(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 728 848 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
06.12.2006 Bulletin 2006/49

(21) Application number: **06112914.4**

(22) Date of filing: **21.04.2006**

(51) Int Cl.:
C10M 161/00 $^{(2006.01)}$ ***C10M 165/00*** $^{(2006.01)}$
C10M 167/00 $^{(2006.01)}$

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK YU

(30) Priority: **01.06.2005 EP 05270020**

(71) Applicant: **Infineum International Limited**
Abingdon,
Oxfordshire OX13 6BB (GB)

(72) Inventors:
- **Irving, Matthew David**
  Oxfordshire OX12 7NA (GB)
- **Scott, Robin**
  Oxfordshire OX14 3XB (GB)
- **Diggs, Nancy Z.**
  07090 New Jersey (US)
- **Gutiérrez, José A.**
  07023 New Jersey (US)
- **Alessi, Michael Louis**
  07921 New Jersey (US)

(54) Use of unsaturated olefin polymers to improve the compatibility between nitrile rubber seals and lubricating oil compositions

(57) A method of improving the seal compatibility and/or copper corrosion performance of lubricating oil compositions for the lubrication of the crankcases of an internal combustion engine, which method includes the step of adding to the lubricating oil compositions a minor amount of a non-hydrogenated (unsaturated) olefin polymer. Also described are lubricating oil compositions for engines and transmissions, which compositions contain sulphur and/or a salicylate soap and a minor amount of a non-hydrogenated (unsaturated) polymer, which compositions are compatible with nitrile rubber engine and transmission seals and copper-containing engine and transmission components.

Printed by Jouve, 75001 PARIS (FR)

Description

FIELD OF THE INVENTION

[0001] This invention relates to a method of improving the seal-compatibility performance of lubricating oil compositions used in engine crankcases and transmissions, particularly lubricating oil compositions having significant sulphur and/or salicylate soap contents, and to lubricating oil compositions having significant sulphur and/or salicylate soap contents that exhibit enhanced seals compatibility performance in engines and transmissions containing nitrile rubber seal materials. The invention further relates to a method of improving copper corrosion performance of lubricating oil compositions used in engine crankcases and transmissions, particularly lubricating oil compositions having significant sulphur contents, and to lubricating oil compositions having significant sulphur contents that exhibit enhanced seals and copper corrosion performance.

BACKGROUND OF THE INVENTION

[0002] Lubricating oil compositions used to lubricate internal combustion engines and transmissions contain a major amount of a base oil of lubricating viscosity, or a mixture of such oils, and additives used to improve the performance characteristics of the oil. For example, additives are used to improve detergency, to reduce engine wear, to provide stability against heat and oxidation, to reduce oil consumption, to inhibit corrosion, to act as a dispersant, and to reduce friction loss. Some additives provide multiple benefits, such as dispersant-viscosity modifiers. Many base oils contain sulfur, and a number of extremely effective additives conventionally used in engine and transmission lubricating oil compositions, including zinc dialkyl dithiophosphates (ZDDP), certain molybdenum-sulfur compounds, ashless dithiocarbamates and sulfonate and some phenate detergents, also contain sulfur and contribute to the overall sulfur content of such formulated lubricants.

[0003] Modern internal combustion engines and transmissions include numerous gaskets and other seals formed of nitrile rubber materials. Lubricant sulfur has been found to contribute to the deterioration of materials. Before certifying a crankcase lubricant for use in their engines, engine manufacturers (oftentimes referred to as "original equipment manufacturers or "OEMs") require passage of a number of performance tests, including tests for compatibility with engine seal materials. It is also suspected that high levels of salicylate soap from salicylate detergents may contribute to the deterioration of nitrile rubber seal materials, particularly in "low ash" lubricants. Therefore, it would be desirable to provide a method of improving the seal compatibility of lubricating oil compositions, particularly lubricating oil compositions having significant sulfur contents and/or high levels of salicylate soap, and lubricating oil compositions having significant sulfur contents and/or high levels of salicylate soap, that provide improved seal-compatibility performance.

[0004] Lubricant sulfur has been found to cause copper corrosion. Prior to granting certification, OEMs also require lubricating oil compositions to pass a copper corrosion test. Therefore, it would be desirable to provide a method of improving the copper corrosion performance of lubricating oil compositions, particularly lubricating oil compositions having significant sulfur contents, and lubricating oil compositions having significant sulfur contents that provide improved copper corrosion performance.

SUMMARY OF THE INVENTION

[0005] It has now been found that the addition of a minor amount of a non-hydrogenated olefin (co)polymer, for example a polyisobutene, to a lubricating oil composition improves the compatibility between the lubricating oil composition and nitrile rubber engine and transmission seals, particularly in lubricating oil compositions containing a significant amount of sulfur, such as a sulfur content greater than about 0.10 mass %, such as greater than about 0.15 mass %, particularly greater than about 0.20 mass % and/or significant amounts of salicylate soap from salicylate detergents, such as 9 or more, particularly 18 or more, more particularly 24 or more mmols of salicylate soap per kilogram of finished lubricant. It has also been found that the addition of a minor amount of a non-hydrogenated olefin (co)polymer, for example a polyisobutene, to a lubricating oil composition improves the copper corrosion performance of lubricating oil compositions, particularly lubricating oil compositions containing a significant amount of sulfur, such as a sulfur content greater than about 0.10 mass %, such as greater than about 0.15 mass %, particularly greater than about 0.20 mass %.

[0006] Therefore, in a first aspect, the invention is directed to a method of improving the seal compatibility performance of lubricating oil compositions for the lubrication of an internal combustion engine or engine transmission, which method comprises adding to such lubricating oil compositions a minor amount of a non-hydrogenated (unsaturated) olefin (co) polymer.

[0007] In a second aspect, the invention is directed to the method of the first aspect in which the lubricating oil composition contains a significant sulfur content, such as a sulfur content greater than about 0.10 mass %, particularly greater than about 0.15 mass %, such as greater than about 0.18 mass %, more particularly greater than about 0.20

mass %, and comprises a major amount of oil of lubricating viscosity; a minor amount of at least one sulphur-containing additive, and from about 0.5 mass % to about 10.0 mass % of a non-hydrogenated olefin (co)polymer, wherein all mass percentages are based on the total mass of the lubricating oil composition.

[0008] In a third aspect, the invention is directed to the method of the first aspect in which the lubricating oil composition comprises a major amount of oil of lubricating viscosity; a minor amount of at least one salicylate detergent in an amount introducing into the lubricating oil composition 9 or more, particularly 18 or more, more particularly 24 or more mmols of salicylate soap per kilogram of lubricating oil composition, and from about 0.5 mass % to about 10.0 mass % of a non-hydrogenated olefin (co)polymer, wherein all mass percentages are based on the total mass of the lubricating oil composition.

[0009] In a fourth aspect, the invention is directed to a lubricating oil composition containing a significant sulfur content, such as a sulfur content greater than about 0.10 mass %, particularly greater than about 0.15 mass %, such as greater than about 0.18 mass %, more particularly greater than about 0.20 mass %, comprising a major amount of oil of lubricating viscosity; a minor amount of at least one sulphur-containing additive, and from about 0.5 mass % to about 10.0 mass % of a non-hydrogenated olefin (co)polymer, wherein all mass percentages are based on the total mass of the lubricating oil composition.

[0010] In a fifth aspect, the invention is directed to a lubricating oil composition comprising a major amount of oil of lubricating viscosity; a minor amount of at least one salicylate detergent in an amount introducing into the lubricating oil composition 9 or more, particularly 18 or more, more particularly 24 or more mmols of salicylate soap per kilogram of lubricating oil composition (finished lubricant), and from about 0.5 mass % to about 10.0 mass % of a non-hydrogenated olefin (co)polymer, wherein all mass percentages are based on the total mass of the lubricating oil composition.

[0011] In a sixth aspect, the invention is directed to a method of the second aspect or a lubricating oil composition of the fourth aspect, wherein the sulphur-containing additives are one or more of a metal salt of a dihydrocarbyl dithiophosphate (e.g., ZDDP), a sulfonate detergent, a sulfurized phenate detergent a molybdenum-sulphur compound and an ashless dithiocarbamate.

[0012] In a seventh aspect, the invention is directed to a method of the second aspect or a lubricating oil composition of the fourth aspect, wherein the lubricating oil composition further contains a salicylate detergent in an amount introducing into the lubricating oil composition at least about 9 mmols of salicylate soap per kilogram of finished lubricant and, preferably, has a sulfated ash content of not greater than about 1.1 mass %, more preferably no greater than 1.05 mass %.

[0013] In an eighth aspect, the invention is directed to a method of the third aspect or a lubricating oil composition of the fifth aspect, wherein the lubricating oil composition contains a significant sulfur content, such as a sulfur content greater than about 0.10 mass %, particularly greater than about 0.15 mass %, such as greater than about 0.18 mass %, more particularly greater than about 0.20 mass %.

