(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
13 February 2014 (13.02.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/025525 A1

(51) International Patent Classification:
C10M 135/04 (2006.01) *C10M 139/02* (2006.01) *C10M 135/08* (2006.01) *C10M 129/42* (2006.01) *C10M 135/36* (2006.01)

(21) International Application Number: PCT/US2013/051602

(22) International Filing Date: 23 July 2013 (23.07.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/679,894 6 August 2012 (06.08.2012) US

(71) Applicant: **EXXONMOBIL RESEARCH AND ENGINEERING COMPANY** [US/US]; 1545 Route 22 East, P.O. Box 900, Annandale, NJ 08801-0900 (US).

(72) Inventors: **SHOUGH, Anne, M.**; 414 Charles Arbors Lane, New Castle, DE 19720 (US). **BAILLARGEON, David, J.**; 112 Morningside Drive, Cherry Hill, NJ 08003 (US). **JETTER, Steven, M.**; 245 Hickory Corner Road, Hightstown, NJ 08520 (US). **DECKMAN, Douglas, Edward**; 5 Peachtree Lane, Mullica Hill, NJ 08062 (US).

(74) Agents: **MIGLIORINI, Robert A.** et al.; Exxonmobil Research And Engineering Company, 1545 Route 22 East, P.o. Box 900, Annandale, NJ 08801-0900 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(54) Title: METHOD FOR IMPROVING NITRILE SEAL COMPATIBILITY WITH LUBRICATING OILS

(57) Abstract: Provided are a lubricating engine oil and a method of improving nitrile seal compatibility with a lubricating oil in an engine lubricated with such lubricating oil. The method includes using as the lubricating oil a formulated oil comprising a lubricating oil base stock as a major component and one or more additives selected from the group consisting of (i) a sulfone, sulfolane, or derivative thereof; (ii) a borate ester, boron amide, or mixtures thereof; (iii) a sulfurized olefin; (iv) a thiadiazole or derivative thereof; and (v) a succinic anhydride or derivative thereof, as a minor component. Nitrile seal compatibility is improved as compared to nitrile seal compatibility achieved using a lubricating oil containing a minor component other than the one or more additives.

WO 2014/025525 A1

METHOD FOR IMPROVING NITRILE SEAL COMPATIBILITY WITH LUBRICATING OILS

FIELD OF THE INVENTION

[0001] This disclosure relates to lubricating engines using formulated lubricating oils that exhibit nitrile seal compatibility in the engine. This disclosure 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 sulphur content, and to lubricating oils having sulphur content that exhibit enhanced seal compatibility performance in engines and transmissions containing nitrile rubber seal materials.

BACKGROUND

[0002] Lubricants in commercial use today are prepared from a variety of natural and synthetic base stocks admixed with various additive packages and solvents depending upon their intended application. The base stocks typically include mineral oils, poly alpha olefins (PAO), gas-to-liquid base oils (GTL), silicone oils, phosphate esters, diesters, polyol esters, and the like.

[0003] Lubricating oils 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.

[0004] Elastomer compatibility is a critical parameter for many lubrication specifications. Currently, the detailed chemistry of elastomer compatibility is relatively unknown, thus adjusting formulations for suitable elastomer compatibility is not straightforward and can lead to significant costs. In particular, nitrile-based elastomers tend to be very challenging materials for lubricant-elastomer compatibility. It is therefore valuable and essential to identifying lubricant base stocks that are capable of improving elastomer compatibility. This will allow not only for improved lubricant formulations but also a greater understanding of elastomer compatibility chemistry.

[0005] 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. Therefore, it would be desirable to provide a method of improving the seal compatibility of lubricating oils, particularly lubricating oils having significant sulfur contents, and lubricating oils having significant sulfur contents that provide improved seal-compatibility performance.

[0006] The present disclosure also provides many additional advantages, which shall become apparent as described below.

SUMMARY

[0007] This disclosure 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 sulphur content, and to lubricating oils having sulphur content that exhibit enhanced seal compatibility performance in engines and transmissions containing nitrile rubber seal materials.

[0008] This disclosure is directed in part to a method of improving nitrile seal compatibility with a lubricating oil in an engine lubricated with the lubricating oil. The method comprises using as the lubricating oil a formulated oil comprising a lubricating oil base stock as a major component and one or more additives selected from the group consisting of (i) a sulfone, sulfolane, or derivative thereof; (ii) a borate ester, boron amide, or mixtures thereof; (iii) a sulfurized olefin; (iv) a thiadiazole or derivative thereof; and (v) a succinic anhydride or derivative thereof, as a minor component. Nitrile seal compatibility is improved as compared to nitrile seal compatibility achieved using a lubricating oil containing a minor component other than the one or more additives.

[0009] This disclosure relates in part to a lubricating engine oil comprising a lubricating oil base stock as a major component and one or more additives selected from the group consisting of (i) a sulfone, sulfolane, or derivative thereof; (ii) a borate ester, boron amide, or mixtures thereof; (iii) a sulfurized olefin; (iv) a thiadiazole or derivative thereof; and (v) a succinic anhydride or derivative thereof, as a minor component. The one or more additives are present in an amount sufficient for the lubricating oil to exhibit improved nitrile seal compatibility as compared to nitrile seal compatibility achieved using a lubricating oil containing a minor component other than the one or more additives.

[0010] In this disclosure, certain additives including (i) a sulfone, sulfolane, or derivative thereof; (ii) a borate ester, boron amide, or mixtures thereof; (iii) a sulfurized olefin; (iv) a thiadiazole or derivative thereof; and (v) a succinic anhydride or derivative thereof, have been found to improve nitrile seal compatibility with lubricating oils when compared to nitrile seal compatibility achieved using a lubricating oil containing an additive other than these additives.

[0011] Further objects, features and advantages of the present disclosure will be understood by reference to the following drawings and detailed description.

DETAILED DESCRIPTION

[0012] All numerical values within the detailed description and the claims herein are modified by "about" or "approximately" the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

[0013] This disclosure provides lubricating oils useful as engine oils and in other applications characterized by an excellent nitrile seal compatibility characteristics. The lubricating oils are based on high quality base stocks including a major portion of a hydrocarbon base fluid such as a PAO or GTL. The lubricating oils also include one or more additives selected from the group consisting of (i) a sulfone, sulfolane, or derivative thereof; (ii) a borate ester, boron amide, or mixtures thereof; (iii) a sulfurized olefin; (iv) a thiadiazole or derivative thereof; and (v) a succinic anhydride or derivative thereof, as a minor component. The Applicants have unexpectedly and surprisingly discovered that certain engine oil compositions including PAO or GTL base stocks with one or more additive indicated in the preceding sentence have yielded unexpected improvements in nitrile seal compatibility characteristics. The lubricating oil base stock can be any oil boiling in the lube oil boiling range, typically between 100 to 600ºC. In the present specification and claims, the terms base oil(s) and base stock(s) are used interchangeably.

Lubricating Oil Base Stocks

[0014] A wide range of lubricating oils is known in the art. Lubricating oils that are useful in the present disclosure are both natural oils and synthetic oils. Natural and synthetic oils (or mixtures thereof) can be used unrefined, refined, or rerefined (the latter is also known as reclaimed or reprocessed oil). Unrefined oils are those obtained directly from a natural or synthetic source and used without added purification. These include shale oil obtained directly from retorting operations, petroleum oil obtained directly from primary distillation, and ester oil obtained directly from an esterification process. Refined oils are similar to the oils discussed for unrefined oils except refined oils are subjected to one or more purification steps to improve the at least one lubricating oil property. One skilled in the art is familiar with many purification processes. These processes include solvent extraction, secondary distillation, acid extraction, base extraction, filtration, and percolation. Rerefined oils are obtained by processes analogous to refined oils but using an oil that has been previously used as a feed stock.

[0015] Natural oils include animal oils, vegetable oils (castor oil and lard oil, for example), and mineral oils. Animal and vegetable oils possessing favorable thermal oxidative stability can be used. Of the natural oils, mineral oils are preferred. Mineral oils vary widely as to their crude source, for example, as to whether they are paraffinic, naphthenic, or mixed paraffinic-naphthenic. Oils derived from coal or shale are also useful in the present disclosure. Natural oils vary also as to the method used for their production and purification, for example, their distillation range and whether they are straight run or cracked, hydrorefined, or solvent extracted.

[0016] API Group I, II, III, IV and V are broad categories of base oil stocks developed and defined by the American Petroleum Institute (API Publication 1509; www.API.org) to create guidelines for lubricant base oils. Group I base stocks have a viscosity index of between 80 to 120 and contain greater than 0.03%

sulfur and less than 90% saturates. Group II base stocks have a viscosity index of between 80 to 120, and contain less than or equal to 0.03% sulfur and greater than or equal to 90% saturates. Group III stock has a viscosity index greater than 120 and contains less than or equal to 0.03% sulfur and greater than 90% saturates. Group IV includes polyalphaolefins (PAO). Group V base stocks include base stocks not included in Groups I-IV. The table below summarizes properties of each of these five groups.

	Base Oil Properties		
	Saturates	Sulfur	Viscosity Index
Group I	<90 and/or	>0.03% and	≥80 and <120
Group II	≥90 and	≤0.03% and	≥80 and <120
Group III	≥90 and	≤0.03% and	≥120
Group IV	Includes polyalphaolefins (PAO)		
Group V	All other base oil stocks not included in Groups I, II, III or IV		

[0017] Group II and/or Group III hydroprocessed or hydrocracked base stocks, as well as synthetic oils such as polyalphaolefins, alkyl aromatics and synthetic esters, i.e. Group IV and Group V oils are also well known base stock oils.

[0018] Synthetic oils include hydrocarbon oil such as polymerized and interpolymerized olefins (polybutylenes, polypropylenes, propylene isobutylene copolymers, ethylene-olefin copolymers, and ethylene-alphaolefin copolymers, for example). Polyalphaolefin (PAO) oil base stocks, the Group IV API base stocks, are a commonly used synthetic hydrocarbon oil. By way of example, PAOs derived from C_8, C_{10}, C_{12}, C_{14} olefins or mixtures thereof may be utilized. See U.S. Patent Nos. 4,956,122; 4,827,064; and 4,827,073, which are incorporated herein by reference in their entirety. Group IV oils, that is, the PAO base stocks have viscosity indices preferably greater than 130, more preferably greater than 135, still more preferably greater than 140.

