



(86) Date de dépôt PCT/PCT Filing Date: 2003/01/31
(87) Date publication PCT/PCT Publication Date: 2003/08/07
(45) Date de délivrance/Issue Date: 2011/07/05
(85) Entrée phase nationale/National Entry: 2004/07/07
(86) N° demande PCT/PCT Application No.: US 2003/002995
(87) N° publication PCT/PCT Publication No.: 2003/064569
(30) Priorités/Priorities: 2002/01/31 (US60/353,735);
2003/01/28 (US10/353,169)

(51) Cl.Int./Int.Cl. *C10M 141/00* (2006.01),
C10M 101/02 (2006.01), *C10M 105/06* (2006.01),
C10M 105/34 (2006.01), *C10M 105/36* (2006.01),
C10M 105/38 (2006.01), *C10M 107/02* (2006.01),
C10M 133/56 (2006.01), *C10M 135/18* (2006.01),
C10M 135/36 (2006.01), *C10M 137/10* (2006.01),
C10M 141/08 (2006.01), *C10M 141/10* (2006.01),
C10M 141/12 (2006.01), *C10M 163/00* (2006.01),
C10M 169/04 (2006.01)

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(54) Titre : COMPOSITION D'HUILE LUBRIFIANTE POUR MOTEURS A COMBUSTION INTERNE AYANT UNE
MEILLEURE RESISTANCE A L'USURE
(54) Title: LUBRICATING OIL COMPOSITIONS FOR INTERNAL COMBUSTION ENGINES WITH IMPROVED WEAR
PERFORMANCE

(57) **Abrégé/Abstract:**

The present invention concerns a lubricating oil composition comprising an oil of lubricating viscosity; about 0.05 to about 5 weight percent of an organo molybdenum compound; and about 0.1 to about 12 weight percent of a borated polyisobutenyl mono- and bis-succinimide wherein the polyisobutenyl group has a molecular weight (Mn) from about 500 to about 2300.

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

REVISED VERSION

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
7 August 2003 (07.08.2003)

PCT

(10) International Publication Number
WO 2003/064569 A1

(51) International Patent Classification⁷: **C10M 141/00**,
169/04 // (C10M 141/00, 133:56, 137:10, 135:18) (C10M
169/04, 101:02, 107:02, 105:06, 105:34, 105:36, 105:38,
133:56, 135:18, 135:36, 137:10), C10N 10:12, 30:06,
60:14

(21) International Application Number:
PCT/US2003/002995

(22) International Filing Date: 31 January 2003 (31.01.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/353,735 31 January 2002 (31.01.2002) US
10/353,169 28 January 2003 (28.01.2003) US

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE,
SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC,
VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI,
SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN,
GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report

(88) Date of publication of the revised international search
report: 22 April 2004

(15) Information about Correction:
see PCT Gazette No. 17/2004 of 22 April 2004, Section II

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: LUBRICATING OIL COMPOSITIONS FOR INTERNAL COMBUSTION ENGINES WITH IMPROVED WEAR
PERFORMANCE

(57) Abstract: The present invention concerns a lubricating oil composition comprising an oil of lubricating viscosity; about 0.05 to about 5 weight percent of an organo molybdenum compound; and about 0.1 to about 12 weight percent of a borated polyisobutenyl mono- and bis-succinimide wherein the polyisobutenyl group has a molecular weight (Mn) from about 500 to about 2300.

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**LUBRICATING OIL COMPOSITIONS FOR INTERNAL
COMBUSTION ENGINES WITH IMPROVED WEAR PERFORMANCE**

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] This invention relates to lubricating oil compositions suitable for use in internal combustion engines.

Background

[0002] Lubricating oils for internal combustion engines contain in addition to at least one base lubricating oil, additives which enhance the performance of the lubricating oil. A variety of additives such as detergents, dispersants, friction reducers, viscosity index improvers, antioxidants, corrosion inhibitors, antiwear additives, pour point depressants, seal swell additives, and antifoam agents are used in lubricating oil compositions.

[0003] During engine operation, oil insoluble oxidation byproducts are produced. Dispersants help keep these byproducts in solution, thus diminishing their deposit on metal surfaces. Dispersants may be ashless or ash-forming in nature. So called ashless dispersants are organic materials that form substantially no ash upon combustion.