[0014] In a ninth aspect, the invention is directed to a method of improving the copper corrosion performance of lubricating oil compositions for the lubrication of an internal combustion engine or engine transmission, which method comprises adding to such lubricating oil compositions a minor amount of a non-hydrogenated (unsaturated) olefin (co) polymer.

[0015] In a tenth aspect, the invention is directed to the method of the ninth aspect in which the lubricating oil composition contains a significant sulfur content, such as a sulfur content greater than about 0.10 mass %, particularly greater than about 0.15 mass %, such as greater than about 0.18 mass %, more particularly greater than about 0.20 mass %, and comprises a major amount of oil of lubricating viscosity; a minor amount of at least one sulphur-containing additive, and from about 0.5 mass % to about 10.0 mass % of a non-hydrogenated olefin (co)polymer, wherein all mass percentages are based on the total mass of the lubricating oil composition.

[0016] In an eleventh aspect, the invention is directed to the method of the tenth aspect wherein the sulphur-containing additives are one or more of a metal salt of a dihydrocarbyl dithiophosphate (e.g., ZDDP), a sulfonate detergent, a sulfurized phenate detergent a molybdenum-sulphur compound and an ashless dithiocarbamate.

[0017] In a twelfth aspect, the invention is directed to a concentrate for preparing a lubricating oil composition of the fourth aspect comprising an oleaginous carrier, a non-hydrogenated olefin (co)polymer, and one or more sulfur-containing additives.

[0018] In a thirteenth aspect, the invention is directed to a concentrate for preparing a lubricating oil composition of the fifth aspect comprising an oleaginous carrier, a non-hydrogenated olefin (co)polymer, and one or more salicylate detergents.

[0019] 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

[0020] The lubricating oil compositions of the present invention are for lubricating the crankcase of an internal combustion engine, preferably a compression-ignited (diesel) engine, more preferably a compression-ignited heavy duty diesel engine. Crankcase lubricating oil compositions for a diesel application, in particular for heavy duty diesel engines, have to be specifically formulated to meet the performance requirements for such an application.

[0021] Oils of lubricating viscosity useful in the context of the present invention may be selected from natural lubricating oils, synthetic lubricating oils and mixtures thereof. The lubricating oil may range in viscosity from light distillate mineral oils to heavy lubricating oils such as gasoline engine oils, mineral lubricating oils and heavy duty diesel oils. Generally, the viscosity of the oil ranges from about 2 centistokes to about 40 centistokes, especially from about 4 centistokes to about 20 centistokes, as measured at 100°C.

[0022] 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.

[0023] Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and derivative, analogs and homologs thereof. Also useful are synthetic oils derived from a gas to liquid process from Fischer-Tropsch synthesized hydrocarbons, which are commonly referred to as gas to liquid, or "GTL" base oils.

[0024] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, and the alkyl and aryl ethers of polyoxyalkylene polymers (e.g., methyl-polyiso-propylene glycol ether having a molecular weight of 1000 or diphenyl ether of poly-ethylene glycol having a molecular weight of 1000 to 1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C_3-C_8 fatty acid esters and C_{13} oxo acid diester of tetraethylene glycol.

[0025] Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebasic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of such esters includes dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0026] Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol esters such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0027] 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.

[0028] Other examples of base oil are gas-to-liquid ("GTL") base oils, i.e. the base oil may be oil derived from Fischer-Tropsch-synthesized hydrocarbons made from synthesis gas containing hydrogen and carbon monoxide using a Fischer-Tropsch catalyst. These hydrocarbons typically require further processing in order to be useful as base oil. For example, they may, by methods known in the art, be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed.

[0029] The oil of lubricating viscosity may comprise a Group I, Group II or Group III, base stock or base oil blends of the aforementioned base stocks. Preferably, the oil of lubricating viscosity is a Group II or Group III base stock, or a mixture thereof, or a mixture of a Group I base stock and one or more a Group II and Group III. Preferably, a major amount of the oil of lubricating viscosity is a Group II, Group III, Group IV or Group V base stock, or a mixture thereof. In one particular embodiment, it is preferred that greater than 50 mass %, such as greater than 60 mass % of the oil of lubricating viscosity is mineral oil. 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 no greater than 0.5 mass % (e.g., from about 0.001 to about 0.5 mass %), such as no greater than 0.1 mass % (e.g., from about 0.001 to about 0.1 mass %), preferably from about 0.005 to about 0.05 mass %.

[0030] Preferably the volatility of the oil or oil blend, as measured by the Noack volatility test (ASTM D5880), is less than or equal to 30 mass %, preferably less than or equal to 25 mass %, more preferably less than or equal to 20 mass %, most preferably less than or equal to 16 mass %. 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.

[0031] 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 I.
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 L
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 I.
d) Group IV base stocks are polyalphaolefins (PAO).
e) Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

Table I - Analytical Methods for Base Stock

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

[0032] The non-hydrogenated olefin (co)polymer useful in the practice of the present invention is preferably a polymer or copolymer of one or more acyclic olefin monomers. Generally, the non-hydrogenated olefin (co)polymers useful in the invention have, or have on average, about one double bond per polymer chain.

[0033] The (co)polymer may be prepared by polymerizing alphaolefin monomer, or mixtures of alpha-olefin monomers, or mixtures comprising ethylene and at least one C_3 to C_{28} alpha-olefin monomer, in the presence of a catalyst system comprising at least one metallocene (e.g., a cyclopentadienyl-transition metal compound) and an alumoxane compound. Using this process, a polymer in which 95 % or more of the polymer chains possess terminal ethenylidene-type unsaturation can be provided. The percentage of polymer chains exhibiting terminal ethenylidene unsaturation may be determined by FTIR spectroscopic analysis, titration, or C^{13} NMR. Interpolymers of this latter type may be characterized by the formula POLY-$C(R^1)=CH_2$ wherein R^1 is C_1 to C_{26} alkyl, preferably C_1 to C_{18} alkyl, more preferably C_1 to C_8 alkyl, and most preferably C_1 to C_2 alkyl, (e.g., methyl or ethyl) and wherein POLY represents the polymer chain. The chain length of the R^1 alkyl group will vary depending on the comonomer(s) selected for use in the polymerization. A minor amount of the polymer chains can contain terminal ethenyl, *i.e.* vinyl, unsaturation, *i.e.* POLY-$CH=CH_2$, and a portion of the polymers can contain internal monounsaturation, e.g., POLY-$CH=CH(R^1)$, wherein R^1 is as defined above. These terminally unsaturated interpolymers may be prepared by known metallocene chemistry and may also be prepared as described in U.S. Patent Nos. 5,498,809; 5,663,130; 5,705,577; 5,814,715; 6,022,929 and 6,030,930.

[0034] Another useful class of (co)polymers is (co)polymers prepared by cationic polymerization of isobutene, styrene, and the like. Common (co)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, with aluminium trichloride preferred. 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 polymer 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).

[0035] In another embodiment, the non-hydrogenated olefin (co)polymer, for example, polyisobutylene, has at most 10, such as 5 to 10, %, of the polymer chains possessing a terminal double bond (or terminal ethenylidene-type or terminal vinylidene unsaturation). Such a polymer is considered not highly reactive, an example of a commercially available polymer is under tradename Napvis™ (from BP-Amoco), and usually obtained by polymerization with aluminium trichloride as catalyst.

[0036] Preferably the (co)polymer is derived from polymerisation of one or more olefins having 2 to 10, such as 3 to 8, carbon atoms. An especially preferred olefin is butene, advantageously isobutene.

[0037] The number average molecular weight of the non-hydrogenated olefin (co)polymer useful in the present invention is preferably in the range of from about 450 to about 2300, such as from about 450 to about 1300, preferably from about 450 to about 950. The molecular weight can be determined by several known techniques. A convenient method for such determination is by 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). Further, it is preferred that the kinemantic viscosity of the non-hydrogenated olefin polymer at 100°C, as measured according to ASTM D445, is at least 9 or 15, such as 100 or 150 to 3000, advantageously 200 to 2500 or 2700 mm^2s^{-1}. In one embodiment of the present invention, a polyisobutylene polymer having a number average molecular weight of 450 to 2300, and a kinematic viscosity at 100°C of from about 200 to 2400 mm^2s^{-1} was found to provide particularly beneficial properties. Lubricating oil compositions of the present invention can contain the non-hydrogenated olefin polymer in an amount of from about 0.2 to about 10.0 mass %, such as from about 0.3 to about 5.0 mass %, particularly from about 0.5 to about 3.0 mass %, preferably from about 1.0 to about 2.5 mass %.

[0038] Dispersants (or dispersant additives), such as ashless (i.e. metal-free) dispersants hold solid and liquid contaminants, resulting from oxidation during use, in suspension and thus preventing sludge flocculation and precipitation or deposition on metal parts; they comprise long-chain hydrocarbons, to confer oil-solubility, with a polar head capable of associating with particles to be dispersed. A noteworthy group is hydrocarbon-substituted succinimides.