[0019] Esters in a minor amount may be useful in the lubricating oils of this disclosure. Additive solvency and seal compatibility characteristics may be secured by the use of esters such as the esters of dibasic acids with monoalkanols and the polyol esters of monocarboxylic acids. Esters of the former type include, for example, the esters of dicarboxylic acids such as phthalic acid, succinic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acid, alkenyl malonic acid, etc., with a variety of alcohols such as butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, etc. Specific examples of these types of esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, etc.

[0020] Particularly useful synthetic esters are those which are obtained by reacting one or more polyhydric alcohols, preferably the hindered polyols such as the neopentyl polyols; e.g., neopentyl glycol, trimethylol ethane, 2-methyl-2-propyl-1,3-propanediol, trimethylol propane (TMP), pentaerythritol and dipentaerythritol with alkanoic acids containing at least 4 carbon atoms, preferably C_5 to C_{30} acids such as saturated straight chain fatty acids including caprylic acid, capric acids, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, and behenic acid, or the corresponding branched chain fatty acids or unsaturated fatty acids such as oleic acid, or mixtures of any of these materials.

[0021] Esters should be used in an amount such that the improved nitrile seal compatibility provided by the lubricating oils of this disclosure is not adversely affected. The esters preferably have a D5293 viscosity of less than 10,000 cP at -35°C.

[0022] Other useful API Group V base stocks include alkylated aromatic base stocks, for example, alkylated naphthalenes and alkylated benzenes. The alkylated aromatic co-base stock can be any hydrocarbyl molecule that contains at least 5% of its weight derived from an aromatic moiety such as a benzenoid moiety or naphthenoid moiety, or their derivatives. These alkylated aromatic co-base stocks include alkyl benzenes, alkyl naphthalenes, alkyl diphenyl oxides, alkyl naphthols, alkyl diphenyl sulfides, alkylated bis-phenol A, alkylated thiodiphenol, and the like. The alkylated aromatic co-base stock can be mono-alkylated, dialkylated, polyalkylated, and the like. The aromatic can be mono- or poly-functionalized. The hydrocarbyl groups can range from C_6 up to C_{60} with a range of C_8 to C_{40} often being preferred. A mixture of hydrocarbyl groups is often preferred. The hydrocarbyl group can optionally contain sulfur, oxygen, and/or nitrogen containing substituents. The aromatic group can also be derived from natural (petroleum) sources, provided at least 5% of the molecule is comprised of an above-type aromatic moiety. Viscosities at 100ºC of approximately 3 cSt to 50 cSt are preferred, with viscosities of approximately 3.4 cSt to 20 cSt often being more preferred for the alkylated aromatic co-base stock. Naphthalene or methyl naphthalene, for example, can be alkylated with olefins such as octene, decene, dodecene, tetradecene or higher, mixtures of similar olefins, and the like.

[0023] Illustrative alkylated naphthalenes useful in the present disclosure are described, for example, in U.S. Patent Publication No. 2008/0300157.

[0024] Examples of typical alkyl naphthalenes are mono-, di-, tri-, tetra-, or penta-C_3 alkyl naphthalene, C_4 alkyl naphthalene, C_5 alkylnaphthalene, C_6 alkyl naphthalene, C_8 alkyl naphthalene, C_{10} alkyl naphthalene, C_{1-2} alkyl naphthalene, C_{1-4} alkyl naphthalene, C_{1-6} alkyl naphthalene, C_{1-8} alkyl naphthalene, etc., C_{10}-C_{14} mixed alkyl naphthalene, C_6-C_{18} mixed alkyl naphthalene, or the mono-, di-, tri-, tetra-, or penta-C_3, C_4, C_5, C_6, C_8, C_{10}, C_{12}, C_{14}, C_{16}, C_{18} or mixture thereof alkyl monomethyl, dimethyl, ethyl, diethyl, or methylethyl naphthalene, or mixtures thereof. The alkyl group can also be branched alkyl group with C_{10} to C_{300}, e.g., C_{24}-C_{56} branched alkyl naphthalene, C_{24}-C_{56} branched alkyl mono-, di-, tri-, tetra- or penta-C_1-C_4 naphthalene. These branched alkyl group substituted naphthalenes or branched alkyl group substituted mono-, di-, tri-, tetra- or penta-C_1-C_4 naphthalene can also be used as mixtures with the previously recited materials. These branched alkyl group can be prepared from oligomerization of small olefins, such as C_5 to C_{24} alpha- or internal-olefins. When the branched alkyl group is very large (that is 8 to 300 carbons), usually only one or two of such alkyl groups are attached to the naphthalene core. The alkyl groups on the naphthalene ring can also be mixtures of the above alkyl groups. Sometimes mixed alkyl groups are advantageous because they provide more improvement of pour points and low temperature fluid properties. The fully hydrogenated fluid alkylnaphthalenes can also be used for blending with GTL base stock/base oil, but the alkyl naphthalenes are preferred.

[0025] Suitable alkylated naphthalenes are available commercially from ExxonMobil under the tradename Synesstic AN or from King Industries under the tradename NA-Lube naphthalene-containing fluids.

[0026] Illustrative alkylated benzenes useful in this disclosure include, for example, those described in U.S. Patent Publication 2008/0300157. Alkylated benzenes having a viscosity at 100ºC of 1.5 to 600 cS, VI of 0 to 200 and pour point of 0ºC or less, preferably -15ºC or less, more preferably -25ºC or less, still more preferably -35ºC or less, most preferably -60ºC or less are useful for this disclosure.

[0027] Illustrative monoalkylated benzenes include, for example, linear C_{10} to C_{30} alkyl benzene or a C_{10}-C_{300} branched alkyl benzene, preferably C_{10}-C_{100} branched alkyl benzene, more preferably C_{15}-C_{50} branched alkyl group. Illustrative miltialkylated benzenes include, for example, those in which one or two of the alkyl groups can be small alkyl radical of C_1 to C_5 alkyl group, preferably C_1-C_2 alkyl group. The other alkyl group or groups can be any combination of linear C_{10}-C_{30} alkyl group, or branched C_{10} and higher up to C_{300} alkyl group, preferably C_{15}-C_{50} branched alkyl group. These branched large alkyl radicals can be prepared from the oligomerization or polymerization of C_3 to C_{20}, internal or alpha-olefins or mixture of these olefins. The total number of carbons in the alkyl substituents ranged from C_{10} to C_{300}. Preferred alkyl benzene fluids can be prepared according to U.S. Patent Nos. 6,071,864 and 6,491,809.

[0028] Non-conventional or unconventional base stocks and/or base oils include one or a mixture of base stock(s) and/or base oil(s) derived from: (1) one or more gas-to-liquids (GTL) materials, as well as (2) hydrodewaxed, or hydroisomerized/cat (and/or solvent) dewaxed base stock(s) and/or base oils derived from synthetic wax, natural wax or waxy feeds, mineral and/or non-mineral oil waxy feed stocks such as gas oils, slack waxes (derived from the solvent dewaxing of natural oils, mineral oils or synthetic oils; e.g., Fischer-Tropsch feed stocks), natural waxes, and waxy stocks such as gas oils, waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, foots oil or other mineral, mineral oil, or even non-petroleum oil derived waxy materials such as waxy materials recovered from coal liquefaction or shale oil, linear or branched hydrocarbyl compounds with carbon number of 20 or greater, preferably 30 or greater and mixtures of such base stocks and/or base oils.

[0029] GTL materials are materials that are derived via one or more synthesis, combination, transformation, rearrangement, and/or degradation/deconstructive processes from gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks such as hydrogen, carbon dioxide, carbon monoxide, water, methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane, butylenes, and butynes. GTL base stocks and/or base oils are GTL materials of lubricating viscosity that are generally derived from hydrocarbons; for example, waxy synthesized hydrocarbons, that are themselves derived from simpler gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks. GTL base stock(s) and/or base oil(s) include oils boiling in the lube oil boiling range (1) separated/fractionated from synthesized GTL materials such as, for example, by distillation and subsequently subjected to a final wax processing step which involves either or both of a catalytic dewaxing process, or a solvent dewaxing process, to produce lube oils of reduced/low pour point; (2) synthesized wax isomerates, comprising, for example, hydrodewaxed or hydroisomerized cat and/or solvent dewaxed synthesized wax or waxy hydrocarbons; (3) hydrodewaxed or hydroisomerized cat and/or solvent dewaxed Fischer-Tropsch (F-T) material (i.e., hydrocarbons, waxy hydrocarbons, waxes and possible analogous oxygenates); preferably hydrodewaxed or hydroisomerized/followed by cat and/or solvent dewaxing dewaxed F-T waxy hydrocarbons, or hydrodewaxed or hydroisomerized/followed by cat (or solvent) dewaxing dewaxed, F-T waxes, or mixtures thereof.

[0030] GTL base stock(s) and/or base oil(s) derived from GTL materials, especially, hydrodewaxed or hydroisomerized/followed by cat and/or solvent dewaxed wax or waxy feed, preferably F-T material derived base stock(s) and/or base oil(s), are characterized typically as having kinematic viscosities at 100ºC of from 2 mm^2/s to 50 mm^2/s (ASTM D445). They are further characterized typically as having pour points of -5ºC to -40ºC or lower (ASTM D97). They are also characterized typically as having viscosity indices of 80 to 140 or greater (ASTM D2270).

[0031] In addition, the GTL base stock(s) and/or base oil(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stock(s) and/or base oil(s) typically have very low sulfur and nitrogen content, generally containing less than 10 ppm, and more typically less than 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock(s) and/or base oil(s) obtained from F-T material, especially F-T wax, is essentially nil. In addition, the absence of phosphorous and aromatics make this materially especially suitable for the formulation of low SAP products.