[0004] A known 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 polyolefin, such

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as ethylene-propylene polymer or 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; 3,2145,707; 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; 3,275,554; 3,438,757; 3,565,804; 3,755,433, 3,822,209, and 5,084,197. Other types of dispersants are described in U.S. Patents 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. 471071.

[0005] Antiwear and extreme pressure additives are also used in lubricating oil compositions. These additives help reduce wear of metal engine parts. Zinc dialkyldithiophosphate (ZDDP) has been used as an antiwear agent for many years. Use of alkylthiocarbamoyl compounds (bis(dibutyl)thiocarbamoyl, for example) in combination with a molybdenum compound (oxymolybdenum diisopropylphosphorodithioate sulfide, for example) and a phosphorous ester (dibutyl hydrogen phosphite, for example) as antiwear additives in lubricants is disclosed in U.S. Patent No. 4,501,678.

[0006] As high performance engines place more demands on lubricating oils, there is a need for oils with improved dispersant function.

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Summary of the Invention

[0007] The present invention concerns a lubricating oil composition comprising an oil of lubricating viscosity; about 0.05 to about 5 weight percent of an organo molybdenum compound; and about 0.1 to about 12 weight percent of a borated polyisobutenyl mono- and bis-succinimide wherein the polyisobutenyl group has a molecular weight (Mn) from about 500 to about 2300.

Detailed Description of the Invention

[0008] Engine oils contain a base lube oil and a variety of additives. These additives include detergents, dispersants, friction reducers, viscosity index improvers, antioxidants, corrosion inhibitors, antiwear additives, pour point depressants, seal compatibility additives, and antifoam agents. To be effective, these additives must be oil-soluble or oil-dispersible. By oil-soluble, it is meant that the compound is soluble in the base oil or lubricating oil composition under normal blending conditions.

[0009] The present invention concerns a lubricating oil composition comprising an oil of lubricating viscosity; about 0.05 to about 5 weight percent of an organo molybdenum compound; and about 0.1 to about 12 weight percent of a borated polyisobutenyl mono- and bis-succinimide wherein the polyisobutenyl group has a molecular weight (Mn) from about 500 to about 2300. The combination of these ingredients shows a significant improvement in engine wear protection and lube related oxidation performance.

[0010] Another aspect of this invention concerns an additive composition comprising an oil of lubricating viscosity; about 0.02 to about 5 weight percent of an organo molybdenum compound; and about 0.1 to about 12 weight percent

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of a borated polyisobutenyl mono- and bis-succinimide wherein the polyisobutenyl group has a molecular weight (Mn) from about 500 to about 2300. Lube oil compositions comprising this additive also show a significant improvements in engine wear protection and lube related oxidation performance. A further aspect of the invention encompasses a method of preparing lubricant oil compositions of the present invention.

[0011] Organic molybdenum sources useful in the present invention include all those commonly available organic molybdenum compositions known in the art, including, but not limited to molybdenum phosphorodithioates, molybdenum complexes of various amines and/or alcohols or esters, molybdenum dithiocarbamates, and/or molybdenum (trimeric) dithiocarbamates or mixtures thereof. Of these, the above molybdenum complexes, molybdenum dithiocarbamates are preferred. Preferred concentration ranges of the molybdenum compounds in the lubricating oil composition range from about 0.05 to about 5 wt% of such molybdenum sources can be effectively used, with concentration ranges of about 0.1 to about 3 wt% often being more preferred, and with concentration ranges of about 0.15 to about 2 wt% often being most preferred.

[0012] The borated moderate molecular weight polyisobutenyl mono- and bis-succinimide compounds of the present invention have an optimal molecular weight range of approximately 500 to about 2300, or preferably 1000 to about 1600, (Mn) for the polyisobutylene portion of the compound. It is observed that a compound of the present invention (approximately 1300 Mn polyisobutylene derived), when used in conjunction with the other elements of this invention, clearly provide improved performance characteristics when compared to the borated higher molecular weight (approximately 2500 Mn polyisobutylene derived) primarily bis-succinimide ashless dispersant. Preferred concentrations of the dispersant(s) of the present invention (or mixtures of such dispersants) are

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about 0.1 to about 12 weight percent or more. Often concentrations of about 0.5 to about 8 weight percent or more are preferred and concentrations of about 2 to about 8 weight percent are most preferred. We believe that at least a significant portion of the succinimide be a mono-succinimide or a mixture of mono and bis-succinimide for maximum performance benefits as described in this instant invention. At least 20% of the mixture is preferably mono-succinimide to provide the synergism of this invention.