[0039] Generally, ashless dispersants form substantially no ash on combustion, in contrast to metal-containing (and thus ash-forming) detergents. Borated, metal-free dispersants are also regarded herein as ashless dispersants. "Substantially no ash" means that the dispersant may give trace amounts of ash on combustion, but amounts which do not have practical or significant effect on the performance of the dispersant. A dispersant additive composition containing two or more dispersants may also be used.

[0040] Ashless, dispersants 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. Suitable dispersants include, for example, derivatives of long chain hydrocarbyl-substituted carboxylic acids, in which the hydrocarbyl group has a number average molecular weight tends of less than 15,000, such as less than 5,000; examples of such derivatives being derivatives of high molecular weight hydrocarbyl-substituted succinic acid. Such hydrocarbyl-substituted carboxylic acids may be derivatized with, for example, a nitrogen-containing compound, advantageously a polyalkylene polyamine or amine-alcohol or amide or ester. Particularly preferred dispersants are the reaction products of polyalkylene amines with alkenyl succinic anhydrides. Examples of specifications disclosing dispersants of the last-mentioned type are U.S. Patent Nos. 3,202,678; 3,154,560; 3,172,892; 3,024,195; 3,024,237; 3,219,666; 3,216,936; and BE-A-662 875.

[0041] The dispersant(s) are preferably non-polymeric (e.g., are mono- or bis-succinimides). The dispersant(s) of the present invention may optionally be borated. Such dispersants 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, in an amount sufficient to provide from about 0.1 to about 20 atomic proportions of boron for each mole of acylated nitrogen composition. Combinations of borated and non-borated dispersants may also be employed.

[0042] An ashless succinimide or a derivative thereof, obtainable from a polyisobutenylsuccinic anhydride produced from polybutene and maleic anhydride by a thermal reaction method using neither chlorine nor a chlorine atom-containing compound, is a preferred dispersant.

[0043] Dispersancy may be provided by polymeric compounds capable of providing viscosity index improving properties and dispersancy, such compounds are known as a dispersant viscosity index improver additive or a multifunctional viscosity index improver. Such polymers differ from conventional viscosity index improvers in that they provide performance properties, such as dispersancy and/or antioxidancy, in addition to viscosity index improvement (see below under viscosity modifiers for further detail on multifunctional viscosity modifiers). In the event, a dispersant viscosity index improver additive is used in the lubricating oil compositions of the present invention, a dispersant additive is, preferably, also present.

[0044] Typically, one or more dispersants and/or dispersant viscosity index improvers, are used in heavy duty diesel (HDD) engine lubricating oil composition in amounts that provide the lubricating oil composition with a nitrogen content of from about 0.08 mass % to about 0.35 mass %, such as from about 0.09 mass % to about 0.25 mass %, preferably from about 0.10 mass % to about 0.20 mass %. In a passenger car diesel engine lubricating oil composition (PCDO), dispersant is generally added in amounts that provide the lubricating oil composition with a nitrogen content of from about 0.04 mass % to about 0.10 mass %, such as from about 0.05 mass % to about 0.09 mass %, preferably from about 0.065 mass % to about 0.085 mass %. In a passenger car motor oil for a spark-ignited engine (PCMO), dispersant is generally added in amounts that provide the lubricating oil composition with a nitrogen of from about 0.02 mass % to about 0.12 mass %, such as from about 0.03 mass % to about 0.08 mass %, preferably from about 0.035 mass % to about 0.05 mass %. In manual transmission fluids (MTF), dispersant is generally added in amounts that provide the lubricating oil composition with a nitrogen content of from about 0.02 mass % to about 0.08 mass %, such as from about 0.025 mass % to about 0.06 mass %, preferably from about 0.03 mass % to about 0.05 mass %. In an automatic transmission fluid (ATF), dispersant is generally added in an amount providing the lubricating oil composition with a nitrogen content of from about 0.02 mass % to about 0.14 mass %, such as from about 0.05 mass % to about 0.11 mass %, preferably from about 0.06 mass % to about 0.08 mass %.

[0045] A detergent (or detergent additive) reduces formation of piston deposits, for example high-temperature varnish and lacquer deposits, by keeping finely divided solids in suspension in engines; it may also have acid-neutralizing properties. A detergent comprises metal salts of organic acids, which are referred herein as soaps or surfactants. A detergent has a polar head, *i.e.* the metal salt of the organic acid, with a long hydrophobic tail for oil solubility. Therefore, the organic acids typically have one or more functional groups, such as OH or COOH or SO_3H, for reacting with a metal, and a hydrocarbyl substituent. A detergent may be overbased, in which case the detergent contains an excess of metal in relation to the stoichiometric quantity needed for the neutralization of the organic acid. This excess is in the form of a colloidal dispersion, typically metal carbonate and/or hydroxide, with the metal salts of organic acids in a micellar structure.

[0046] Examples of organic acids include sulfonic acids, phenols and sulfurized derivatives thereof, and carboxylic acids including aromatic carboxylic acids.

[0047] Phenols may be non-sulfurized or sulfurized. Further, the term "phenol" as used herein includes phenols containing more than one hydroxyl group (for example, alkyl catechols) or fused aromatic rings (for example, alkyl naphthols) and phenols which have been modified by chemical reaction, for example, alkylene-bridged phenols and Mannich base-condensed phenols; and saligenin-type phenols (produced by the reaction of a phenol and an aldehyde under basic conditions). The phenols are frequently used in sulfurized form. Details of sulfurization processes are known to those skilled in the art, for example, see U.S. Patent Nos.4,228,022 and 4,309,293.

[0048] As indicated above, the term "phenol" as used herein includes phenols which have been modified by chemical reaction with, for example, an aldehyde, and Mannich base-condensed phenols. Aldehydes with which phenols may be modified include, for example, formaldehyde, propionaldehyde and butyraldehyde. The preferred aldehyde is formaldehyde. Aldehyde-modified phenols suitable for use in accordance with the present invention are described in, for example, U.S. Patent Nos. 5 259 967 and 6,310,009. Mannich base-condensed phenols are prepared by the reaction of a phenol, an aldehyde and an amine. Examples of suitable Mannich base-condensed phenols are described in U.S. Patent Nos. 4,708,809 and 4,740,321. In general, the phenols may include substituents other than those mentioned above. Examples of such substituents are methoxy groups and halogen atoms.

[0049] Sulfonic acids are typically obtained by sulfonation of hydrocarbyl-substituted, especially alkyl-substituted, aromatic hydrocarbons, for example, those obtained from the fractionation of petroleum by distillation and/or extraction, or by the alkylation of aromatic hydrocarbons. The alkylaryl sulfonic acids usually contain from about 22 to about 100 or more carbon atoms. The sulfonic acids may be substituted by more than one alkyl group on the aromatic moiety, for example they may be dialkylaryl sulfonic acids. Preferably the sulfonic acid has a number average molecular weight of 350 or greater, more preferably 400 or greater, especially 500 or greater, such as 600 or greater. Number average molecular weight may be determined by ASTM D3712. Another type of sulfonic acid which may be used in accordance with the invention comprises alkyl phenol sulfonic acids. Such sulfonic acids can be sulfurized.

[0050] Carboxylic acids include mono- and dicarboxylic acids. Preferred monocarboxylic acids are those containing 8 to 30, especially 8 to 24, carbon atoms. (Where this specification indicates the number of carbon atoms in a carboxylic acid, the carbon atom(s) in the carboxylic group(s) is/are included in that number). Examples of monocarboxylic acids are iso-octanoic acid, stearic acid, oleic acid, palmitic acid and behenic acid. Iso-octanoic acid may, if desired, be used in the form of the mixture of C8 acid isomers sold by Exxon Chemical under the trade name "Cekanoic". Other suitable acids are those with tertiary substitution at the α-carbon atom and dicarboxylic acids with 2 or more carbon atoms separating the carboxylic groups. Further, dicarboxylic acids with more than 35 carbon atoms, for example, 36 to 100 carbon atoms, are also suitable. Unsaturated carboxylic acids can be sulfurized.

[0051] A preferred type of carboxylic acid is an aromatic carboxylic acid. 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.

[0052] 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. The aromatic moiety may also contain a second functional group, such as a hydroxyl group or a sulfonate group, which can be attached directly or indirectly to a carbon atom on the aromatic moiety. 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.

[0053] 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.

[0054] Preferred substituents for 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.

[0055] The metal detergent may be neutral or overbased, such terms are known in the art. A detergent additive composition may comprise one or more detergent additives, which can be a neutral detergent, an overbased detergent or a mixture of both. The Total Base Number (TBN) of detergents will conventionally range from 15 to 600.

[0056] Detergents generally useful in the formulation of lubricating oil compositions also include "hybrid" detergents formed with mixed surfactant systems, e.g., phenate/salicylates (sometimes referred to as "phenalates"), sulfonate/phenates, sulfonate/salicylates, sulfonates/phenates/salicylates, as described, for example, in U.S. Patent Nos. 6,153,565; 6,281,179; 6,429,178; and 6,429,179.