[0032] The term GTL base stock and/or base oil and/or wax isomerate base stock and/or base oil is to be understood as embracing individual fractions of such materials of wide viscosity range as recovered in the production process, mixtures of two or more of such fractions, as well as mixtures of one or two or more low viscosity fractions with one, two or more higher viscosity fractions to produce a blend wherein the blend exhibits a target kinematic viscosity.

[0033] The GTL material, from which the GTL base stock(s) and/or base oil(s) is/are derived is preferably an F-T material (i.e., hydrocarbons, waxy hydrocarbons, wax).

[0034] Base oils for use in the formulated lubricating oils useful in the present disclosure are any of the variety of oils corresponding to API Group I, Group II, Group III, Group IV, Group V and Group VI oils and mixtures thereof, preferably API Group II, Group III, Group IV, Group V and Group VI oils and mixtures thereof, more preferably the Group III to Group VI base oils due to their exceptional volatility, stability, viscometric and cleanliness features. Minor quantities of Group I stock, such as the amount used to dilute additives for blending into formulated lube oil products, can be tolerated but should be kept to a minimum, i.e. amounts only associated with their use as diluent/carrier oil for additives used on an “as-received” basis. Even in regard to the Group II stocks, it is preferred that the Group II stock be in the higher quality range associated with that stock, i.e. a Group II stock having a viscosity index in the range $100 < VI < 120$.

[0035] In addition, the GTL base stock(s) and/or base oil(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stock(s) and/or base oil(s) and hydrodewaxed, or hydroisomerized/cat (and/or solvent) dewaxed base stock(s) and/or base oil(s) typically have very low sulfur and nitrogen content, generally containing less than 10 ppm, and more typically less than 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock(s) and/or base oil(s) obtained from F-T material, especially F-T wax, is essentially nil. In addition, the absence of phosphorous and aromatics make this material especially suitable for the formulation of low sulfur, sulfated ash, and phosphorus (low SAP) products.

[0036] The base stock component can preferably be a mixture of one or more of the API Group I, II, III, IV and V base oil stocks. The base stock component of the present lubricating oils will typically be from 80 to 99 weight percent of the total composition (all proportions and percentages set out in this specification are by weight unless the contrary is stated) and more usually in the range of 90 to 99 weight percent.

Nitrile Seal Compatibility Additives

Sulfones, Sulfolanes, and Derivatives Thereof

[0037] A sulfone, sulfolane, or derivative thereof can be used as a nitrile seal compatibility additive in the formulations of this disclosure. A sulfone, sulfolane, or derivative thereof such as a substituted sulfolane from Lubrizol, Inc., Afton Corp., for example Lubrizol® 730, can be used in an effective amount up to 1.0 volume percent, and more preferably from 0.03 to 1.0 percent by weight of the complete motor oil formula and up to 5 times that amount in the concentrate.

Other sulfone, sulfolane, or derivative thereof include 3-alkoxysulfolane or the like, in which the alkoxy group contains at least 4 and preferably 4 to 25 carbon atoms. See U.S. Patent Nos. 4,029,587 and 4,116,877, the disclosures of which are incorporated herein by reference.

[0038] The sulfone and sulfolane compounds and particularly the substituted sulfones and sulfolanes, are a preferred additives in the formulations of this disclosure. The sulfone and sulfolane compounds are also useful as seal swell additives.

[0039] More particularly, nitrile seal compatibility additives suitable in the present disclosure include 3-isodecoxysulfolane, and other substituted sulfolanes including those having: i) a hydrocarbon-based radical having at least 4 carbon atoms such as aliphatic, (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl or cycloalkenyl), aromatic, aliphatic- and alicyclic-substituted aromatic, aromatic-substituted aliphatic and alicyclic radicals, and the like; examples include butyl, pentyl, hexyl, octyl, decyl, dodecyl, eicosyl, decenyl, cyclohexyl, phenyl, tolyl, heptylphenyl, isopropenylphenyl and naphthyl; ii) substituted hydrocarbon radicals containing non-hydrocarbon substituents which, do not alter the predominantly hydrocarbon character of the radical such as halo, nitro, and cyano compounds; and iii) hetero radicals which are hydrocarbons which contain atoms other than carbon present in a chain or ring otherwise composed of carbon atoms such as oxygen, nitrogen and sulfur.

[0040] Other preferred substituted sulfolanes are those in which a hydrocarbon radical is selected free from acetylenic unsaturation and which contains 4-100 carbon atoms. Examples (all isomers being included) are butyl, amyl, hexyl, octyl, decyl, dodecyl, eicosyl, triacontanyl, butenyl, dodecenyl, phenyl, naphthyl, tolyl, dodecylphenyl, tetrapropene-alkylated phenyl, phenethyl, cyclohexyl and methylcyclohexyl. Each of substituted hydrocarbon radicals and hetero radicals are hydrogen or a lower alkylbased (and usually a lower alkyl) radical, the word "lower" denoting radicals containing up to 7 carbon atoms. Examples of lower alkyl radicals (all isomers being included, but especially the straight chain radicals) are methyl, ethyl, propyl, butyl and hexyl, with methyl being preferred.

[0041] The above-described substituted sulfolanes comprise a class of compounds which may be prepared by the reaction of 3-sulfolene or a substituted derivative thereof with an organic hydroxy compound, ordinarily an alcohol. This method for their preparation is described, for example, in U.S. Patent No. 2,393,925. The 3-sulfolenes may be prepared by reaction of sulfur dioxide with a conjugated diene such as butadiene or isoprene.

[0042] Moreover, aliphatic alcohols of 8 to 13 carbon atoms, e.g., tridecyl alcohol in combination with an oil-soluble, saturated hydrocarbyl ester of 10 to 60 carbon atoms and 2 to 3 ester linkages, e.g., dihexyl phthalate are useful.

[0043] Furthermore, C_1-C_8 alkyl substituted phosphites, C_1 to C_4 alkyl substituted phenols or aromatic secondary amine and a dispersant copolymer containing N-vinyl-2-pyrrolidone, an organophosphite, such as tris(nonylphenyl) phosphite and mixtures of organic phosphite ester and methylene bisphenol are useful for oxidation inhibitors for lubricating oils and for elastomers, including nitrile rubbers.

<u>Borate Esters, Boron Amides, and Mixtures Thereof</u>

[0044] Illustrative borate esters and boron amides useful in this disclosure include, for example, borate esters and boronate esters derived from boric acids or boronic acids, amides and glycerides, and mixtures thereof. In addition to providing nitrile seal compatibility, the borate esters and boronate esters can provide ashless, almost phosphorus-free and sulfur-free antiwear, extreme pressure friction modifying additives for lubricating oils and fuels. Useful borate esters and boron amides are disclosed, for example, in EP 1 625 193, U.S. Patent

Nos. 4,389,322, 4,406,802, 4,478,732, 4,722,894, 4,975,211, 5,006,272 and 7,291,581, U.S. Patent Application Publication No. 2003/0234105, the disclosures of which are incorporated herein by reference.

[0045] Borate esters and boron amides may include borated alkyl diethanol amides, borated mono glycerides, and Vanlube® 289 available from R.T. Vanderbilt Company. Preferred borate esters and boron amides include mixtures of borated alkyl diethanol amides and borated mono glycerides. The borate esters are also useful as antiwear additives and dispersants.

Sulfurized Olefins

[0046] The sulfurized olefins useful in the present disclosure can be prepared by a number of known methods. They are characterized by the type of olefin used in their production and their final sulfur content. High molecular weight olefins, i.e., those olefins having an average molecular weight of 168 to 351 g/mole, are preferred. Examples of olefins that may be used include alpha-olefins, isomerized alpha-olefins, branched olefins, cyclic olefins, and combinations of these.

[0047] Suitable alpha-olefins include any C_4-C_{25} alpha-olefins. Alpha-olefins may be isomerized before the sulfurization reaction or during the sulfurization reaction. Structural and/or conformational isomers of the alpha olefin that contain internal double bonds and/or branching may also be used. For example, isobutylene is the branched olefin counterpart of the alphaolefin 1-butene.

[0048] Sulfur sources that may be used in the sulfurization reaction include: elemental sulfur, sulfur monochloride, sulfur dichloride, sodium sulfide, sodium hydrosulfide, sodium polysulfide, and mixtures of these added together or at different stages of the sulfurization process.

[0049] Unsaturated fatty acids and oils, because of their unsaturation, may also be sulfurized and used in this disclosure. Examples of fatty acids that may be used include lauroleic acid, myristoleic acid, palmitoleic acid, oleic acid, elaidic acid, vaccenic acid, linoleic acid, linolenic acid, gadoleic acid, arachidonic acid, erucic acid, and mixtures of these. Examples of oils or fats that may be used include corn oil, cottonseed oil, grapeseed oil, olive oil, palm oil, peanut oil, rapeseed oil, safflower seed oil, sesame seed oil, soyabean oil, sunflower seed oil, and combinations of these. Unsaturated oils include oleyl oleate, jojoba oil, and the like. Unsaturated fats include lard, and the like.

[0050] The concentration of sulfurized olefin in the formulated lubricant oil can vary depending upon the applications, and the desired level of nitrile seal compatibility required for the specific formulated oil. An important criteria for selecting the concentration of the sulfurized olefin used in the formulated oil is the sulfur concentration of the sulfurized olefin itself. The sulfurized olefin should deliver between 0.05 wt% and 0.30 wt% of sulfur to the finished lubricant formulation. For example, a sulfurized olefin containing 20 wt% sulfur content should be used at levels between 0.25 wt% and 1.5 wt% to deliver between 0.05 wt% and 0.30 wt% sulfur to the finished oil. A sulfurized olefin containing 10 wt% sulfur content should be used between 0.5 wt% and 3.0 wt% to deliver between 0.05 wt% and 0.30 wt% sulfur to the finished oil.

