phenol were removed from the reaction mixture under reduced pressure at 200°C. Finally, the temperature was decreased to 120°C at which point diluent oil (SN 150) was added to produce the desired level of active ingredient.

Table 1. Compositional Information for the Examples

Component	Ex. 1	Ex. 2	Ex.3	Ex.4
STAR5 ¹	37.4	43.9	37.9	44.4
STAR8 ²	37.4	43.9	37.9	44.4
Infineum SV155 ³	13.0	0.0	13.0	0.0
Infineum V351 ⁴	0.2	0.2	0.2	0.2
Ashless methylene-bridged alkyl phenol	0.0	0.0	2.022	2.022
Low Base No. non-bridged salicylate detergent	3.0	3.0	0.0	0.0
Soap [%] ⁵	1.011	1.011	1.011	1.011
¹ Group II base oil available commercially from Motiva. ² Group II base oil available commercially from Motiva. ³ Styrene/polyolefin diblock copolymer (6% Al) commercially available from Infineum, USA. ⁴ Commercially available pour point depressant from Infineum USA. ⁵ mass % surfactant in the product.				

[0095] Examples 1 through 4 were evaluated for soot dispersing performance in the manner described below. In the test, carbon black was used as a surrogate for the soot produced in diesel engines.

[0096] Each of the exemplified lubricant compositions was placed in a vessel and heated to a temperature of 160° C under air for 96 hours. The vessels containing the compositions were fitted with condensers to return volatiles to the lubricant compositions. Next, Cabot "Vulcan XC-72R" carbon black was added to the compositions to achieve lubricant compositions having 8 mass % of carbon black. The dispersion of carbon black in oil was stirred overnight at 90° C to equilibrate. The shear stress as a function of shear rate was measured with a rotational viscometer.

[0097] The log of the measured shear stress was then plotted versus the log of the shear rate, and the slope of the line was determined. The slope of the resulting line is hereafter referred to as the viscosity index of the lubricant com-

position and can have a value ranging from 0 and 1.0. As the value of the viscosity index approaches 1.0, the carbon black is completely dispersed in the composition because there is no dependence of stress on shear rate. A viscosity index of substantially less than 1 indicates that the carbon black is not thoroughly dispersed; when the carbon black is poorly dispersed, it forms agglomerates that become sheared when subjected to stress.

[0098] The practical effect of agglomerate formation is to thicken the lubricant composition which can result in engine failure because the composition is too thick to pump. Although carbon black agglomerates cause the lubricant composition to thicken, the agglomerates will break up when subjected to shear.

Table 2. Soot Dispersing Performance of the Examples

	Ex. 1	Ex. 2	Ex. 3	Ex.4
Viscosity Index	0.702	0.485	0.893	0.778

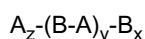
[0099] Example 3 is representative of the present invention and contained a block copolymers of hydrogenated poly (monovinyl aromatic hydrocarbon) and poly (conjugated diene), as a viscosity modifier and a bridged, phenol condensate detergent.

[0100] As shown by the resulting viscosity index, the lubricating oil composition of Example 3, containing the claimed combination of viscosity modifier and detergent demonstrated superior soot dispersancy compared to the comparative Examples containing a combination of the claimed viscosity modifier and a salicylate detergent (Example 1); the salicylate detergent, alone (Example 2), and the claimed detergent, in the absence of the claimed viscosity modifier (Example 4).