[0057] A detergent additive composition may contain two or more detergents, for example, an alkali metal, such as sodium, detergent, and an alkaline earth metal, such as calcium and/or magnesium, detergent. The detergent additive composition may also comprise an ashless detergent, *i.e.* a non-metal containing detergent, typically in the form of an organic salt of an organic acid. The detergents are preferably metal containing and Group 1 and Group 2 metals are preferred as metals in the detergents, more preferably calcium and magnesium, especially calcium.

[0058] Typically, one or more detergents are used in heavy duty diesel (HDD) engine lubricating oil composition in amounts that provide the lubricating oil composition with a TBN of from about 4.0 to about 11.5, such as from about 6.0 to about 9.5, preferably from about 7.0 to about 8.25. In a passenger car diesel engine lubricating oil composition (PCDO), detergent is generally added in amounts that provide the lubricating oil composition with a TBN of from about 5.0 to about 12.0, such as from about 6.0 to about 11.0, preferably from about 7.0 to about 10.5. In a passenger car motor oil for a spark-ignited engine (PCMO), detergent(s) is generally added in amounts that provide the lubricating oil composition with a TBN of from about 2.5 to about 9.9, such as from about 4.0 to about 8.0, preferably from about 4.5 to about 7.25. In a power transmission fluid (PTF), detergent(s) is generally added in amounts that provide the lubricating oil composition with a TBN of from about 0.0 to about 10.0, such as from about 0.5 to about 5.0, preferably from about 1.0 to about 2.5. Where the detergent is a sulfonate detergent, a sulfurized phenate detergent, or a hybrid detergent containing a sulfurized phenate and/or sulfonate component, the use of a conventional amount of such detergents can introduce into the lubricating oil composition as much as 0.04 mass %, even as much as 0.15 mass %, such as from about 0.06 to about 0.12 mass % of sulfur.

[0059] In one embodiment, the invention is directed specifically to lubricating oil compositions containing salicylate detergent in an amount introducing at least about 9 mmols (e.g, about 12 to about 50 mmols), such as at least about 18 mmols (e.g. about 18 to about 33 mmols) particularly at least about 24 mmols of salicylate soap per kilogram of finished lubricant and from about 1.0 mass % to about 2.5 mass % of the non-hydrogenated polymer described *supra.*

[0060] In another embodiment, the invention is directed specifically to low ash compositions having an ash (reported as sulfated ash or SASH) content of less than 1.1 mass %, such as less than 1.05 mass%, preferably less than 0.8 mass %; and a sulfur content of from about 0.10 mass % to about 0.40 mass %, such as from about 0.15 mass % to about 0.35 mass %, preferably from about 0.20 mass % to about 0.30 mass % of sulfur, which compositions contain salicylate detergent in an amount introducing at least about 9 mmols, such as at least about 18 mmols, preferably at least about 24 mmols, of salicylate soap per kilogram of finished lubricant and from about 1.0 mass % to about 2.5 mass % of the non-hydrogenated polymer described *supra.*

[0061] Anti-wear agents reduce friction and excessive wear and are usually based on compounds containing sulfur or phosphorus or both. Dihydrocarbyl dithiophosphate metal salts are frequently used as anti-wear 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 (ZDDP) are most commonly used in lubricating oil in amounts of 0.1 to 10, preferably 0.2 to 2 mass %, 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 having 1 to 18, preferably 2 to 12, carbon atoms. 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 use of an excess of the basic zinc compound in the neutralization reaction.

[0062] ZDDP provides excellent wear protection at a comparatively low cost and also functions as an antioxidant. Preferably a zinc dialky dithiophosphate composition comprising one or more zinc dialkyl dithiophosphate, which composition especially contains a mixture of primary and secondary alkyl groups, wherein the secondary alkyl groups are in a major molar proportion, such as at least 60, advantageously at least 75, more especially at least 85, mole %, based on the amount of alkyl groups, is useful in the present invention. Preferably a zinc dithiophosphate composition has 90 mole % secondary alkyl groups and 10 mole % primary alkyl groups.

[0063] When used in conventional amounts, sulfur-containing antiwear agents can introduce into the lubricating oil composition as much as 0.15 mass %, and even as much as 0.30 mass %, such as from about 0.16 to about 0.25 mass % of sulfur.

[0064] Anti-oxidants increase the composition's resistance to oxidation and may work by combining with and modifying peroxides to render them harmless by decomposing peroxides or by rendering an oxidation catalyst inert. They may be classified as radical scavengers (e.g. sterically hindered phenols, secondary aromatic amines, and organo-copper salts); hydroperoxide decomposers (e.g. organo-sulfur and organophosphorus additives); and multifunctionals. Such anti-oxidants (or oxidation inhibitors) include hindered phenols, aromatic amine compounds, alkaline earth metal and metal-free alkylphenolthioesters having preferably C_5 to C_{12} alkyl side chains, ashless alkylene bridged phenols, phosphosulfurized and sulfurized hydrocarbons, phosphorous esters, metal and metal-free thiocarbamates & derivatives thereof, oil soluble copper compound as described in U.S. Patent No. 4,867,890, and molybdenum containing compounds. In the practice of the present invention, the use or otherwise of certain anti-oxidants may confer certain benefits. For example, in one embodiment it is preferred that an anti-oxidant composition comprising a hindered phenol with an ester group is used. In another embodiment, it is preferred to employ an anti-oxidant composition comprising a secondary aromatic amine and said hindered phenol. Preferably an antioxidant composition comprising an aromatic amine, such as diphenylamine and/or a hindered phenol compound, such as 3,5-*bis*(alkyl)-4-hydroxyphenyl carboxylic acid esters, e.g. IRGANOX® L135 as sold by Ciba Speciality Chemicals, is useful.

[0065] Friction modifiers include boundary additives that lower friction coefficients and hence improve fuel economy. Examples are esters of polyhydric alcohols such as glycerol monoesters of higher fatty acids, for example glycerol monooleate; esters of long chain polycarboxylic acids with diols, for example the butane diol esters of dimerized unsaturated fatty acids; oxazoline compounds; and alkoxylated alkyl-substituted mono-amines, and alkyl ether amines, for example, ethoxylated tallow amine and ethoxylated tallow ether amine. Molybdenum-containing compounds and ashless dithiocarbamates are also examples of known friction modifiers. Conventionally, one or more organic friction modifiers are used in an amount of 0.1 to 0.5, such as 0.2 to 0.4, mass %, based on the mass of the oil composition.

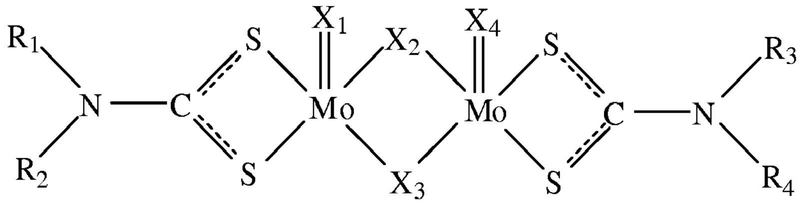
[0066] The molybdenum-containing compounds, preferably molybdenum-sulfur compounds, useful in the present invention may be mononuclear or polynuclear. In the event that the compound is polynuclear, the compound contains a molybdenum core consisting of non-metallic atoms, such as sulfur, oxygen and selenium, preferably consisting essentially of sulfur.

[0067] To enable the molybdenum-sulfur compound to be oil-soluble or oil-dispersible, one or more ligands are bonded to a molybdenum atom in the compound. The bonding of the ligands includes bonding by electrostatic interaction as in the case of a counter-ion and forms of bonding intermediate between covalent and electrostatic bonding. Ligands within the same compound may be differently bonded. For example, a ligand may be covalently bonded and another ligand may be electrostatically bonded.

[0068] Preferably, the or each ligand is monoanionic and examples of such ligands are dithiophosphates, dithiocarbamates, xanthates, carboxylates, thioxanthates, phosphates and hydrocarbyl, preferably alkyl, derivatives thereof. Preferably, the ratio of the number of molybdenum atoms, for example, in the core in the event that the molybdenum-sulfur compound is a polynuclear compound, to the number of monoanionic ligands, capable of rendering the compound oil-soluble or oil-dispersible, is greater than 1 to 1, such as at least 3 to 2.

[0069] The molybdenum-sulfur compound's oil-solubility or oil-dispersibility may be influenced by the total number of carbon atoms present among all of the compound's ligands. The total number of carbon atoms present among all of the hydrocarbyl groups of the compound's ligands typically will be at least 21, e.g., 21 to 800, such as at least 25, at least 30 or at least 35. For example, the number of carbon atoms in each alkyl group will generally range between 1 and 100, preferably 1 and 40, and more preferably between 3 and 20. Examples of molybdenum-sulfur compounds include dinuclear molybdenum-sulfur compounds and trinuclear molybdenum-sulfur compounds.