[0051] Examples of commercial sulfurized olefins which may be used in the present disclosure include Hitec® 7084 which contains approximately 20 wt% sulfur content, Hitec® 7188 which contains approximately 12 wt% sulfur content, Hitec® 312 which contains approximately 47.5 wt% sulfur content, and Hitec® 313 which contains approximately 47.5 wt% sulfur content, all from Afton Corporation, and Additin® RC 2540-A which contains approximately 38 wt% sulfur content, from Rhein Chemie Corporation. Commercially available sulfurized fatty oils, or mixtures of sulfurized fatty oils and olefins, that may be used in the present disclosure include Additin® R 4410 which contains approximately 9.5 wt% sulfur content, Additin® R 4412-F which contains approximately 12.5 wt% sulfur content, Additin® R 4417 which contains approximately 17.5 wt% sulfur content, Additin® RC 2515 which contains approximately 15 wt% sulfur content, Additin® RC 2526 which contains approximately 26 wt% sulfur content, Additin® RC 2810-A which contains approximately 10 wt% sulfur content, Additin® RC 2814-A which contains approximately 14 wt% sulfur content, and Additin® RC 2818-A which contains approximately 16 wt% sulfur content, all from Rhein Chemie Corporation. It is preferred that the sulfurized olefin and/or fatty oil be a liquid of low corrosivity and low active sulfur content as determined by ASTM D1662.

[0052] Sulfurized olefins, which may also be employed in the present disclosure, are typically prepared by the reaction of a C_3-C_6 olefin, including sulfurized isobutylene, or a low-molecular-weight polyolefin derived therefrom with a sulfur-containing compound such as sulfur, sulfur monochloride, and/or sulfur dichloride. Sulfurized olefins are also useful as antioxidants.

<u>Thiadiazoles</u>

[0053] The thiadiazole component of the present additive composition is a non-polycarboxylate moiety-containing thiadiazole. Preferably, the thiadiazole comprises at least one of 2,5-dimercapto-1,3,4-thiadiazole; 2-mercapto-5-hydrocarbylthio-1,3,4-thiadiazoles; 2-mercapto-5-hydrocarbyl- dithio-1,3,4-thiadiazoles; 2,5-bis(hydrocarbylthio and 2,5-bis(hydrocarbyldithio)-1,3,4-thiadiazoles. The more preferred compounds are the 1,3,4-thiadiazoles, especially the 2-hydrocarbyidithio-5-mercapto-1,3,4-dithiadiazoles and the 2,5-bis(hydrocarbyidithio)-1,3,4-thiadiazoles, a number of which are available as articles of commerce. Most preferably, a non-polycarboxylate-containing thiadiazole containing 4.0 wt % 2,5-dimercapto-1,3,4-thiadiazole, which may be either Afton Corporation's Hitec® 4313 or Lubrizol Corporation's Lubrizol®

5955A, is used. Hitec® 4313 may be obtained from Afton Corporation, Richmond, Va. and Lubrizol® 5955A may be obtained from Lubrizol Corporation, Wycliiffe, Ohio. Thiadiazoles are also useful as antioxidants and sulfur scavengers.

Succinic Anhydrides

[0054] The succinic anhydride component of the present gear oil additive composition is an alkyl or alkenyl succinic anhydride, wherein the alkyl or alkenyl group has a number average molecular weight of 160 to 700. Preferably, the succinic anhydride is an alkenyl succinic anhydride. Preferred alkenyl succinic anhydrides include tetrapropenyl succinic anhydride and polyisobutenyl succinic anhydride. When the alkenyl succinic anhydride is a polyisobutenyl succinic anhydride, the polyisobutenyl group will preferably have a molecular weight of 250 to 700, more preferably 450 to 650, and most preferably 500 to 600. A particularly preferred polyisobutenyl group will have a molecular weight of 550. If polyisobutenyl succinic anhydride (PIBSA) is used, then the PIBSA can be prepared by a number of methods. One example of preparing PIBSA by a thermal reaction is disclosed in U.S. Patent No. 6,156,850. Other methods of PIBSA preparation include using a chlorinated polyisobutene as disclosed in U.S. Patent No. 4,234,435. The succinic anhydrides are also useful as dispersants.

[0055] The nitrile seal compatibility additives are typically used in an amount from 0.01 wt% to 2 wt%, preferably 0.025 wt% to 1.5 wt%, and more preferably 0.5 wt% to 1.25 wt%, depending on the particular formulation.

[0056] The nitrile seal compatibility additive is preferably present in an amount sufficient for the lubricating oil to exhibit improved nitrile seal compatibility with a lubricating oil in an engine lubricated with the lubricating oil, as compared to nitrile seal compatibility achieved using a lubricating oil containing other than the nitrile seal compatibility additive, preferably improved change in tensile strength (%) and elongation at break (%) as determined by Nitrile-NBR34 (MB VDA 675301 Method).

Other Additives

[0057] The formulated lubricating oil useful in the present disclosure may additionally contain one or more of the other commonly used lubricating oil performance additives including but not limited to dispersants, other detergents, corrosion inhibitors, rust inhibitors, metal deactivators, other anti-wear agents and/or extreme pressure additives, anti-seizure agents, wax modifiers, viscosity index improvers, viscosity modifiers, fluid-loss additives, seal compatibility agents, other friction modifiers, lubricity agents, anti-staining agents, chromophoric agents, defoamants, demulsifiers, emulsifiers, densifiers, wetting agents, gelling agents, tackiness agents, colorants, and others. For a review of many commonly used additives, see Klamann in Lubricants and Related Products, Verlag Chemie, Deerfield Beach, FL; ISBN 0-89573-177-0. Reference is also made to "Lubricant Additives" by M. W. Ranney, published by Noyes Data Corporation of Parkridge, NJ (1973).

[0058] The types and quantities of performance additives used in combination with the instant disclosure in lubricant compositions are not limited by the examples shown herein as illustrations.

Viscosity Improvers

[0059] Viscosity improvers (also known as Viscosity Index modifiers, and VI improvers) increase the viscosity of the oil composition at elevated temperatures which increases film thickness, while having limited effect on viscosity at low temperatures.

[0060] Suitable viscosity improvers include high molecular weight hydrocarbons, polyesters and viscosity index improver dispersants that function as both a viscosity index improver and a dispersant. Typical molecular weights of these polymers are between 10,000 to 1,000,000, more typically 20,000 to 500,000, and even more typically between 50,000 and 200,000.

[0061] Examples of suitable viscosity improvers are polymers and copolymers of methacrylate, butadiene, olefins, or alkylated styrenes. Polyisobutylene is a commonly used viscosity index improver. Another suitable viscosity index improver is polymethacrylate (copolymers of various chain length alkyl methacrylates, for example), some formulations of which also serve as pour point depressants. Other suitable viscosity index improvers include copolymers of ethylene and propylene, hydrogenated block copolymers of styrene and isoprene, and polyacrylates (copolymers of various chain length acrylates, for example). Specific examples include styrene-isoprene or styrene-butadiene based polymers of 50,000 to 200,000 molecular weight.

[0062] The amount of viscosity modifier may range from zero to 8 wt%, preferably zero to 4 wt%, more preferably zero to 2 wt% based on active ingredient and depending on the specific viscosity modifier used.

Antioxidants

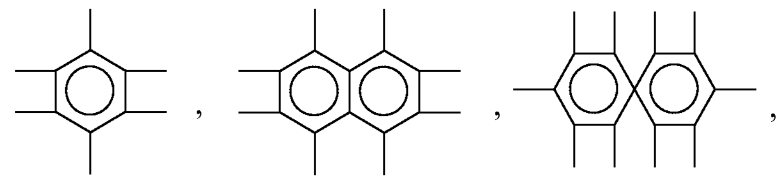
[0063] Typical antioxidant include phenolic antioxidants, aminic antioxidants and oil-soluble copper complexes.

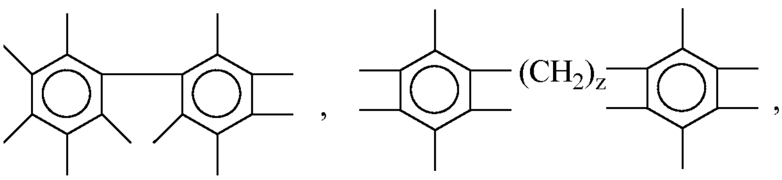
[0064] The phenolic antioxidants include sulfurized and non-sulfurized phenolic antioxidants. The terms “phenolic type” or “phenolic antioxidant” used herein includes compounds having one or more than one hydroxyl group bound to an aromatic ring which may itself be mononuclear, e.g., benzyl, or poly-nuclear, e.g., naphthyl and spiro aromatic compounds. Thus “phenol type” includes phenol per se, catechol, resorcinol, hydroquinone, naphthol, etc., as well as alkyl or alkenyl and sulfurized alkyl or alkenyl derivatives thereof, and bisphenol type compounds including such bi-phenol compounds linked by alkylene bridges sulfuric bridges or oxygen bridges. Alkyl phenols include mono- and poly-alkyl or alkenyl phenols, the alkyl or alkenyl group containing from 3-100 carbons, preferably 4 to 50 carbons and sulfurized derivatives thereof, the number of alkyl or alkenyl groups present in the aromatic ring ranging from 1 to up to the available unsatisfied valences of the aromatic ring remaining after counting the number of hydroxyl groups bound to the aromatic ring.