[0101] The disclosures of all patents, articles and other materials described herein are hereby incorporated, in their entirety, into this specification by reference. Many of the components described above may react under conditions of formulation, storage or use and therefore, compositions described as "comprising", "consisting essentially of" or "consisting of" a plurality of defined components are to be construed as including compositions obtained or obtainable by admixing the defined plurality of defined components. The 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 oil of lubricating viscosity, and minor amounts of a viscosity modifier comprising one or more block copolymers of hydrogenated poly(monovinyl aromatic hydrocarbon) and poly(conjugated diene) and one or more detergents comprising one or more optionally substituted bridged hydrocarbyl phenol condensates, or metal salts thereof.
2. A lubricating composition according to claim 1, wherein the monovinyl aromatic hydrocarbon block of said block copolymer of hydrogenated poly(monovinyl aromatic hydrocarbon) and poly (conjugated diene) is derived from monomer containing from 8 to about 16 carbon atoms selected from the group consisting of aryl-substituted styrene, alkoxy-substituted styrene, vinyl naphthalene and alkyl-substituted vinyl naphthalene.
3. A lubricating composition according to claim 1 or 2, wherein the conjugated diene block of said block copolymer of hydrogenated poly(monovinyl aromatic hydrocarbon) and poly (conjugated diene) is derived from monomer containing 2 to 16 carbon atoms selected from the group consisting of 1,3-butadiene, isoprene, piperylene, methylpentadiene, phenylbutadiene, 3,4-dimethyl-1,3-hexadiene, and 4,5-diethyl-1,3-octadiene.
4. A lubricating oil composition according to claim 1, 2 or 3, wherein said block copolymer of hydrogenated poly (monovinyl aromatic hydrocarbon) and poly (conjugated diene) is represented by the following formula:



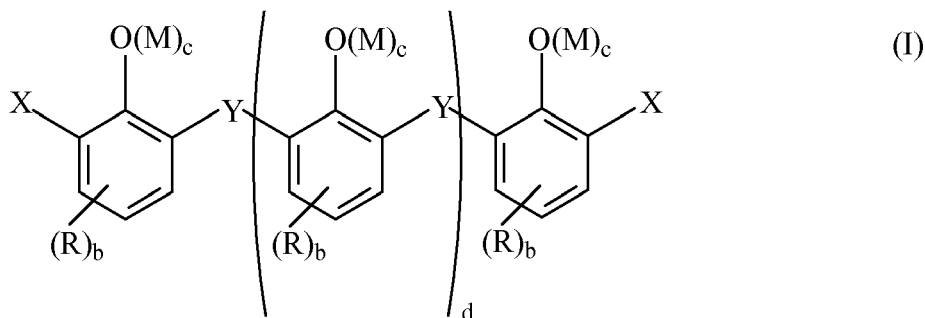
wherein: A is a polymeric block derived predominantly from vinyl aromatic hydrocarbon monomer; B is a polymeric block derived predominantly from conjugated diene monomer; x and z are, independently, a number equal to 0 or 1; and y is a whole number ranging from 1 to about 15.

5. A lubricating oil composition according to any one of the preceding claims, wherein said block copolymer of hydrogenated poly(monovinyl aromatic hydrocarbon) and poly (conjugated diene) is represented by the following formula:



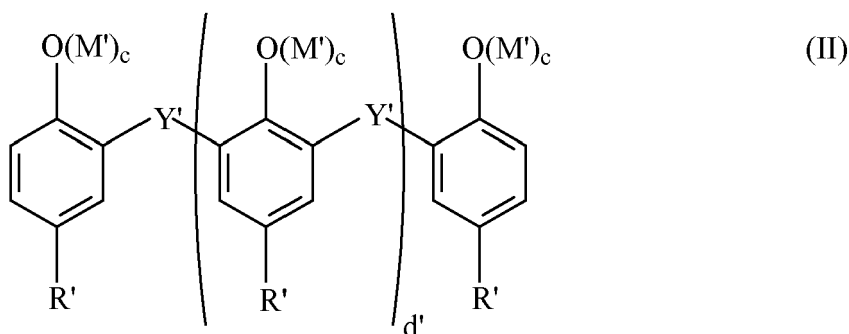
wherein: A is a polymeric block derived predominantly from vinyl aromatic hydrocarbon monomer; B is a polymeric block derived predominantly from conjugated diolefin monomer; and A/B is a tapered segment derived from both vinyl aromatic hydrocarbon monomer and conjugated diolefin monomer.