[0070] An example of a dinuclear molybdenum-sulfur compound is represented by the formula:



where R_1 to R_4 independently denote a straight chain, branched chain or aromatic hydrocarbyl group having 1 to 24 carbon atoms; and X_1 to X_4 independently denote an oxygen atom or a sulfur atom. The four hydrocarbyl groups, R_1 to R_4, may be identical or different from one another.

[0071] In a preferred embodiment, the molybdenum-sulfur compound is an oil-soluble or oil-dispersible trinuclear molybdenum-sulfur compound. Examples of trinuclear molybdenum-sulfur compounds are disclosed in U.S. Patent Nos. 5,888,945; 5,906,968; 6,010,987; 6,110,878; 6,153,564; 6,232,276; 6,358,894; 6,541,429; 6,569,820; and European patent application no. 02078011, each of which are incorporated into the present description by reference, particularly with respect to the characteristics of the molybdenum compound or additive disclosed therein.

[0072] Preferably, the trinuclear molybdenum-sulfur compounds are represented by the formula $Mo_3S_kE_xL_nA_pQ_z$, wherein k is an integer of at least 1; E represents a non-metallic atom selected from oxygen and selenium; x can be 0 or an integer, and preferably k + x is at least 4, more preferably in the range of 4 to 10, such as 4 to 7, most preferably 4 or 7; L represents a ligand that confers oil-solubility or oil-dispersibility on the molybdenum-sulfur compound, preferably L is a monoanionic ligand; n is an integer in the range of 1 to 4; A represents an anion other than L, if L is an anionic ligand; p can be 0 or an integer; Q represents a neutral electron-donating compound; and z is in the range of 0 to 5 and includes non-stoichiometric values.

[0073] Those skilled in the art will realize that formation of the trinuclear molybdenum-sulfur compound will require selection of appropriate ligands (L) and other anions (A), depending on, for example, the number of sulfur and E atoms present in the core, *i.e.* the total anionic charge contributed by sulfur atom(s), E atom(s), if present, L and A, if present, must be -12. The trinuclear molybdenum-sulfur compound may also have a cation other than molybdenum, for example, (alkyl)ammonium, amine or sodium, if the anionic charge exceeds -12.

[0074] Examples of Q include water, alcohol, amine, ether and phosphine. It is believed that the electron-donating compound, Q, is merely present to fill any vacant coordination sites on the trinuclear molybdenum-sulfur compound. Examples of A can be of any valence, for example, monovalent and divalent and include disulfide, hydroxide, alkoxide, amide and thiocyanate or derivative thereof; preferably A represents a disulfide ion. Preferably, L is monoanionic ligand, such as dithiophosphates, dithiocarbamates, xanthates, carboxylates, thioxanthates, phosphates and hydrocarbyl, preferably alkyl, derivatives thereof. When n is 2 or more, the ligands can be the same or different. In an embodiment, independently of the other embodiments, k is 4 or 7, n is either 1 or 2, L is a monoanionic ligand, p is an integer to confer electrical neutrality on the compound based on the anionic charge on A and each of x and z is 0. In a further embodiment, independently of the other embodiments, k is 4 or 7, L is a monoanionic ligand, n is 4 and each of p, x and z is 0. Other examples of molybdenum containing compounds include molybdenum carboxylates and molybdenum nitrogen complexes, both of which may be sulfurised.

[0075] Where a sulfur-containing molybdenum compound is employed as a friction modifier and/or antioxidant, and used in a conventional amount such as an amount providing from about 20 ppm to about 250 ppm, such as from about 50 ppm to about 125ppm of Mo, such compounds can introduce into the lubricating oil composition about 0.004 mass % or more, or about 0.008 mass % or more, such as from about 0.004 mass % to about 0.090 mass %, e.g., from about 0.008 to about 0.025 mass % of sulfur.

[0076] Boron may also be present in the lubricating oil compositions of the present invention. Boron-containing additives may be prepared by reacting a boron compound with an oil-soluble or oil-dispersible additive or compound. Boron compounds include boron oxide, boron oxide hydrate, boron trioxide, boron trifluoride, boron tribromide, boron trichloride, boron acid such as boronic acid, boric acid, tetraboric acid and metaboric acid, boron hydrides, boron amides and various esters of boron acids. Examples of boron-containing additives include a borated dispersant; a borated dispersant VI improver; an alkali metal or a mixed alkali metal or an alkaline earth metal borate; a borated overbased metal detergent; a borated epoxide; a borate ester; a sulfurized borate ester; and a borate amide. A preferred boron-containing additive is a borated dispersant.

[0077] Examples of other additives include rust inhibitors, corrosion inhibitors, pour point depressants, anti-foaming agents and viscosity modifiers.

[0078] Rust inhibitors selected from the group consisting of nonionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, and anionic alkyl sulfonic acids may be used.

[0079] Copper and lead bearing corrosion inhibitors may be used, but are typically not required with the formulation of the present invention. Typically such compounds are the thiadiazole polysulfides containing from 5 to 50 carbon atoms, their derivatives and polymers thereof. Derivatives of 1, 3, 4-thiadiazoles, such as those described in U.S. Patent Nos. 2,719,125; 2,719,126; and 3,087,932; are typical. Other similar materials are described in U.S. Patent Nos. 3,821,236; 3,904,537; 4,097,387; 4,107,059; 4,136,043; 4,188,299; and 4,193,882. Other additives are the thio and polythio sulfenamides of thiadiazoles such as those described in U.K. Patent Specification No. 1,560,830. Benzotriazoles derivatives also fall within this class of additives. When these compounds are included in the lubricating composition, they are preferably present in an amount not exceeding 0.2 mass % (A.I.).

[0080] A small amount of a demulsifying component may be used. A preferred demulsifying component is described in EP 330,522. It is obtained by reacting an alkylene oxide with an adduct obtained by reacting a bis-epoxide with a polyhydric alcohol. The demulsifier should be used at a level not exceeding 0.1 mass % A.I. A treat rate of 0.001 to 0.05 mass % (A.I.) is convenient.

[0081] Pour point depressants, otherwise known as lube oil improvers, lower the minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Typical of those additives which improve the low temperature fluidity of the fluid are C_8 and C_{18} dialkyl fumarate/vinyl acetate copolymers, polyalkylmethacrylates and the like.

[0082] Foam control can be provided by many compounds including an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

[0083] Viscosity index improvers (or viscosity modifiers) impart high and low temperature operability to a lubricating oil and permit it to remain shear stable at elevated temperatures and also exhibit acceptable viscosity or fluidity at low temperatures. Suitable compounds for use as viscosity modifiers are generally high molecular weight hydrocarbon polymers, e.g. polyisobutylene, copolymers of ethylene and propylene and higher alpha-olefins; polyesters, such as polymethacrylates; hydrogenated poly(styrene-co-butadiene or-isoprene) polymers and modifications (e.g., star polymers); and esterified poly(styrene-co-maleic anhydride) polymers. Oil-soluble viscosity modifying polymers generally have number average molecular weights of at least 15,000 to 1,000,000, preferably 20,000 to 600,000, as determined by gel permeation chromatography or light scattering methods. The disclosure in Chapter 5 of "Chemistry & Technology of Lubricants", edited by R.M. Mortier and S.T. Orzulik, First edition, 1992, Blackie Academic & Professional, is incorporated herein. The VM used may have that sole function, or may be multifunctional, such as demonstrating viscosity index improving properties as well as dispersant properties. Dispersant olefin copolymers and dispersant polymethacrylates are examples of dispersant viscosity index improver additives. Dispersant viscosity index improver additives are prepared by chemically attaching various functional moieties, for example amines, alcohols and amides, onto polymers, which polymers preferably tend to have a number average molecular weight of at least 15,000, such in the range from 20,000 to 600,000, as determined by gel permeation chromatography or light scattering methods. The polymers used may be those described below with respect to viscosity modifiers. Therefore, amine molecules may be incorporated to impart dispersancy and/or antioxidancy characteristics, whereas phenolic molecules may be incorporated to improve antioxidant properties. A specific example, therefore, is an inter-polymer of ethylene-propylene post grafted with an active monomer such as maleic anhydride and then derivatized with, for example, an alcohol or amine. In the event a dispersant viscosity modifier is used in the present invention, the nitrogen content of the lubricating oil composition also includes that derived from the dispersant viscosity modifier. An example of a dispersant viscosity modifier is Hitec® 5777, which is manufactured and sold by Afton Corp. U.S. Patent Nos.4,867,890 and 5,958,848 describe examples of dispersant viscosity index improvers, which are accordingly incorporated herein. Generally, viscosity modifiers, whether multifunctional or not, are used in an amount depending on the desired viscometric grade (e.g., SAE 10W-40) of the lubricating oil composition, for example, an amount of 0.001 to 2, preferably 0.01 to 1.5, such as 0.1 to 1, mass % of the polymer, based on the mass of the oil composition.