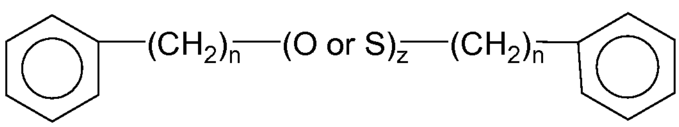
[0065] Generally, therefore, the phenolic anti-oxidant may be represented by the general formula:

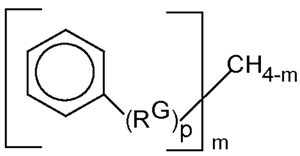
$$(R)_x\text{—Ar—}(OH)_y$$

where Ar is selected from the group consisting of:



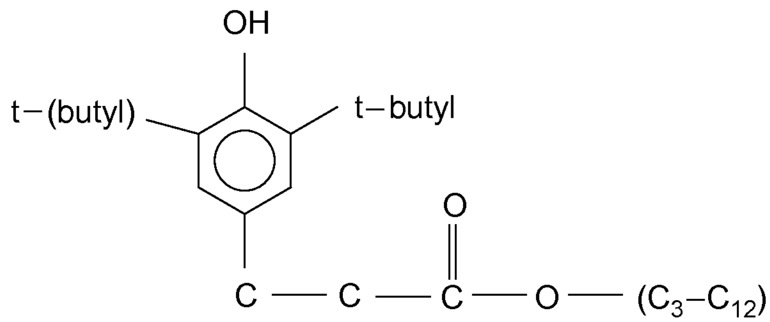






wherein R is a C_3-C_{100} alkyl or alkenyl group, a sulfur substituted alkyl or alkenyl group, preferably a C_4-C_{50} alkyl or alkenyl group or sulfur substituted alkyl or alkenyl group, more preferably C_3-C_{100} alkyl or sulfur substituted alkyl group, most preferably a C_4-C_{50} alkyl group, R^g is a C_1-C_{100} alkylene or sulfur substituted alkylene group, preferably a C_2-C_{50} alkylene or sulfur substituted alkylene group, more preferably a C_2-C_2 alkylene or sulfur substituted alkylene group, y is at least 1 to up to the available valences of Ar, x ranges from 0 to up to the available valances of Ar-y, z ranges from 1 to 10, n ranges from 0 to 20, and m is 0 to 4 and p is 0 or 1, preferably y ranges from 1 to 3, x ranges from 0 to 3, z ranges from 1 to 4 and n ranges from 0 to 5, and p is 0.

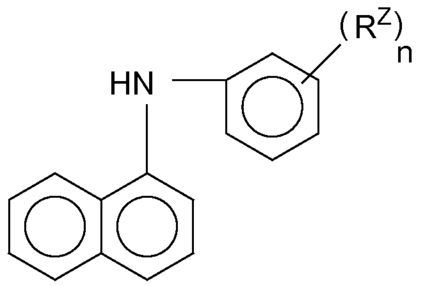
[0066] Preferred phenolic antioxidant compounds are the hindered phenolics and phenolic esters which contain a sterically hindered hydroxyl group, and these include those derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or p-position to each other. Typical phenolic antioxidants include the hindered phenols substituted with C_1+ alkyl groups and the alkylene coupled derivatives of these hindered phenols. Examples of phenolic materials of this type 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-t-butyl-4-heptyl phenol; 2-methyl-6-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-methyl phenol; 2,6-di-t-butyl-4-ethyl phenol; and 2,6-di-t-butyl-4-alkoxy phenol; and



[0067] Phenolic type antioxidants are well known in the lubricating industry and commercial examples such as Ethanox® 4710, Irganox® 1076, Irganox® L1035, Irganox® 1010, Irganox® L109, Irganox® L118, Irganox® L135 and the like are familiar to those skilled in the art. The above is presented only by way of exemplification, not limitation on the type of phenolic antioxidants which can be used.

[0068] The phenolic antioxidant can be employed in an amount in the range of 0.1 to 3 wt%, preferably 0.25 to 2.5 wt%, more preferably 0.5 to 2 wt% on an active ingredient basis.

[0069] Aromatic amine antioxidants include phenyl-α-naphthyl amine which is described by the following molecular structure:



wherein R^z is hydrogen or a C_1 to C_{14} linear or C_3 to C_{14} branched alkyl group, preferably C_1 to C_{10} linear or C_3 to C_{10} branched alkyl group, more preferably linear or branched C_6 to C_8 and n is an integer ranging from 1 to 5 preferably 1. A particular example is Irganox L06.

[0070] Other aromatic amine antioxidants include other alkylated and non-alkylated aromatic amines such as aromatic monoamines of the formula $R^8R^9R^{10}N$ where R^8 is an aliphatic, aromatic or substituted aromatic group, R^9 is an aromatic or a substituted aromatic group, and R^{10} is H, alkyl, aryl or $R^{11}S(O)_XR^{12}$ where R^{11} is an alkylene, alkenylene, or aralkylene group, R^{12} is a higher alkyl group, or an alkenyl, aryl, or alkaryl group, and x is 0, 1 or 2. The aliphatic group R^8 may contain from 1 to 20 carbon atoms, and preferably contains from 6 to 12 carbon atoms. The aliphatic group is a saturated aliphatic group. Preferably, both R^8 and R^9 are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring aromatic group such as naphthyl. Aromatic groups R^8 and R^9 may be joined together with other groups such as S.

[0071] Typical aromatic amines anti-oxidants have alkyl substituent groups of at least 6 carbon atoms. Examples of aliphatic groups include hexyl, heptyl, octyl, nonyl, and decyl. Generally, the aliphatic groups will not contain more than 14 carbon atoms. The general types of such other additional amine antioxidants which may be present include diphenylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more of such other additional aromatic amines may also be present. Polymeric amine antioxidants can also be used.

[0072] Another class of antioxidant used in lubricating oil compositions and which may also be present are oil-soluble copper compounds. Any oil-soluble suitable copper compound may be blended into the lubricating oil. Examples of suitable copper antioxidants include copper dihydrocarbyl thio- or dithio-phosphates and copper salts of carboxylic acid (naturally occurring or synthetic). Other suitable copper salts include copper dithiacarbamates, sulphonates, phenates, and acetylacetonates. Basic, neutral, or acidic copper Cu(I) and or Cu(II) salts derived from alkenyl succinic acids or anhydrides are known to be particularly useful.

[0073] Such antioxidants may be used individually or as mixtures of one or more types of antioxidants, the total amount employed being an amount of 0.50 to 5 wt%, preferably 0.75 to 3 wt% (on an as-received basis).

<u>Detergents</u>

[0074] In addition to the alkali or alkaline earth metal salicylate detergent which is an optional component in the present disclosure, other detergents may also be present. While such other detergents can be present, it is preferred that the amount employed be such as to not interfere with the synergistic effect attributable to the presence of the salicylate. Therefore, most preferably such other detergents are not employed.

[0075] If such additional detergents are present, they can include alkali and alkaline earth metal phenates, sulfonates, carboxylates, phosphonates and mixtures thereof. These supplemental detergents can have total base number (TBN) ranging from neutral to highly overbased, i.e. TBN of 0 to over 500, preferably 2 to 400, more preferably 5 to 300, and they can be present either individually or in combination with each other in an amount in the range of from 0 to 10 wt%, preferably 0.5 to 5 wt% (active ingredient) based on the total weight of the formulated lubricating oil. As previously stated, however, it is preferred that such other detergent not be present in the formulation.

[0076] Such additional other detergents include by way of example and not limitation calcium phenates, calcium sulfonates, magnesium phenates, magnesium sulfonates and other related components (including borated detergents).

Dispersants

[0077] During engine operation, oil-insoluble oxidation byproducts are produced. Dispersants help keep these byproducts in solution, thus diminishing their deposition on metal surfaces. Dispersants may be ashless or ash-forming in nature. Preferably, the dispersant is ashless. So-called ashless dispersants are organic materials that form substantially no ash upon combustion. For example, non-metal-containing or borated metal-free dispersants are considered ashless. In contrast, metal-containing detergents discussed above form ash upon combustion.

[0078] Suitable dispersants typically contain a polar group attached to a relatively high molecular weight hydrocarbon chain. The polar group typically contains at least one element of nitrogen, oxygen, and/or phosphorus. Typical hydrocarbon chains contain 50 to 400 carbon atoms.

[0079] A particularly useful class of dispersants are the alkenylsuccinic derivatives, typically produced by the reaction of a long chain substituted alkenyl succinic compound, usually a substituted succinic anhydride, with a polyhydroxy or polyamino compound. The long chain group constituting the oleophilic portion of the molecule which confers solubility in the oil, is normally a polyisobutylene group. Many examples of this type of dispersant are well known commercially and in the literature. Exemplary U.S. patents describing such dispersants are 3,172,892; 3,215,707; 3,219,666; 3,316,177; 3,341,542; 3,444,170; 3,454,607; 3,541,012; 3,630,904; 3,632,511; 3,787,374 and 4,234,435. Other types of dispersant are described in U.S. Pat. Nos. 3,036,003; 3,200,107; 3,254,025; 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,413,347; 3,697,574; 3,725,277; 3,725,480; 3,726,882; 4,454,059; 3,329,658; 3,449,250; 3,519,565; 3,666,730; 3,687,849; 3,702,300; 4,100,082; 5,705,458. A further description of dispersants may be found, for example, in European Patent Application No. 471 071, to which reference is made for this purpose.

[0080] Hydrocarbyl-substituted succinic acid compounds are popular dispersants. In particular, succinimide, succinate esters, or succinate ester amides prepared by the reaction of a hydrocarbon-substituted succinic acid compound preferably having at least 50 carbon atoms in the hydrocarbon substituent, with at least one equivalent of an alkylene amine are particularly useful.

[0081] Succinimides are formed by the condensation reaction between alkenyl succinic anhydrides and amines. Molar ratios can vary depending on the amine or polyamine. For example, the molar ratio of alkenyl succinic anhydride to TEPA can vary from 1:1 to 5:1.

[0082] Succinate esters are formed by the condensation reaction between alkenyl succinic anhydrides and alcohols or polyols. Molar ratios can vary depending on the alcohol or polyol used. For example, the condensation product of an alkenyl succinic anhydride and pentaerythritol is a useful dispersant.

[0083] Succinate ester amides are formed by condensation reaction between alkenyl succinic anhydrides and alkanol amines. For example, suitable alkanol amines include ethoxylated polyalkylpolyamines, propoxylated polyalkylpolyamines and polyalkenylpolyamines such as polyethylene polyamines. One example is propoxylated hexamethylenediamine.