6. A lubricating oil composition according to any one of the preceding claims, wherein said block copolymer of hydrogenated poly(monovinyl aromatic hydrocarbon) and poly(conjugated diene) has a number average molecular weight ranging from 85,000 to 1,500,000.
7. A lubricating oil composition according to any one of the preceding claims, wherein said block copolymer of hydrogenated poly(monovinyl aromatic hydrocarbon) and poly(conjugated diene) has an SSI value of 2% to 50% after 90 cycles in the testing apparatus specified in the ASTM D6278-98 protocol with a diesel injector nozzle.
8. A lubricating oil composition according to any one of the preceding claims, wherein said one or more optionally substituted bridged hydrocarbyl phenol condensates, or metal salts thereof are compounds represented by formula (I):



wherein d is 0 to 10; Y is a divalent hydrocarbyl or ether bridging group; each R is independently a hydrocarbyl group having from 4 to 30 carbon atoms, each b is independently 0, 1, 2 or 3, provided that at least one aromatic group has an R substituent and the total number of carbon atoms in all R groups is at least 7; each M is independently an alkali or alkaline earth metal ion; each c is 0 or 1, provided that, when c is 0, M is replaced with H; and each X is independently H, -CHO or CH₂OH.

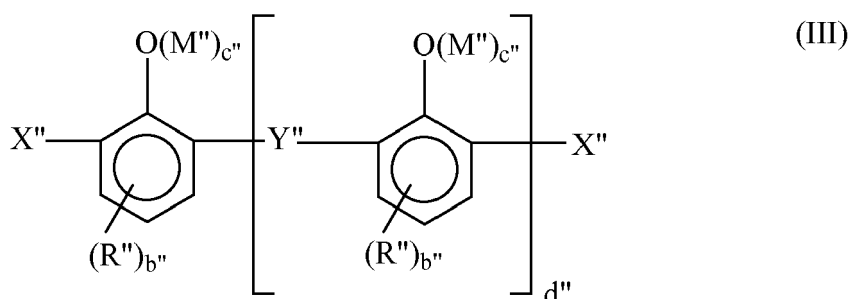
9. A lubricating oil composition according to claim 8, wherein said one or more optionally substituted bridged hydrocarbyl phenol condensates, or metal salts thereof are compounds represented by formula (II):



wherein d' is 0 to 10; each Y' is a divalent hydrocarbyl or ether bridging group; each R' is independently a hydrocarbyl

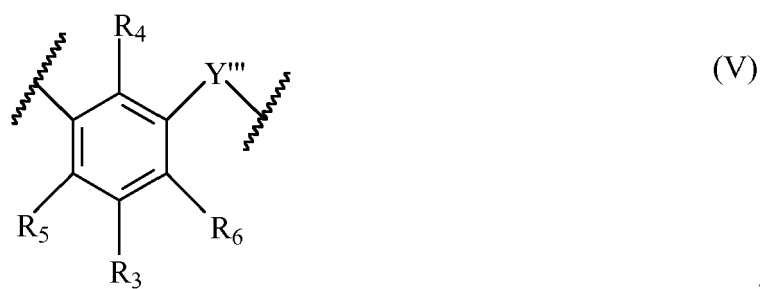
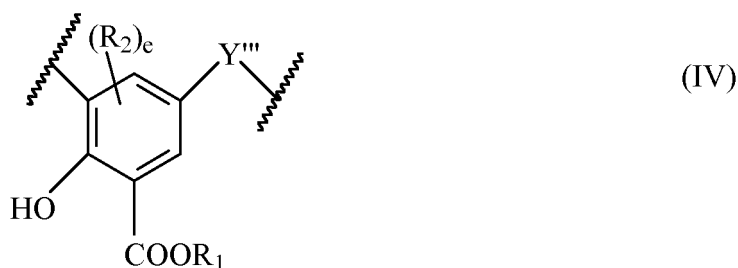
group having from 4 to 30 carbon atoms, provided that the total number of carbon atoms in all R' groups is at least 7; each M' is independently an alkali or alkaline earth metal ion; and each c' is 0 or 1, provided that, when c' is 0, M' is replaced with H.