[0013] It is often advantageous to use mixtures of the dispersants described above and other related dispersants, such as those that are boron-free, those that are primarily of higher molecular weight, those that consist of primarily mono-succinimide, bis-succinimide, or mixtures of above, those made with different amines, those that are end-capped, dispersants wherein the back-bone is derived from polymers such as other polyolefins other than polyisobutylene, such as ethylene, propylene, and all mixtures thereof and the like.

[0014] The above products can be post-reacted with various reagents such as sulfur, oxygen, formaldehyde, carboxylic acids such as oleic acid, anhydrides, polycyclic carbonates, and boron compounds such as borate esters or highly borated dispersants. The dispersants can be borated with from about 0.1 to about 5 moles of boron per mole of dispersant reaction product.

[0015] Other aspects of this invention are the additional performance advantages for wear protection (i.e., anti-wear performance) in low- to non-phosphorus lubricant compositions. Low- to non-phosphorus encompasses compositions in which the phosphorus concentration is 0% to about 0.05% by weight of the lubricant composition.

Base Oil

[0016] A wide range of lubricating oils is known in the art. Lubricating oils that are useful in the present invention 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.

[0017] Groups I, II, III, IV and V are broad categories of base oil stocks developed and defined by the American Petroleum Institute (API Publication 1509) to create guidelines for lubricant base oils. Group I base stock generally have a viscosity index of between about 80 to 120 and contains greater than about 0.03% sulfur and/or less than about 90% saturates. Group II base stocks generally have a viscosity index of between about 80 to 120, and contain less than or equal to about 0.03% sulfur and greater than or equal to about 90% saturates. Group III stock generally has a viscosity index greater than about 120 and contain less than or equal to about 0.03% sulfur and greater than about 90% saturates. Group IV includes polyalphaolefins (POA). Group V base

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stock includes base stocks not included in Groups I-IV. The table below summarizes properties of each of these five groups.

Base Stock Properties

	Saturates	Sulfur	Viscosity Index
Group I	< 90 &/or	> 0.03% &	≥ 80 & < 120
Group II	≥ 90 &	$\leq 0.03\%$ &	≥ 80 & < 120
Group III	≥ 90 &	$\leq 0.03\%$ &	≥ 120
Group IV	Defined as polyalphaolefins (PAO)		
Group V	All other base oil stocks not included in Groups I, II, III, or IV		

[0018] Natural oils include animal oils, vegetable oils (castor oil and lard oil, for example), and mineral oils. In regard to animal and vegetable oils, those 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 invention. 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.

[0019] Synthetic oils include hydrocarbon oil. Hydrocarbon oils include oils 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 are a commonly used synthetic hydrocarbon oil. By way of example, PAOs derived from C₈, C₁₀, C₁₂, C₁₄ olefins or mixtures thereof may be utilized. See U.S. Patents 4,956,122; 4,827,064; and 4,827,073.

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[0020] The number average molecular weights of the PAOs, which are known materials and generally available on a major commercial scale from suppliers such as ExxonMobil Chemical Company, Chevron-Phillips, BP-Amoco, and others, typically vary from about 250 to about 3,000, although PAO's may be made in viscosities up to about 100 cSt (100°C). The PAOs are typically comprised of relatively low molecular weight hydrogenated polymers or oligomers of alphaolefins which include, but are not limited to, C₂ to about C₃₂ alphaolefins with C₈ to about C₁₆ alphaolefins, such as 1-octene, 1-decene, 1-dodecene and the like, being preferred. The preferred polyalphaolefins are poly-1-octene, poly-1-decene and poly-1-dodecene and mixtures thereof and mixed olefin-derived polyolefins. However, the dimers of higher olefins in the range of C₁₄ to C₁₈ may be used to provide low viscosity basestocks of acceptably low volatility. Depending on the viscosity grade and the starting oligomer, the PAOs may be predominantly trimers and tetramers of the starting olefins, with minor amounts of the higher oligomers, having a viscosity range of about 1.5 to 12 cSt.