[0084] The molecular weight of the alkenyl succinic anhydrides will typically range between 800 and 2,500. The above products can be post-reacted with various reagents such as sulfur, oxygen, formaldehyde, carboxylic acids such as oleic acid, and boron compounds such as borate esters or highly borated dispersants. The dispersants can be borated with from 0.1 to 5 moles of boron per mole of dispersant reaction product.

[0085] Mannich base dispersants are made from the reaction of alkylphenols, formaldehyde, and amines. Process aids and catalysts, such as oleic acid and sulfonic acids, can also be part of the reaction mixture. Molecular weights of the alkylphenols range from 800 to 2,500 or more.

[0086] Typical high molecular weight aliphatic acid modified Mannich condensation products can be prepared from high molecular weight alkyl-substituted hydroxyaromatics or $HN(R)_2$ group-containing reactants.

[0087] Examples of high molecular weight alkyl-substituted hydroxyaromatic compounds are polypropylphenol, polybutylphenol, and other polyalkylphenols. These polyalkylphenols can be obtained by the alkylation, in the presence of an alkylating catalyst, such as BF_3, of phenol with high molecular weight polypropylene, polybutylene, and other polyalkylene compounds to give alkyl substituents on the benzene ring of phenol having an average 600-100,000 molecular weight.

[0088] Examples of $HN(R)_2$ group-containing reactants are alkylene polyamines, principally polyethylene polyamines. Other representative organic compounds containing at least one $HN(R)_2$ group suitable for use in the preparation of Mannich condensation products are well known and include the mono- and di-amino alkanes and their substituted analogs, e.g., ethylamine and diethanol amine; aromatic diamines, e.g., phenylene diamine, diamino naphthalenes; heterocyclic amines, e.g., morpholine, pyrrole, pyrrolidine, imidazole, imidazolidine, and piperidine; melamine and their substituted analogs.

[0089] Examples of alkylene polyamine reactants include ethylenediamine, diethylene triamine, triethylene tetraamine, tetraethylene pentaamine, pentaethylene hexamine, hexaethylene heptaamine, heptaethylene octaamine, octaethylene nonaamine, nonaethylene decamine, and decaethylene undecamine and mixture of such amines having nitrogen contents corresponding to the alkylene polyamines, in the formula $H_2N\text{-}(Z\text{-}NH\text{-})_nH$, mentioned before, Z is a divalent ethylene and n is 1 to 10 of the foregoing formula. Corresponding propylene polyamines such as propylene diamine and di-, tri-, tetra-, pentapropylene tri-, tetra-, penta- and hexaamines are also suitable reactants. The alkylene polyamines are usually obtained by the reaction of ammonia and dihalo alkanes, such as dichloro alkanes. Thus the alkylene polyamines obtained from the reaction of 2 to 11 moles of ammonia with 1 to 10 moles of dichloroalkanes having 2 to 6 carbon atoms and the chlorines on different carbons are suitable alkylene polyamine reactants.

[0090] Aldehyde reactants useful in the preparation of the high molecular products useful in this disclosure include the aliphatic aldehydes such as formaldehyde (also as paraformaldehyde and formalin), acetaldehyde and aldol (β-hydroxybutyraldehyde). Formaldehyde or a formaldehyde-yielding reactant is preferred.

[0091] Preferred dispersants include borated and non-borated succinimides, including those derivatives from mono-succinimides, bis-succinimides, and/or mixtures of mono- and bis-succinimides, wherein the hydrocarbyl succinimide is derived from a hydrocarbylene group such as polyisobutylene having a Mn of from 500 to 5000 or more or a mixture of such hydrocarbylene groups. Other preferred dispersants include succinic acid-esters and amides, alkylphenol-polyamine-coupled Mannich adducts, their capped derivatives, and other related components. Such additives may be used in an amount of 0.1 to 20 wt%, preferably 0.1 to 8 wt%, more preferably 1 to 6 wt% (on an as-received basis) based on the weight of the total lubricant.

Pour Point Depressants

[0092] Conventional pour point depressants (also known as lube oil flow improvers) may also be present. Pour point depressant may be added to lower the minimum temperature at which the fluid will flow or can be poured. Examples of suitable pour point depressants include alkylated naphthalenes polymethacrylates, polyacrylates, polyarylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, and terpolymers of dialkylfumarates, vinyl esters of fatty acids and allyl vinyl ethers. Such additives may be used in amount of 0.0 to 0.5 wt%, preferably 0 to 0.3 wt%, more preferably 0.001 to 0.1 wt% on an as-received basis.

Corrosion Inhibitors/Metal Deactivators

[0093] Corrosion inhibitors are used to reduce the degradation of metallic parts that are in contact with the lubricating oil composition. Suitable corrosion inhibitors include aryl thiazines, alkyl substituted dimercapto thiodiazoles thiadiazoles and mixtures thereof. Such additives may be used in an amount of 0.01 to 5 wt%, preferably 0.01 to 1.5 wt%, more preferably 0.01 to 0.2 wt%, still more preferably 0.01 to 0.1 wt% (on an as-received basis) based on the total weight of the lubricating oil composition.

Seal Compatibility Additives

[0094] Seal compatibility agents help to swell elastomeric seals by causing a chemical reaction in the fluid or physical change in the elastomer. Suitable seal compatibility agents for lubricating oils include organic phosphates, aromatic esters, aromatic hydrocarbons, esters (butylbenzyl phthalate, for example), and polybutenyl succinic anhydride and sulfolane-type seal swell agents such as Lubrizol 730-type seal swell additives. Such additives may be used in an amount of 0.01 to 3 wt%, preferably 0.01 to 2 wt% on an as-received basis.

AntiFoam Agents

[0095] Antifoam agents may advantageously be added to lubricant compositions. These agents retard the formation of stable foams. Silicones and organic polymers are typical antifoam agents. For example, polysiloxanes, such as silicon oil or polydimethyl siloxane, provide antifoam properties. Antifoam agents are commercially available and may be used in conventional minor amounts along with other additives such as demulsifiers; usually the amount of these additives combined is less than 1 percent, preferably 0.001 to 0.5 wt%, more preferably 0.001 to 0.2 wt%, still more preferably 0.0001 to 0.15 wt% (on an as-received basis) based on the total weight of the lubricating oil composition.

Inhibitors and Antirust Additives

[0096] Anti-rust additives (or corrosion inhibitors) are additives that protect lubricated metal surfaces against chemical attack by water or other contaminants.

One type of anti-rust additive is a polar compound that wets the metal surface preferentially, protecting it with a film of oil. Another type of anti-rust additive absorbs water by incorporating it in a water-in-oil emulsion so that only the oil touches the surface. Yet another type of anti-rust additive chemically adheres to the metal to produce a non-reactive surface. Examples of suitable additives include zinc dithiophosphates, metal phenolates, basic metal sulfonates, fatty acids and amines. Such additives may be used in an amount of 0.01 to 5 wt%, preferably 0.01 to 1.5 wt% on an as-received basis.

[0097] In addition to the ZDDP anti-wear additives which are essential components of the present disclosure, other anti-wear additives can be present, including zinc dithiocarbamates, molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, other organo molybdenum-nitrogen complexes, sulfurized olefins, etc.

[0098] The term “organo molybdenum-nitrogen complexes” embraces the organo molybdenum-nitrogen complexes described in U.S. Patent 4,889,647. The complexes are reaction products of a fatty oil, dithanolamine and a molybdenum source. Specific chemical structures have not been assigned to the complexes. U.S. Patent 4,889,647 reports an infrared spectrum for a typical reaction product of that disclosure; the spectrum identifies an ester carbonyl band at 1740 cm^{-1} and an amide carbonyl band at 1620 cm^{-1}. The fatty oils are glyceryl esters of higher fatty acids containing at least 12 carbon atoms up to 22 carbon atoms or more. The molybdenum source is an oxygen-containing compound such as ammonium molybdates, molybdenum oxides and mixtures.

[0099] Other organo molybdenum complexes which can be used in the present disclosure are tri-nuclear molybdenum-sulfur compounds described in EP 1 040 115 and WO 99/31113 and the molybdenum complexes described in U.S. Patent 4,978,464.

[00100] In the above detailed description, the specific embodiments of this disclosure have been described in connection with its preferred embodiments. However, to the extent that the above description is specific to a particular embodiment or a particular use of this disclosure, this is intended to be illustrative only and merely provides a concise description of the exemplary embodiments. Accordingly, the disclosure is not limited to the specific embodiments described above, but rather, the disclosure includes all alternatives, modifications, and equivalents falling within the true scope of the appended claims. Various modifications and variations of this disclosure will be obvious to a worker skilled in the art and it is to be understood that such modifications and variations are to be included within the purview of this application and the spirit and scope of the claims.

EXAMPLES

[00101] PCMO (passenger car motor oil) formulations (1.1% ash) were prepared having the ingredients and the amounts listed in Table 1. The amounts are given in weight percent based on the total weight percent of the formulation. DDI is a detergent-dispersant-inhibitor package containing detergents, dispersants, ZDDP, antioxidants, defoamant, and friction modifiers. The isoprene star copolymer concentrate has a shear stability index (SSI) of 4. The Group III base stock has a viscosity of 4 cSt and a viscosity index of 133. The second Group III base stock has a viscosity of 6 cSt and a viscosity index of 146. C_8/C_{10} TMP ester is a polyol ester API Group V base stock with a KV at 100°C of 4.4 cSt. The olefin copolymer viscosity modifier (OCP VM) has a 50 SSI. Lubrizol® 730 is an alkyl sulfone and sulfolane available from Lubrizol Corporation. Vanlube® 289 is a mixture of borated alkyl diethanol amides and borated mono glycerides available from R.T. Vanderbilt Company. Hitec® 7188 is a sulfurized olefin available from Afton Corporation. Hitec® 4313 is a thiadiazole derivative available from Afton Corporation. All of the ingredients are commercially available. The MB Seal Test raw data for PCMO formulations (1.1% ash) is set forth in Table 2. A comparison of MB seal performance benefit vs. comparative example is set forth in Table 3. The sulfated ash (%) was determined by D874 test method. The data set forth in Tables 2 and 3 was generated by the Nitrile-NBR34 (MB VDA 675301 Method).