10. A lubricating oil composition according to claim 8, wherein said one or more optionally substituted bridged hydrocarbyl phenol condensates, or metal salts thereof are compounds represented by formula (III):

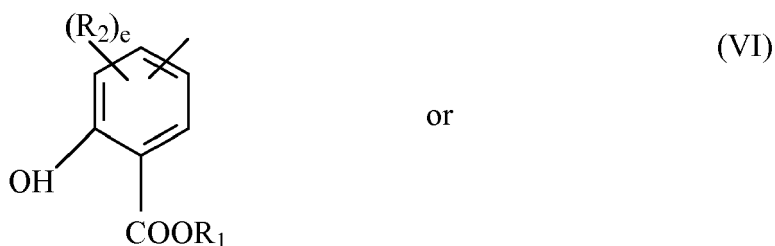


wherein each X'' is independently -CHO or -CH₂OH; each Y'' is a divalent hydrocarbyl or ether bridging group; provided that -CHO groups comprise at least about 10 mole percent of the X'' and Y'' groups; each M'' is independently an alkali or alkaline earth metal ion; each R'' is independently a hydrocarbyl group containing 1 to about 60 carbon atoms; d'' is 1 to about 10; c'' is 0 or 1 provided that when c'' is 0 the M'' is replaced with H; and each b'' is independently 0, 1, 2, or 3; provided that at least one aromatic ring contains an R'' substituent and the total number of carbon atoms in all R'' groups is at least 7; and further provided that if d'' is 1 or greater, then one of the X'' groups can be -H.

11. A lubricating oil composition according to any one of claims 1 to 7, wherein said one or more optionally substituted bridged hydrocarbyl phenol condensates, or metal salts thereof are optionally substituted bridged phenol/salicylate condensates, comprising one or more units of formula (IV) and/or formula (V):



each end of the compound having a terminal group which is independently a unit of formula (VI) or formula (VII):



with the proviso that said condensate must have at least one unit of formula (IV) or formula (VI) and one unit of either formula (V) or formula (VII); wherein in formulae (IV) through (VII), Y''' is a divalent hydrocarbyl or ether bridging group R₁ is hydrogen or a hydrocarbyl group; R₂ is hydrogen or a hydrocarbyl group; e is 1 or 2; R₃ is hydrogen, a hydrocarbyl group or a hetero-substituted hydrocarbyl group; either R₁ is hydroxyl and R₂ and R₄ are independently either hydrogen, hydrocarbyl or hetero-substituted hydrocarbyl, or R₂ and R₄ are hydroxyl and R₁ is either hydrogen, a hydrocarbyl group or a hetero-substituted hydrocarbyl group; with the proviso that Y''' may optionally be sulfur in up to 50% of the units, such that the amount of sulfur incorporated in the molecule is up to 50 mole % of the Y groups; or metal salts of said condensates

12. A lubricating oil composition according to any one of the preceding claims, comprising from about 0.5 to about 30 mass %, based on the total mass of the lubricating oil composition, of said optionally substituted bridged hydrocarbyl phenol condensates, or metal salts thereof, and from about 0.01 to about 10 mass %, based on the total mass of the lubricating oil composition, of said one or more block copolymers of hydrogenated poly(monovinyl aromatic hydrocarbon) and poly(conjugated diene).
13. A lubricating oil composition according to any one of the preceding claims, comprising one or more additional additives selected from the group consisting of dispersants, supplemental metallic detergents, supplemental viscosity modifiers, oxidation inhibitors, friction modifiers, antifoamants, antiwear agents and pour point depressants.
14. A method of reducing soot-induced viscosity increase in engines, which method comprises the step lubricating a crankcase of the engine with a lubricating oil composition according to any one of the preceding claims, and operating the engine.



EUROPEAN SEARCH REPORT

Application Number
EP 10 15 8694

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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 23 August 2010	Examiner Renoth, Heinz
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