[0021] The PAO fluids may be conveniently made by the polymerization of an alphaolefin in the presence of a polymerization catalyst such as the Friedel-Crafts catalysts including, for example, aluminum trichloride, boron trifluoride or complexes of boron trifluoride with water, alcohols such as ethanol, propanol or butanol, carboxylic acids or esters such as ethyl acetate or ethyl propionate. For example the methods disclosed by U.S. Patent No. 4,149,178 or U.S. Patent No. 3,382,291 may be conveniently used herein. Other descriptions of PAO synthesis are found in the following U.S. Patent Nos. 3,742,082; 3,769,363; 3,876,720; 4,239,930; 4,367,352; 4,413,156; 4,434,408; 4,910,355; 4,956,122; and 5,068,487. The dimers of the C₁₄ to C₁₈ olefins are described in U.S.

4,218,330.

[0022] Other useful synthetic lubricating oils may also be utilized, for example, those described in the work "*Synthetic Lubricants*", Gunderson and hart, Reinhold Publ. Corp., New York, 1962.

[0023] In alkylated aromatic stocks (hydrocarbyl aromatics, for example), the alkyl substituents are typically alkyl groups of about 8 to 25 carbon atoms, usually from about 10 to 18 carbon atoms and up to three such substituents may be present, as described for the alkyl benzenes in ACS Petroleum Chemistry Preprint 1053-1058, "*Poly n-Alkylbenzene Compounds: A Class of Thermally Stable and Wide Liquid Range Fluids*", Eapen et al, Phila. 1984. Tri-alkyl benzenes may be produced by the cyclodimerization of 1-alkynes of 8 to 12 carbon atoms as described in U.S. Patent No. 5,055,626. Other alkylbenzenes are described in European Patent Application No. 168534 and U.S. Patent No. 4,658,072. Alkylbenzenes are used as lubricant basestocks, especially for low-temperature applications (arctic vehicle service and refrigeration oils) and in papermaking oils. They are commercially available from producers of linear alkylbenzenes (LABs) such as Vista Chem. Co, Huntsman Chemical Co., Chevron Chemical Co., and Nippon Oil Co. The linear alkylbenzenes typically have good low pour points and low temperature viscosities and VI values greater than 100 together with good solvency for additives. Other alkylated aromatics which may be used when desirable are described, for example, in "*Synthetic Lubricants and High Performance Functional Fluids*", Dressler, H., chap 5, (R. L. Shubkin (Ed.)), Marcel Dekker, N.Y. 1993.

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[0024] Other useful lubricant oil base stocks include wax isomerate base stocks and base oils, comprising hydroisomerized waxy stocks (e.g. waxy stocks such as gas oils, slack waxes, fuels hydrocracker bottoms, etc.), hydroisomerized Fischer-Tropsch waxes, Gas-to-Liquids (GTL) base stocks and base oils, and other wax isomerate hydroisomerized base stocks and base oils, or mixtures thereof. Fischer-Tropsch waxes, the high boiling point residues of Fischer-Tropsch synthesis, are highly paraffinic hydrocarbons with very low sulfur content. The hydroprocessing used for the production of such base stocks may use an amorphous hydrocracking/ hydroisomerization catalyst, such as one of the specialized lube hydrocracking (LHDC) catalysts or a crystalline hydrocracking/hydroisomerization catalyst, preferably a zeolitic catalyst. For example, one useful catalyst is ZSM-48 as described in U.S. Patent 5,075,269. Processes for making hydrocracked/ hydroisomerized distillates and hydrocracked/hydroisomerized waxes are described, for example, in U.S. Patents Nos. 2,817,693; 4,975,177; 4,921,594 and 4,897,178 as well as in British Patent Nos. 1,429,494; 1,350,257; 1,440,230 and 1,390,359. Particularly favorable processes are described in European Patent Application Nos. 464546 and 464547. Processes using Fischer-Tropsch wax feeds are described in US 4,594,172 and 4,943,672. Gas-to-Liquids (GTL) base oils, Fischer-Tropsch wax derived base oils, and other wax-derived hydroisomerized (wax isomerate) base oils be advantageously used in the instant invention, and may have useful kinematic viscosities at 100°C of about 3 cSt to about 50 cSt, preferably about 3 cSt to about 30 cSt, more preferably about 3.5 cSt to about 25 cSt, as exemplified by GTL 4 with kinematic viscosity of about 4.0 cSt at 100°C and a viscosity index of about 141. These Gas-to-Liquids (GTL) base oils, Fischer-Tropsch wax derived base oils, and other wax-derived hydroisomerized base oils may have useful pour points of about -20°C or lower, and under some conditions may have advantageous pour points of about -25°C or lower, with useful pour points of about -30°C to about -40°C or lower. Useful compositions

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of Gas-to-Liquids (GTL) base oils, Fischer-Tropsch wax derived base oils, and wax-derived hydroisomerized base oils are recited in U.S. Patent Nos. 6,080,301; 6,090,989, and 6,165,949 for example.