[0084] Representative effective amounts of such additives, when used in lubricating oil compositions, are as follows:

Additive	**Mass % a.i.* (Broad)**	**Mass % a.i.* (Preferred)**
Viscosity Modifier	0.01-6	0.01-4
Corrosion Inhibitor	0.0-5	0.01-1.5
Oxidation Inhibitor	0.01-5	0.01-3
Friction Reducer	0.01-5	0.01-1.5
Dispersant	0.1-20	0.1-8
Multifuctional Viscosity Modifier	0.0 -5	0.05-5
Detergent	0.01-6	0.01-4
Anti-wear Agent	0.01-6	0.01-4

(continued)

Additive	Mass % a.i.* (Broad)	Mass % a.i.* (Preferred)
Pour Point Depressant	0.01-5	0.01-1.5
Rust Inhibitor	0.0-0.5	0.001-0.2
Anti-Foaming Agent	0.001-0.3	0.001-0.15
Demulsifier	0.0-0.5	0.001-0.2
*mass % active ingredient based on the final lubricating oil composition.		

[0085] An additive concentrate constitutes a convenient means of handling two or more additives before their use, as well as facilitating solution or dispersion of the additives in lubricant compositions. When preparing a lubricant composition that contains more than one type of additive (sometimes referred to as "additive components"), each additive may be incorporated separately. In many instances, however, it is convenient to incorporate the additives as an additive concentrate (a so-called additive "package" (also referred to as an "adpack")) comprising two or more additives).

[0086] In the preparation of the lubricant oil compositions, it is common practice to introduce additives in the form of additive concentrate(s) containing the additives. When a plurality of additives are employed it may be desirable, although not essential, to prepare one or more additive concentrates (also known as additive packages) comprising the additives, whereby several additives, with the exception of viscosity modifiers, multifunctional viscosity modifiers and pour point depressants, can be added simultaneously to the oil of lubricating viscosity to form the lubricating oil composition. Dissolution of the additive concentrate(s) into the lubricating oil may be facilitated by diluent or solvents and by mixing accompanied with mild heating, but this is not essential. The additive concentrate(s) will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration in the final formulation when the additive concentrate(s) is/are combined with a predetermined amount of oil of lubricating viscosity. If required, the viscosity modifiers, or multifunctional viscosity modifiers, and pour point depressants are then separately added to form a lubricating oil composition.

[0087] An additive concentrate may contain 1 to 90, such as 10 to 80, preferably 20 to 80, more preferably 40 to 70, mass % based on active ingredient, of the additives, the remainder being an oleaginous carrier or diluent fluid (for example, an oil of lubricating viscosity). The final lubricating oil composition may typically contain 5 to 40 mass % of the additive concentrate(s).

[0088] The amount of additives in the final lubricating oil composition is generally dependent on the type of the oil composition, for example, a heavy duty diesel engine lubricating oil composition preferably has 7 to 25, more preferably 8 to 23, such as 8 to 20, mass % of additives (including any diluent fluid), based on the mass of the oil composition. A passenger car engine lubricating oil composition, for example, a gasoline or a diesel engine oil composition, tends to have a lower amount of additives, for example 2 to 16, such as 3 or 4 to 14, preferably 5 to 12, especially 6 to 10, mass % of additives, based on the mass of the oil composition. The amounts expressed above exclude non-hydrogenated olefin polymer, viscosity modifier and pour point depressant additives.

[0089] Generally the viscosity of the additive concentrate is higher than that of the lubricating oil composition. Typically, the kinematic viscosity at 100 °C of the additive concentrate is at least 50, such as in the range 100 to 200, preferably 120 to 180, mm^2s^{-1} (or cSt).

[0090] Thus, a method of preparing a lubricating oil composition according to the present invention can involve admixing an oil of lubricating viscosity and one or more of additives or additive concentrates that comprises two or more of additives and then, admixing other additive components, such as viscosity modifier, and optionally a multifunctional viscosity modifier and pour point depressant.

[0091] Lubricating oil compositions of the present invention may also be prepared by admixing an oil of lubricating viscosity, an additive concentrate containing two or more additive components, a non-hydrogenated olefin polymer and a viscosity modifier, and optionally a multifunctional viscosity modifier and pour point depressant.

[0092] It is preferred that lubricating oil compositions of the invention are multigrade oil compositions having a viscometric grade of SAE 10W-X, SAE 5W-X and SAE 0W-X, where X represents 20, 30 and 40; the characteristics of the different grades can be found in the SAE J300 classification.

Fully formulated lubricating oil compositions of the present invention preferably have a sulfur content of from about 0.15 mass % to about 1.0 mass %, such as from about 0.20 mass % to about 0.35 mass %. Preferably, the Noack volatility of the fully formulated lubricating oil composition (oil of lubricating viscosity plus all additives) 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 a phosphorus content of less than about 1500 ppm, such as from about 500 to 1500 ppm, preferably less than 1250 ppm, such as from about 500 to about 1250 ppm, more preferably less than about 1200 ppm, such as from about 500 to about 1200 ppm, still more preferably less than about 850 ppm , such as from about 500 to

850 ppm, based on the total mass of the lubricating oil composition.

[0093] Fully formulated lubricating oil compositions of the present invention preferably have a sulfated ash (SASH) content of about 1.9 mass % or less, preferably about 1.1 mass % or less, such as about 1.05 mass % or less.

[0094] The amount of phosphorus and sulfur are determined according to method ASTM D5185; "TBN" is Total Base Number as measured by ASTM D2896; the amount of nitrogen is determined according to method ASTM D4629; and sulfated ash is measured according to method ASTM D874.

[0095] Where the lubricating oil compositions of the present invention are for HDD use, the lubricating oil compositions preferably satisfy at least the performance requirements of the ACEA E2-96#5, more preferably at least the ACEA E7-04 and/or API CI-4, such as at least the ACEA E4-99#3, especially at least the ACEA E6-04 and/or API CJ-4 specification. Where the lubricating oil compositions of the present invention are for PCDO use, the lubricating oil compositions preferably satisfy at least the performance requirements of the ACEA B2-98#2, more preferably at least the ACEA B3-04, such as at least the ACEA B4-04/ ACEA C3-04, especially at least the ACEA B5-04/ ACEA C3-04/ ACEA C2-04 specification(s). Where the lubricating oil compositions of the present invention are for PCMO use, the lubricating oil compositions preferably satisfy at least the performance requirements of the ACEA A2-96#3/ API SJ, more preferably at least the ACEA A3-04/ ACEA C3-04, such as at least the API SL/ ILSAC GF-3, especially at least the ACEA AS-04/ ACEA C2-04/ ACEA C3-04/ API SM/ ILSAC GF-4 specification(s).

[0096] It should be appreciated that interaction may take place between any two or more of the additives, including any two or more detergents, after they have been incorporated into the oil composition. The interaction may take place in either the process of mixing or any subsequent condition to which the composition is exposed, including the use of the composition in its working environment. Interactions may also take place when further auxiliary additives are added to the compositions of the invention or with components of oil. Such interaction may include interaction which alters the chemical constitution of the additives. Thus, the compositions of the invention include compositions in which interaction, for example, between any of the additives, has occurred, as well as compositions in which no interaction has occurred, for example, between the components mixed in the oil.

[0097] The lubricating oil compositions may be used to lubricate mechanical engine components, particularly an internal combustion, such as a compression-ignited (diesel) engine, or a spark-ignited (gasoline) engine or a manual or automatic transmission unit, by adding the lubricating oil thereto and operating the engine/transmission.

[0098] In this specification the term "hydrocarbyl" as used herein means that the group concerned is primarily composed of hydrogen and carbon atoms and is bonded to the remainder of the molecule via a carbon atom, but does not exclude the presence of other atoms or groups in a proportion insufficient to detract from the substantially hydrocarbon characteristics of the group. The term "comprising" or "comprises" when used herein is taken to specify the presence of stated features, integers, steps or components, but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof. In the instance the term "comprising" or comprises" is used herein, the term "consisting essentially of" and its cognates are a preferred embodiment, while the term "consisting of" and its cognates are a preferred embodiment of the term "consisting essentially of". The term "oil-soluble" or "oil-dispersible", as used herein, does not mean that the additives are soluble, dissolvable, miscible or capable of being suspended in the oil in all proportions. They do mean, however, that the additives are, for instance, soluble or stable dispersible in the oil to an extent sufficient to exert their intended effect in the environment in which the oil composition is employed. Moreover, the additional incorporation of other additives such as those described above may affect the solubility or dispersibility of the additives. "Major amount" means in excess of 50, such as greater than 70, preferably 75 to 97, especially 80 to 95 or 90, mass %, of the composition. "Minor amount" means less than 50, such as less than 30, for example, 3 to 25, preferably 5 or 10 to 20, mass %, of the composition mass % of the composition. All percentages reported are mass % on an active ingredient basis, *i.e.* without regard to carrier or diluent oil, unless otherwise stated. The abbreviation SAE stands for Society of Automotive Engineers, an organization that classifies lubricants by viscosity grades.