Table 1

PCMO Formulations (1.1% Ash)

Ingredients	Comp. Ex. A	Ex. 1	Ex. 2
Group III Base Stock (4 cSt)	52.98	52.63	52.76
C_8/C_{10} TMP Ester	5.00	5.00	5.00
Group III Base Stock (6 cSt)	21.00	20.85	20.92
Isoprene Star Polymer Concentrate	4.70	4.70	4.70
OCP VM Concentrate	4.50	4.50	4.50
DDI	11.82	11.82	11.82
Lubrizol® 730		0.50	
Vanlube® 289			0.30
Hitec® 7188			
Hitec® 4313			
PIB Succinic Anhydride			

Ingredients	Ex. 3	Ex. 4	Ex. 5
Group III Base Stock (4 cSt)	52.88	52.92	52.63
C_8/C_{10} TMP Ester	5.00	5.00	5.00
Group III Base Stock (6 cSt)	21.00	21.01	20.85
Isoprene Star Polymer Concentrate	4.70	4.70	4.70
OCP VM Concentrate	4.50	4.50	4.50
DDI	11.82	11.82	11.82
Lubrizol® 730			
Vanlube® 289			
Hitec® 7188	0.10		
Hitec® 4313		0.05	
PIB Succinic Anhydride			0.50

Table 2

MB Seal Test Raw Data for PCMO Formulations (1.1% Ash)

Method Description	Comp. Ex. A	Ex. 1	Ex. 2
Change in Tensile Strength (%)	-29	-16	-16
Elongation at Break (%)	-46	-36	-31
Shore-A Hardness (%)	-0.5	-2	0
Change in Volume (%)	2	3.7	2.2

Method Description	Ex. 3	Ex. 4	Ex. 5
Change in Tensile Strength (%)	-14	-4.8	-15
Elongation at Break (%)	-33	-25	-40
Shore-A Hardness (%)	-1	-1	0
Change in Volume (%)	1.9	1.9	2

Table 3

MB Seal Performance Benefit vs. Comparative Example for PCMO Formulations (1.1% Ash)

% Change vs. Comparative Example	Comp. Ex. A	Ex. 1	Ex. 2
Improvement in Tensile Strength (%)		44	44
Improvement in Elongation at Break (%)		22	33

% Change vs. Comparative Example	Ex. 3	Ex. 4	Ex. 5
Improvement in Tensile Strength (%)	51	83	48
Improvement in Elongation at Break (%)	29	46	14

[00102] Tables 1, 2 and 3 show engine oil formulations where a 1.1% ash reference formulation is treated with different additives at relatively low concentrations. Different additive chemistries are shown which provide a significant improvement in MB NBR 34 nitrile seal performance in the areas of change in tensile strength (44-83%) and elongation at break (14-46%). These improvements in NBR 34 seal performance as measured by tensile strength and elongation at break are surprising and unexpected for the inventive formulations with respect to the prior art comparative example.

[00103] PCMO formulations (0.8% ash) were prepared having the ingredients and the amounts listed in Table 4. The amounts are given in weight percent based on the total weight percent of the formulation. DDI is a detergent-dispersant-inhibitor package containing detergents, dispersants, ZDDP, antioxidants, defoamant, pour point depressant, and friction modifiers. The isoprene star copolymer concentrate has a shear stability index (SSI) of 4. The Group III base stock has a viscosity of 4 cSt and a viscosity index of 133. The second Group III base stock has a viscosity of 6 cSt and a viscosity index of 146. C_8/C_{10} TMP ester is a polyol ester API Group V base stock with a KV at 100°C of 4.4 cSt. The olefin copolymer viscosity modifier (OCP VM) has a 50 SSI. Vanlube® 289 is a mixture of borated alkyl diethanol amides and borated mono glycerides available from R.T. Vanderbilt Company. Hitec® 7188 is a sulfurized olefin available from Afton Corporation. All of the ingredients are commercially available. The MB Seal Test raw data for PCMO formulations (0.8% ash) is set forth in Table 5. A comparison of MB seal performance benefit vs. comparative example is set forth in Table 6. The sulfated ash (%) was determined by D874 test method. The data set forth in Tables 5 and 6 was generated by the Nitrile-NBR34 (MB VDA 675301 Method).

Table 4

PCMO Formulations (0.8% Ash)

Ingredients	Comp. Ex. B	Ex. 6	Ex. 7	Ex. 8
Group III Base Stock (4 cSt)	54.38	53.58	53.38	53.78
C_8/C_{10} TMP Ester	5	5	5	5
Group III Base Stock (6 cSt)	21	21	21	21
Isoprene Star Polymer Concentrate	6.5	6.6	6.6	6.6
OCP VM Concentrate	2.3	2.35	2.35	2.35
DDI	10.82	11.47	11.67	11.27
Vanlube® 289		0.30	0.50	
Hitec® 7188				0.10

Table 5

MB Seal Test Raw Data for PCMO Formulations (0.8% Ash)

Method Description	Comp. Ex. B	Ex. 6	Ex. 7	Ex. 8
Change in Tensile Strength (%)	-30	-16	-14	-12
Elongation at Break (%)	-48	-41	-33	-37
Shore-A Hardness (%)	-1	-2	-2	-1
Change in Volume (%)	2.1	2.3	2.5	2

Table 6

MB Seal Performance Benefit vs. Comparative Example for PCMO Formulations (0.8% Ash)

% Change vs. Comparative Example	Comp. Ex. B	Ex. 6	Ex. 7	Ex. 8
Improvement in Tensile Strength (%)		47	53	60
Improvement in Elongation at Break (%)		15	31	23

[00104] Tables 4, 5 and 6 show engine formulations where a 0.8% ash reference formulation is treated with different additives at relatively low concentrations. Different additive chemistries are shown which provide a significant improvement in MB nitrile seal performance in the areas of change in tensile strength (47-60%) and elongation at break (15-23%). Again, these improvements in NBR 34 seal performance as measured by tensile strength and elongation at break are surprising and unexpected for the inventive formulations with respect to the prior art comparative example.

[00105] PCMO formulations (1.4% ash) were prepared having the ingredients and the amounts listed in Table 7. The amounts are given in weight percent based on the total weight percent of the formulation. DDI is a detergent-dispersant-inhibitor package containing detergents, dispersants, ZDDP, antioxidants, defoamant, and friction modifier. The isoprene star copolymer concentrate has a shear stability index (SSI) of 4. The Group III base stock has a viscosity of 4 cSt and a viscosity index of 133. The Group IV base stock has a viscosity of 5.8 cSt at 100°C and a viscosity index of 137. C_8/C_{10} TMP ester is polyol ester API Group V base stock with a KV at 100°C of 4.4 cSt. Hitec® 4313 is a thiadiazole derivative available from Afton Corporation. All of the ingredients are commercially available. The ACEA RE-4 Seal Test raw data for PCMO formulations (1.4% ash) is set forth in Table 8. A comparison of ACEA RE-4 seal performance benefit vs. comparative example is set forth in Table 9. The sulfated ash (%) was determined by D874 test method. The data set forth in Tables 8 and 9 was generated by the CEC L-39-96 elastomer test using the RE-4 nitrile elastomer.

Table 7

PCMO Formulations (1.4% Ash)

Ingredients	Comp. Ex. C	Ex. 9
Group III Base Stock (4 cSt)	30	30
C_8/C_{10} TMP Ester	10	10
Group IV Base Stock	36.72	36.62
Alkylated Naphthalene	0.75	0.75
Isoprene Star Polymer Concentrate	4	4
DDI	18.525	18.525
Hitec® 4313		0.10

Table 8

ACEA RE-4 Nitrile Seal Test Raw Data for PCMO Formulations (1.4% Ash)

Method Description	Comp. Ex. C	Ex. 9
Change in Tensile Strength (%)	-12	0.4
Elongation at Break (%)	-38	-21
Shore-A Hardness (%)	-2	-2
Change in Volume (%)	3.4	3.6

Table 9

ACEA RE-4 Nitrile Seal Performance Benefit vs. Comparative Example for PCMO Formulations (1.4% Ash)

% Change vs. Comparative Example	Comp. Ex. C	Ex. 9
Improvement in Tensile Strength (%)		103
Improvement in Elongation at Break (%)		45

Table 10

MB Nitrile Seal Test Raw Data for PCMO Formulations (1.4% Ash)

Method Description	Comp. Ex. C	Ex. 9
Change in Tensile Strength (%)	-11	-0.4
Elongation at Break (%)	-30	-19
Shore-A Hardness (%)	-3	-4
Change in Volume (%)	4.1	4.2

Table 11

MB Nitrile Seal Performance Benefit vs. Comparative Example for PCMO Formulations (1.4% Ash)

% Change vs. Comparative Example	Comp. Ex. C	Ex. 9
Improvement in Tensile Strength (%)		96
Improvement in Elongation at Break (%)		37

[00106] Tables 7-11 show engine formulations where a 1.4% ash reference formulation is treated with a thiadiazole additive at a relatively low concentration (0.1%). Table 9 shows a significant improvement in MB nitrile seal performance in the areas of change in tensile strength (103%) and elongation at break (45%). Table 11 shows a significant improvement in MB NBR 34 nitrile seal performance in the areas of change in tensile strength (96%) and elongation at break (37%). Again, these improvements in NBR 34 seal performance as measured by tensile strength and elongation at break are surprising and unexpected for the inventive formulations with respect to the prior art comparative example.

CLAIMS:

1. A method of improving nitrile seal compatibility with a lubricating oil in an engine lubricated with the lubricating oil, said method comprising using as the lubricating oil a formulated oil comprising a lubricating oil base stock as a major component and one or more additives selected from the group consisting of (i) a sulfone, sulfolane, or derivative thereof; (ii) a borate ester, boron amide, or mixtures thereof; (iii) a sulfurized olefin; (iv) a thiadiazole or derivative thereof; and (v) a succinic anhydride or derivative thereof, as a minor component; wherein nitrile seal compatibility is improved as compared to nitrile seal compatibility achieved using a lubricating oil containing a minor component other than the one or more additives.