[0025] Gas-to-Liquids (GTL) base oils, Fischer-Tropsch wax derived base oils, have a beneficial kinematic viscosity advantage over conventional Group II and Group III base oils, which may be very advantageously used with the instant invention. Gas-to-Liquids (GTL) base oils can have significantly higher kinematic viscosities, up to about 20-50 cSt at 100°C, whereas by comparison commercial Group II base oils can have kinematic viscosities, up to about 15 cSt at 100°C, and commercial Group III base oils can have kinematic viscosities, up to about 10 cSt at 100°C. The higher kinematic viscosity range of Gas-to-Liquids (GTL) base oils, compared to the more limited kinematic viscosity range of Group II and Group III base oils, in combination with the instant invention can provide additional beneficial advantages in formulating lubricant compositions. Also, the exceptionally low sulfur content of Gas-to-Liquids (GTL) base oils, and other wax-derived hydroisomerized base oils, in combination with the low sulfur content of suitable olefin oligomers and/or alkyl aromatics base oils, and in combination with the instant invention can provide additional advantages in lubricant compositions where very low overall sulfur content can beneficially impact lubricant performance.

[0026] Alkylene oxide polymers and interpolymers and their derivatives containing modified terminal hydroxyl groups obtained by, for example, esterification or etherification are useful synthetic lubricating oils. By way of example, these oils may be obtained by polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (methyl-polyisopropylene glycol ether having an average molecular weight of

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about 1000, diphenyl ether of polyethylene glycol having a molecular weight of about 500-1000, and the diethyl ether of polypropylene glycol having a molecular weight of about 1000 to 1500, for example) or mono- and polycarboxylic esters thereof (the acidic acid esters, mixed C₃₋₈ fatty acid esters, or the C₁₃Oxo acid diester of tetraethylene glycol, for example).

[0027] Esters comprise a useful base stock. 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, alkyl succinic acid, alkenyl succinic acid, maleic acid, azelaic acid, suberic 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.

[0028] 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, pentaerythritol and dipentaerythritol) with alkanoic acids containing at least about 4 carbon atoms such as C₅ to C₃₀ acids (such as saturated straight chain fatty acids including caprylic acid, capric acid, 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 thereof).

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[0029] Suitable synthetic ester components include esters of trimethylol propane, trimethylol butane, trimethylol ethane, pentaerythritol and/or dipentaerythritol with one or more monocarboxylic acids containing from about 5 to about 10 carbon atoms. Such esters are widely available commercially, for example, the Mobil P-41 and P-51^{*} esters (ExxonMobil Chemical Company).

[0030] Silicon-based oils are another class of useful synthetic lubricating oils. These oils include polyalkyl-, polyaryl-, polyalkoxy-, and polyaryloxy-siloxane oils and silicate oils. Examples of suitable silicon-based oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methylhexyl)silicate, tetra-(p-tert-butylphenyl) silicate, hexyl-(4-methyl-2-pentoxy) disiloxane, poly(methyl) siloxanes, and poly-(methyl-2-methylphenyl) siloxanes.

[0031] Another class of synthetic lubricating oil is esters of phosphorous-containing acids. These include, for example, tricresyl phosphate, trioctyl phosphate, diethyl ester of decanephosphonic acid.

[0032] Another class of oils includes polymeric tetrahydrofurans and the like.

[0033] In the present invention, base stocks having a high paraffinic nature are preferred. For example, Group II and/or Group III hydroprocessed or hydrocracked base stocks, or their synthetic counterparts such as polyalphaolefin lubricating oils, or similar base oils or mixtures of similar base oils are often preferred as lubricating base stocks when used in conjunction with the components of the above inventions. Preferably, at least about 20% of the total composition should consist of such Group II or Group III base stocks, with at least about 30%, often being more preferable, and more than about 80% often being even more preferable. Gas to liquid base stocks can also be preferentially used with the components of this invention as a portion or all of the base stocks

^{*}=trade-mark

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used to formulate the finished lubricant. A mixture of all or some of such base may be used and may be preferred. In one preferred mode, the base oil that is added to lubricating systems is comprised of primarily Group II and/or Group III base stocks. Preferably, 20% of such Group II and/or Group III base stocks may be used to achieve the advantages of this invention. Optionally in this mode, lesser quantities of alternate fluids such as the above described hydrocarbyl aromatics (C_{16} monoalkylated naphthalene, for example) may be added.