EXAMPLES

[0099] The invention will now be particularly described, by way of example only, as follows:

Example 1

[0100] A lubricating oil composition representing a conventional 10W40 crankcase lubricant for a heavy duty diesel engine meeting the requirements of the ACEA E4-99#3 specification was prepared by blending a base stock oil of lubricating viscosity, a detergent/inhibitor (DI) package including salicylate detergent, dispersant, ZDDP and antifoamant; a viscosity modifier (VM) and lubricating oil flow improver (LOFI). The resulting composition had a nitrogen content of 0.1 mass %; a sulfur content of 0.3 mass %, a sulfated ash (SASH) content of 1.9 mass %, 1250 ppm of phosphorus and 43 mmols of salicylate soap per kilogram of finished lubricant.

[0101] Four lubricating oil compositions were prepared based on the above recipe. Example 1, a comparative example, contained no added 450 M_n polybutene (PIB). Examples 2, 3 and 4, which represent the invention, contained 0.5, 1 and 2 mass % of 450 M_n PIB, respectively. The four samples were then tested for compatibility with nitrile rubber using the bench tests used by Mercedes Benz (MB) or Daimler Chrysler (DC), specifically Test Method VDA6753014; Maschinenfabrik Augsburg & Nürnberg (MAN), specifically Test Method DIN 53521 (nitrile seal); and Motoren und Turbinen Union (MTU); specifically Test Method DIN 53521 (for nitrile seals). The results are shown below in Table II. Where the tests were repeated a number of times, an average result is provided.

Table II

Bench Test	Property	Limit	Ex. 1 (0)	Ex. 2 (0.5)	Ex. 3 (1)	Ex. 4 (2)
MBSEAL NBR	EAB*	-35% max	-45	-44	-37	
	TS**	-20% max	-20	-19	-11	
	V***	0 to 10%	0	0	0	
	H****	-8 to +2 pts.	0	0	0	
	# of tests	---	>5	2	3	0
MANSEAL NBR	EAB	-30% max	-43	---	-36	-32
	TS	-20% max	-23	---	-12	-12
	V	0 to +10%	2	---	2	2
	H	-10 pts. max	-1	---	-1	-1
	# of tests	---	>5	0	3	2
MTUSEAL NBR	EAB	-35% max	-40	-34	-36	-33
	TS	-20% max	-23	-11	-16	-17
	V	0 to 10%	2	2	2	2
	H	0 to -10 pts.	-1	-1	-1	-2
	# of tests	---	>5	2	2	2
*elongation at break; **tensile strength; ***volume; ****hardness						

[0102] As shown, in each of the bench tests, the addition of PIB resulted in improved performance, particularly in terms of EAB and TS, sufficiently to provide a passing result, where the base formulation failed.

Example 2

[0103] A lubricating oil composition representing a low SAPS (sulfated ash, phosphorus, sulfur) 1OW40 crankcase lubricant for a heavy duty diesel engine meeting the requirements of the ACEA E6-04 specification was prepared by blending a base stock oil of lubricating viscosity, a detergent/inhibitor (DI) package including salicylate detergent, dispersant, ZDDP and antifoamant; a viscosity modifier and LOFI (lube oil flow improver). The resulting composition had a nitrogen content of 0.16 mass %; a sulfur content of 0.25 mass %, a sulfated ash (SASH) content of 0.25 mass % and 800 ppm of phosphorus and 24 mmol of salicylate soap per kilogram of finished lubricant.

[0104] Four lubricating oil compositions were prepared based on the above recipe. Example 5, a comparative example, contained no added 450 M_n polybutene (PIB). Examples 2, 3 and 4, which represent the invention, contained 2.1, 2.5 and 3.0 mass % of 950 M_n PIB, respectively. The four samples were then tested for compatibility with nitrile rubber the bench tests described in Example 1. The results are shown below in Table III.

Table III

Bench Test	Property	Limit	Ex. 5 (0)	Ex. 6 (2.1)	Ex. 7 (2.5)	Ex. 8 (3.0)
MBSEAL NBR	EAB*	-35% max.	-57	-31	-33	-27
	TS**	-20% max.	-35	-11	-12	-11
	V***	0 to +10 %	2	2	2	2

(continued)

Bench Test	Property	Limit	Ex. 5 (0)	Ex. 6 (2.1)	Ex. 7 (2.5)	Ex. 8 (3.0)
	H****	-8 to +2 pts.	1	-2	1	-1
MANSEAL NBR	EAB	-30% max.	-55	-28	---	-27
	TS	-20% max.	-48	-10	---	-10
	V	0 to +10 %	5	5	---	5
	H	-10 pts. max	-2	-3	---	-4

[0105] As shown, the effects of the invention are particularly apparent in low SAPS HDD lubricants formulated with salicylate detergents. Again, in each of the bench tests, the addition of PIB resulted in improved performance, particularly in terms of EAB and TS, sufficiently to provide a passing result, where the base formulation failed.

Example 3

[0106] A lubricating oil composition representing a 15W40 crankcase lubricant for a heavy duty diesel engine meeting the requirements of the PC-10 specification was prepared by blending a base stock oil of lubricating viscosity, a detergent/inhibitor (DI) package including sulfonate and sulfurized phenate detergent, dispersant, ZDDP, a molybdenum-sulfur compound, and antifoamant; a dispersant/viscosity modifier and LOFI (lube oil flow improver). The resulting composition had a sulfur content of 0.31 mass %, a nitrogen content of 0.14, a SASH content of 0.94; 50 ppm of molybdenum and 1000 ppm of phosphorus.

[0107] Four lubricating oil compositions were prepared based on the above recipe. Example 9, a comparative example, contained no added 950 M_n polybutene (PIB). Examples 10, 11 and 12, which represent the invention, contained 0.5, 1.0 and 2.0 mass % of 950 M_n PIB, respectively. The four samples were then tested for compatibility with nitrile rubber in the bench tests described in Example 1. The results are shown below in Table IV.

Table IV

Bench Test	Property	Limit	Ex. 9 (0)	Ex. 10 (0.5)	Ex. 11 (1.0)	Ex. 12 (2.0)
MBSEAL NBR	EAB*	-35% max.	-37	-29	-23	-21
	TS**	-20% max.	-18	-13	-9	-7
	V***	0 to +10 %	2.1	2	2	2
	H****	-8 to +2 pts.	-2	-2	-2	-2

[0108] As shown, the effects of the invention are also apparent in lubricants formulated with phenate and sulfonate detergents. The addition of PIB resulted in improved performance, specifically in terms of EAB, sufficient to provide a passing result, where the base formulation failed.

Example 4

[0109] Five lubricating oil compositions were prepared based on the recipe provided in Example 3. Example 13, a comparative example, contained no added 950 M_n polybutene (PIB). Examples 14, 15, 16 and 17, which represent the invention, contained 2, 3, 4 and 5 mass % of 950 M_n PIB, respectively. The five samples were then tested for corrosion, particularly copper corrosion, using the High Temperature Corrosion Bench Test described in ASTM D6594. The results are shown below in Table V.

Table V

Property	Limit	Ex. 13	Ex. 14 (2)	Ex. 15 (3)	Ex. 16 (4)	Ex. 12 (5)
Cu	20 max	111	24	13	12	9
Pb	120 max	44	36	37	38	42
Sn	50 max	0	2	2	2	2

(continued)

Property	Limit	Ex. 13	Ex. 14 (2)	Ex. 15 (3)	Ex. 16 (4)	Ex. 12 (5)
Cu Strip	3	4B	1A	1A	1A	1A

[0110] As demonstrated, the addition of PIB to a lubricating oil composition containing a significant sulfur content further improves copper corrosion performance and allows passage of the HTCBT with a formulation that fails the test in the absence of the PIB.

[0111] The disclosures of all patents, articles and other materials described herein are hereby incorporated, in their entirety, into this specification by reference. A description of a composition comprising, consisting of, or consisting essentially of multiple specified components, as presented herein and in the appended claims, should be construed to also encompass compositions made by admixing said multiple specified 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 method of improving copper corrosion properties and/or nitrile seal compatibility in or with a lubricating oil composition comprising a major amount of oil of lubricating viscosity and a minor amount of one or more additives, said composition having a sulfur content of at least 0.1 mass %, particularly from 0.15 to 0.40 mass %, more particularly from 0.20 to 0.35 mass %, based on the total mass of lubricating oil composition, which method comprises adding to and/or incorporating into the lubricating oil composition an effective amount, such as from 0.2 to 10.0 mass %, preferably from 0.5 to 5 mass %, more preferably from 1.0 to 2.5 mass %, based on the total mass of said lubricating oil composition, of at least one non-hydrogenated polymer, preferably an olefin polymer or copolymer, such as polybutene and/or polyisobutene.

2. The method of claim 1 wherein the oil of lubricating viscosity has a sulfur content of from 0.001 to 0.10 mass %, preferably from 0.005 to 0.05 mass % sulfur, based on the total mass of oil of lubricating viscosity, and optionally, at least one of the said additives comprising a sulfur-containing compound providing at least 0.005 mass % sulfur based on the mass of said composition.