2. The method of claim 1 wherein the lubricating oil base stock comprises a Group I, II, III, IV, or V base oil stock, or mixtures thereof.

3. The method of claims 1 and 2 wherein the lubricating oil base stock is present in an amount from 80 weight percent to 99 weight percent, based on the total weight of the lubricating oil.

4. The method of claims 1-3 wherein (i) the sulfone, sulfolane, or derivative thereof comprises an alkyl sulfone or alkyl sulfolane; (ii) the borate ester, boron amide, or mixtures thereof comprises a mixture of borated alkyl diethanol amides and borated mono glycerides; (iii) the sulfurized olefin comprises sulfurized alpha-olefin, sulfurized isomerized alpha-olefin, sulfurized branched olefin, sulfurized cyclic olefin, or combinations of these; (iv) the thiadiazole or derivative thereof comprises an alkyl thiadiazole; and (v) the succinic anhydride or derivative thereof comprises polyisobutylene (PIB) succinic anhydride.

5. The method of claims 1-4 wherein the one or more additives are present in an amount from 0.01 weight percent to 2.0 weight percent, based on the total weight of the lubricating oil.

6. The method of claims 1-5 wherein the one or more additives are present in an amount sufficient for the lubricating oil to exhibit at least one of improved tensile strength (%) and elongation at break (%) as determined by Nitrile-NBR34 (MB VDA 675301 Method) or CEC L-39-96 elastomer test using RE-4 nitrile elastomer.

7. A lubricating engine oil comprising a lubricating oil base stock as a major component and one or more additives selected from the group consisting of (i) a sulfone, sulfolane, or derivative thereof; (ii) a borate ester, boron amide, or mixtures thereof; (iii) a sulfurized olefin; (iv) a thiadiazole or derivative thereof; and (v) a succinic anhydride or derivative thereof, as a minor component; wherein the one or more additives are present in an amount sufficient for the lubricating oil to exhibit improved nitrile seal compatibility as compared to nitrile seal compatibility achieved using a lubricating oil containing a minor component other than the one or more additives.

8. The lubricating engine oil of claim 7 wherein the lubricating oil base stock comprises a Group I, II, III, IV, or V base oil stock, or mixtures thereof.

9. The lubricating engine oil of claims 7 and 8 wherein the lubricating oil base stock comprises a poly alpha olefin (PAO) or gas-to-liquid (GTL) oil base stock.

10. The lubricating engine oil of claims 7-9 wherein the lubricating oil base stock is present in an amount from 80 weight percent to 99 weight percent, based on the total weight of the lubricating oil.

11. The lubricating engine oil of claims 7-10 wherein (i) the sulfone, sulfolane, or derivative thereof comprises an alkyl sulfone or alkyl sulfolane; (ii) the borate ester, boron amide, or mixtures thereof comprises a mixture of borated alkyl diethanol amides and borated mono glycerides; (iii) the sulfurized olefin comprises sulfurized alpha-olefin, sulfurized isomerized alpha-olefin, sulfurized branched olefin, sulfurized cyclic olefin, or combinations of these; (iv) the thiadiazole or derivative thereof comprises an alkyl thiadiazole; and (v) the succinic anhydride or derivative thereof comprises polyisobutylene (PIB) succinic anhydride.

12. The lubricating engine oil of claims 7-11 wherein the one or more additives are present in an amount from 0.01 weight percent to 2.0 weight percent, based on the total weight of the lubricating oil.

13. The lubricating engine oil of claims 7-12 wherein the one or more additives are present in an amount sufficient for the lubricating oil to exhibit at least one of improved tensile strength (%) and elongation at break (%) as determined by Nitrile-NBR34 (MB VDA 675301 Method) or CEC L-39-96 elastomer test using RE-4 nitrile elastomer.

14. The lubricating engine oil of claims 7-13 wherein the lubricating oil further comprises one or more of a viscosity improver, antioxidant, detergent, dispersant, pour point depressant, corrosion inhibitor, metal deactivator, seal compatibility additive, anti-foam agent, inhibitor, and anti-rust additive.

15. The lubricating engine oil of claims 7-14 in which the lubricating oil is a passenger vehicle engine oil.

All patents and patent applications, test procedures (such as ASTM methods, UL methods, and the like), and other documents cited herein are fully incorporated by reference to the extent such disclosure is not inconsistent with this disclosure and for all jurisdictions in which such incorporation is permitted.

When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated. While the illustrative embodiments of the disclosure have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the disclosure. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present disclosure, including all features which would be treated as equivalents thereof by those skilled in the art to which the disclosure pertains.

The present disclosure has been described above with reference to numerous embodiments and specific examples. Many variations will suggest themselves to those skilled in this art in light of the above detailed description. All such obvious variations are within the full intended scope of the appended claims.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/051602

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M135/04 C10M135/08 C10M135/36 C10M139/02 C10M129/42
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10M C10N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/213235 A1 (SAINI MANDEEP S [US] ET AL) 13 September 2007 (2007-09-13) paragraph [0059] - paragraphs [0062], [0099]; claim 1; figure 3; tables II-VIII	1-15
X	EP 1 777 285 A1 (AFTON CHEMICAL CORP [US]) 25 April 2007 (2007-04-25) paragraph [0041] - paragraph [0045]; claims 1,5,9,11,16,20,21; table 1	1-15
X	WO 2006/023317 A1 (LUBRIZOL CORP [US]; KONZMAN EDWARD [US]; LANGE RICHARD M [US]) 2 March 2006 (2006-03-02) page 2, line 3 - line 21 page 8, line 1 - page 9, line 12 page 18, line 11 - page 19, line 2; claims 1,6,11,12,14,15,16	1-15

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 November 2013	14/11/2013

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Pöllmann, Klaus

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/051602

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/051602

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 094 763 A (TOCHIGI HIROSHI [JP] ET AL) 10 March 1992 (1992-03-10) tables 1,2	1-8, 10-14
X	US 5 840 672 A (GATTO VINCENT JAMES [US]) 24 November 1998 (1998-11-24) column 1, line 15 - line 28 example 5; table 5	1-8, 10-15
X	EP 0 638 632 A2 (ETHYL PETROLEUM ADDITIVES LTD [GB]) 15 February 1995 (1995-02-15) page 2, line 1 - page 3, line 54; examples I,IV pages 4,5, line 11 - line 19; examples 5,6	1-8, 10-15
X	US 4 973 412 A (MIGDAL CYRIL A [US] ET AL) 27 November 1990 (1990-11-27) column 8, line 33 - column 9, line 39; table VI	1-4,6-8, 10-12, 14,15
X	US 6 362 136 B1 (RICHARDSON ROBERT C [US] ET AL) 26 March 2002 (2002-03-26) column 1, line 10 - line 47 column 48, line 44 - line 66; claims 13,4,21,29,30; table 1	1-5,7,8, 10-12, 14,15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2013/051602

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
US 2007213235	A1	13-09-2007	NONE			
EP 1777285	A1	25-04-2007	AT	502995	T	15-04-2011
			CN	1952090	A	25-04-2007
			EP	1777285	A1	25-04-2007
			JP	4773921	B2	14-09-2011
			JP	2007113006	A	10-05-2007
			KR	20070042446	A	23-04-2007
			US	2007087947	A1	19-04-2007
WO 2006023317	A1	02-03-2006	US	2007298984	A1	27-12-2007
			WO	2006023317	A1	02-03-2006
US 5094763	A	10-03-1992	CA	2009746	A1	10-08-1990
			DE	69004282	D1	09-12-1993
			DE	69004282	T2	28-04-1994
			EP	0382242	A1	16-08-1990
			JP	H0699701	B2	07-12-1994
			JP	H02212596	A	23-08-1990
			US	5094763	A	10-03-1992
US 5840672	A	24-11-1998	CA	2240973	A1	17-01-1999
			CN	1206041	A	27-01-1999
			DE	892037	T1	19-08-1999
			DE	69802148	D1	29-11-2001
			DE	69802148	T2	20-06-2002
			EP	0892037	A1	20-01-1999
			JP	3135229	B2	13-02-2001
			JP	3812637	B2	23-08-2006
			JP	H11228981	A	24-08-1999
			JP	2001089782	A	03-04-2001
			SG	64492	A1	27-04-1999
			US	5840672	A	24-11-1998
EP 0638632	A2	15-02-1995	AU	670883	B2	01-08-1996
			AU	7025094	A	23-02-1995
			CA	2130035	A1	14-02-1995
			DE	69423153	D1	06-04-2000
			EP	0638632	A2	15-02-1995
			GB	2280907	A	15-02-1995
			JP	H07150185	A	13-06-1995
US 4973412	A	27-11-1990	NONE			
US 6362136	B1	26-03-2002	CA	2149827	A1	24-11-1995
			EP	0684298	A2	29-11-1995
			US	6362136	B1	26-03-2002

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-15(partially)

   A method of improving nitrile seal compatibility in an engine with a lubricating oil comprising a base stock and a sulfolane or sulfone additive and a lubricating engine oil comprising a base stock and a sulfolane or sulfone additive.

   ---

2. claims: 1-15(partially)

   A method of improving nitrile seal compatibility in an engine with a lubricating oil comprising a base stock and a borate ester or boron amide additive and a lubricating engine oil comprising a base stock and a borate ester or boron amide.

   ---

3. claims: 1-15(partially)

   A method of improving nitrile seal compatibility in an engine with a lubricating oil comprising a base stock and sulfurized olefin additive and a lubricating engine oil comprising a base stock and a sulfurized olefin.

   ---

4. claims: 1-15(partially)

   A method of improving nitrile seal compatibility in an engine with a lubricating oil comprising a base stock and a thiadiazole additive and a lubricating engine oil comprising a base stock and a thiadiazole.

   ---

5. claims: 1-15(partially)

   A method of improving nitrile seal compatibility in an engine with a lubricating oil comprising a base stock and a succinic anhydride additive and a lubricating engine oil comprising a base stock and a succinic anhydride.