[0034] Co-base stocks can also advantageously used at concentrations lower than those of the primary base stock(s) without detracting from the elements of this invention. These co-base stocks include polyalphaolefin oligomeric low and moderate and high viscosity oils, dibasic acid esters, polyol esters, other hydrocarbon oils, supplementary hydrocarbyl aromatics and the like. These co-base stocks can also include some quantity of decene-derived trimers and tetramers, and also some quantity of Group I base stocks, provided that the above Group II and or Group III type base stocks predominate and make up at least about 50% of the total base stocks contained in fluids of the present invention.

Performance Additives

[0035] The instant invention can be used with additional lubricant components in effective amounts in lubricant compositions, such as for example polar and/or non-polar lubricant base oils, and performance additives such as for example, but not limited to, oxidation inhibitors, metallic and non-metallic dispersants, metallic and non-metallic detergents, corrosion and rust inhibitors, metal deactivators, anti-wear agents (metallic and non-metallic, phosphorus-containing and non-phosphorus, sulfur-containing and non-sulfur types), extreme pressure additives (metallic and non-metallic, phosphorus-containing and non-phosphorus, sulfur-containing and non-sulfur types), anti-seizure

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agents, pour point depressants, wax modifiers, viscosity modifiers, seal compatibility agents, friction modifiers, lubricity agents, anti-staining agents, chromophoric agents, defoamants, demulsifiers, 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, which also gives a good discussion of a number of the lubricant additives discussed mentioned below. Reference is also made "*Lubricant Additives*" by M. W. Ranney, published by Noyes Data Corporation of Parkridge, N.J. (1973).

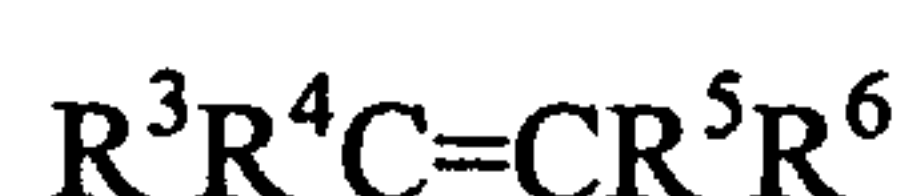
Antiwear and Extreme Pressure Additives

[0036] Additional antiwear additives may be used with the present invention. While there are many different types of antiwear additives, for several decades the principal antiwear additive for internal combustion engine crankcase oils is a metal alkylthiophosphate and more particularly a metal dialkyldithiophosphate in which the primary metal constituent is zinc, or zinc dialkyldithiophosphate (ZDDP). ZDDP compounds generally are of the formula $\text{Zn}[\text{SP}(\text{S})(\text{OR}^1)(\text{OR}^2)]_2$ where R^1 and R^2 are C_1 - C_{18} alkyl groups, preferably C_2 - C_{12} alkyl groups. These alkyl groups may be straight chain or branched. For example, suitable alkyl groups include isopropyl, 4-methyl-2-pentyl, and isooctyl. The ZDDP is typically used in amounts of from about 0.4% to about 1.4 wt% of the total lube oil composition, although more or less can often be used advantageously.

[0037] However, it is found that the phosphorus from these additives has a deleterious effect on the catalyst in catalytic converters and also on oxygen sensors in automobiles. One way to minimize this effect is to replace some or all of the ZDDP with phosphorus-free antiwear additives.

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[0038] A variety of non-phosphorous additives are also used as antiwear additives. Sulfurized olefins are useful as antiwear and EP additives. Sulfur-containing olefins can be prepared by sulfurization or various organic materials including aliphatic, arylaliphatic or alicyclic olefinic hydrocarbons containing from about 3 to 30 carbon atoms, preferably 3-20 carbon atoms. The olefinic compounds contain at least one non-aromatic double bond. Such compounds are defined by the formula



where each of R^3 - R^6 are independently hydrogen or a hydrocarbon radical. Preferred hydrocarbon radicals are alkyl or alkenyl radicals. Any two of R^3 - R^6 may be connected so as to form a cyclic ring. Additional information concerning sulfurized olefins and their preparation can be found in U.S. Patent No. 4,941,984, incorporated by reference herein in its entirety.