3. The method of claim 1 or claim 2 wherein at least one additive comprising a sulfur-containing compound is selected from metal salts of dihydrocarbyl dithiphosphates, sulfonate detergents, sulfurized phenate detergents, sulfur-containing molybdenum compounds, ashless dithiocarbamates, and combinations thereof.

4. The method of any of claims 1 to 3 wherein said lubricating oil composition has at least one of, preferably both of, (a) a sulphated ash (SASH) content of from 0.5 to 1.9 mass %, such as from 0.8 to 1.1 mass %, preferably from 0.90 to 1.05 mass %, e.g., no greater than 1.1 mass %, preferably no more than 1.05 mass %, and/or (b) a phosphorus content of less than 1500 ppm, preferably less than 1250 ppm, such as from 500 to 1250 ppm, more preferably less than 1200 ppm, such as 500 to 1200 ppm, still more preferably less than 850 ppm, such as from 500 to 850 ppm, based on the total mass of the composition.

5. The method of any of claims 1 to 4 wherein said lubricating oil composition comprises a salicylate detergent in an amount providing said composition with at least 9 mmoles, such as at least 18 mmoles, preferably at least 24 mmoles, e.g., 12 to 50 mmoles, preferably 18 to 33 mmoles, of salicylate soap per kg of said composition.

6. The method of any of claims 1 to 5 wherein said lubricating oil composition comprises a nitrogen-containing dispersant and/or dispersant-viscosity modifier in an amount providing in said composition from 0.08 to 0.35 mass %, such as from 0.09 to 0.25 mass %, preferably from 0.10 to 0.20 mass % of nitrogen.

7. The method of any of claims 1 to 6 wherein said lubricating oil composition has a phosphorus content of less than 1500 ppm, such as from 500 to 1500 ppm, preferably less than 1250 ppm, such as from 500 to 1250 ppm, more preferably less than 1200 ppm, such as from 500 to 1200 ppm, still more preferably less than 850 ppm, such as from 500 to 850 ppm, based on the total mass of said composition.

8. The method of any of claims 1 to 7 wherein said oil of lubricating viscosity comprises at least 50 mass %, such as at least 60 mass %, particularly at least 70 mass %, of mineral oil, based on the total mass of said composition.

9. The method of any of claims 1 to 8 wherein said composition is a power transmission fluid or a crankcase lubricating oil composition for an internal combustion engine such as a heavy duty diesel (HDD) engine and optionally, said composition meets the performance requirements of ACEA E2-96#5, such as at least one of ACEA E7-04 and API CI-4, preferably ACEA E4-99#3, more preferably at least one of ACEA E6-04 and API CJ-4.

10. The method of any one of claims 1 to 9 wherein the said non-hydrogenated (co-) polymer has a number average molecular weight in the range of from 450 to 2300, such as from 450 to 1300, e.g., from 450 to 950.

11. A lubricating oil composition comprising a sulfur content of at least 0.15 mas %, such as from 0.15 to 0.49 mass %, preferably from 0.20 to 0.35 mass %, comprising a major amount of an oil of lubricating viscosity, a minor amount of additive(s) including at least one additive having sulfur content, and a minor amount, such as at least 0.2 mass %, such as from 0.5 to 5.0 mass %, preferably from 1.0 to 2.5 mass %, of a non-hydrogenated olefin polymer, such as polybutene or polyisobutene, and optionally, one or more of the following: (i) a sulfur-containing additive selected from metal salts of dihydrocarbyl dithiphosphates, sulfonate detergents, sulfurized phenate detergents, sulfur-containing molybdenum compounds, ashless dithiocarbamates, (ii) a sulfated ash (SASH) content of from 0.5 to 1.9 mass % based on the mass of the composition; (iii) a phosphorus content of less than 1500 ppm, such as from 500 to 1250 ppm, based on the mass of said composition, (iv) a nitrogen-containing dispersant and/or dispersant-viscosity modifier providing from 0.08 to 0.35 mass % nitrogen in said composition; (v) a salicylate detergent providing at least 9 mmols, such as 12 to 50 mmols salicylate soap per kilogram of composition.

12. An additive concentrate comprising a major amount of lubricant additives which, when admixed with oil of lubricating viscosity, yields a lubricating oil composition according to claim 11.

13. The use of a non-hydrogenated olefin polymer, preferably polybutene or polyisobutene, to improve the copper corrosion properties of a sulfur-containing lubricating oil composition and/or to improve the compatibility between a lubricating oil composition containing sulfur and/or salicylate soap and nitrile rubber, particularly nitrile rubber engine and transmission seals.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 11 2914

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 0 835 923 A (IDEMITSU KOSAN COMPANY LIMITED) 15 April 1998 (1998-04-15) * abstract * * page 2, lines 6-52 * * page 3, lines 19-28 * * page 4, lines 20-33 * * claims 1,3 * -----	1-13	INV. C10M161/00 C10M165/00 C10M167/00
X	US 2004/102335 A1 (CARRICK VIRGINIA A ET AL) 27 May 2004 (2004-05-27)	11	
A	* paragraphs [0008], [0088], [0130], [0135], [0136], [0147], [0148], [0190]; table 1 * -----	1-10,12,13	
X	EP 0 331 359 A (EXXON CHEMICAL PATENTS INC) 6 September 1989 (1989-09-06) * examples 1-3,7-9 * -----	11	
A	EP 0 978 555 A (ETHYL CORPORATION) 9 February 2000 (2000-02-09) * page 2, paragraphs 1,8 * * page 3, lines 12-16 * * pages 5-6, paragraph 42 * * page 7, paragraph 51-53 * * claims 1-5 * -----	1-13	

TECHNICAL FIELDS SEARCHED (IPC)
C10M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	25 September 2006	Glod, Guy

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

3

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 06 11 2914

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

25-09-2006

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0835923 A	15-04-1998	DE 69732886 D1	04-05-2005
		DE 69732886 T2	18-08-2005
		JP 10114895 A	06-05-1998
		US 5858932 A	12-01-1999
US 2004102335 A1	27-05-2004	AU 2003302425 A1	18-06-2004
		CA 2506632 A1	10-06-2004
		EP 1587902 A1	26-10-2005
		JP 2006507394 T	02-03-2006
		WO 2004048503 A1	10-06-2004
EP 0331359 A	06-09-1989	DE 68901549 D1	25-06-1992
		ES 2033089 T3	01-03-1993
		GR 3005497 T3	24-05-1993
		HK 99894 A	23-09-1994
		JP 2008296 A	11-01-1990
		US 4948522 A	14-08-1990
EP 0978555 A	09-02-2000	AU 3583499 A	24-02-2000
		CA 2275835 A1	03-02-2000
		CN 1243863 A	09-02-2000
		DE 69921245 D1	25-11-2004
		DE 69921245 T2	09-03-2006
		JP 2000063877 A	29-02-2000
		US 6034040 A	07-03-2000

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 5498809 A **[0033]**
- US 5663130 A **[0033]**
- US 5705577 A **[0033]**
- US 5814715 A **[0033]**
- US 6022929 A **[0033]**
- US 6030930 A **[0033]**
- US 4952739 A **[0034]**
- US 4152499 A **[0034]**
- US 3202678 A **[0040]**
- US 3154560 A **[0040]**
- US 3172892 A **[0040]**
- US 3024195 A **[0040]**
- US 3024237 A **[0040]**
- US 3219666 A **[0040]**
- US 3216936 A **[0040]**
- BE 662875 A **[0040]**
- US 3087936 A **[0041]**
- US 3254025 A **[0041]**
- US 5430105 A **[0041]**
- US 4228022 A **[0047]**
- US 4309293 A **[0047]**
- US 5259967 A **[0048]**
- US 6310009 B **[0048]**
- US 4708809 A **[0048]**
- US 4740321 A **[0048]**
- US 6153565 A **[0056]**
- US 6281179 B **[0056]**
- US 6429178 B **[0056]**
- US 6429179 B **[0056]**
- US 4867890 A **[0064] [0083]**
- US 5888945 A **[0071]**
- US 5906968 A **[0071]**
- US 6010987 A **[0071]**
- US 6110878 A **[0071]**
- US 6153564 A **[0071]**
- US 6232276 B **[0071]**
- US 6358894 B **[0071]**
- US 6541429 B **[0071]**
- US 6569820 B **[0071]**
- EP 02078011 A **[0071]**
- US 2719125 A **[0079]**
- US 2719126 A **[0079]**
- US 3087932 A **[0079]**
- US 3821236 A **[0079]**
- US 3904537 A **[0079]**
- US 4097387 A **[0079]**
- US 4107059 A **[0079]**
- US 4136043 A **[0079]**
- US 4188299 A **[0079]**
- US 4193882 A **[0079]**
- GB 1560830 A **[0079]**
- EP 330522 A **[0080]**
- US 5958848 A **[0083]**

Non-patent literature cited in the description

- **W.W. YAU ; J.J KIRKLAND ; D.D BLY.** *Modern Size Exclusion Liquid Chromatography,* 1979 **[0037]**