[0039] The use of polysulfides of thiophosphorous acids and thiophosphorous acid esters as lubricant additives is disclosed in U.S. Patent Nos. 2,443,264; 2,471,115; 2,526,497; and 2,591,577. Addition of phosphorothionyl disulfides as an antiwear, antioxidant, and EP additives is disclosed in U.S. Patent No. 3,770,854. Use of alkylthiocarbamoyl compounds (bis(dibutyl)thiocarbamoyl, for example) in combination with a molybdenum compound (oxymolybdenum diisopropylphosphorodithioate sulfide, for example) and a phosphorous ester (dibutyl hydrogen phosphite, for example) as antiwear additives in lubricants is disclosed in U.S. Patent No. 4,501,678. U.S. Patent No. 4,758,362 discloses use of a carbamate additive to provide improved antiwear and extreme pressure properties. The use of thiocarbamate as an antiwear additive is disclosed in U.S. Patent No. 5,693,598. Thiocarbamate/molybdenum complexes such as moly-sulfur alkyl dithiocarbamate trimer complex ($R=C_8-C_{18}$ alkyl) are also useful

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antiwear agents.

[0040] Esters of glycerol may be used as antiwear agents. For example, mono-, di, and tri-oleates, mono-palmitates and mono-myristates may be used.

[0041] ZDDP is combined with other compositions that provide antiwear properties. U.S. Patent No. 5,034,141 discloses that a combination of a thiodixanthogen compound (octylthiodixanthogen, for example) and a metal thiophosphate (ZDDP, for example) can improve antiwear properties. U.S. Patent No. 5,034,142 discloses that use of a metal alkyoxyalkylxanthate (nickel ethoxyethylxanthate, for example) and a dixanthogen (diethoxyethyl dixanthogen, for example) in combination with ZDDP improves antiwear properties.

[0042] Antiwear additives may be used in an amount of about 0.01 to 6 wt%, preferably about 0.01 to 4 wt%.

Viscosity Index Improvers

[0043] Viscosity index improvers (also known as VI improvers, viscosity modifiers, and viscosity improvers) provide lubricants with high and low temperature operability. These additives impart shear stability at elevated temperatures and acceptable viscosity at low temperatures.

[0044] Suitable viscosity index 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

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of these polymers are between about 10,000 to 1,000,000, more typically about 20,000 to 500,00, and even more typically between about 50,000 and 200,000.

[0045] Examples of suitable viscosity index 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 about 50,000 to 200,000 molecular weight.

[0046] Viscosity index improvers may be used in an amount of about 0.01 to 6 weight percent, preferably about 0.01 to 4 weight percent.

Antioxidants

[0047] Antioxidants retard the oxidative degradation of base oils during service. Such degradation may result in deposits on metal surfaces, the presence of sludge, or a viscosity increase in the lubricant. One skilled in the art knows a wide variety of oxidation inhibitors that are useful in lubricating oil compositions. See, Klamann in *Lubricants and Related Products*, *op cite*, and U.S. Patent Nos. 4,798,684 and 5,084,197, for example. Useful antioxidants include hindered phenols. These phenolic antioxidants may be ashless (metal-free) phenolic compounds or neutral or basic metal salts of certain phenolic compounds. Typical phenolic antioxidant compounds are the hindered phenolics

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which are the ones 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 C₆+ 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; and 2-methyl-6-t-butyl-4-dodecyl phenol. Other useful hindered mono-phenolic antioxidants may include for example hindered 2,6-di-alkyl-phenolic propionic ester derivatives. Bis-phenolic antioxidants may also be advantageously used in combination with the instant invention. Examples of ortho coupled phenols include: 2,2'-bis(6-t-butyl-4-heptyl phenol); 2,2'-bis(6-t-butyl-4-octyl phenol); and 2,2'-bis(6-t-butyl-4-dodecyl phenol). Para coupled bis phenols include for example 4,4'-bis(2,6-di-t-butyl phenol) and 4,4'-methylene-bis(2,6-di-t-butyl phenol).

[0048] Non-phenolic oxidation inhibitors which may be used include aromatic amine antioxidants and these may be used either as such or in combination with phenolics. Typical examples of non-phenolic antioxidants include: alkylated and non-alkylated aromatic amines such as aromatic monoamines of the formula R⁸R⁹R¹⁰N where R⁸ is an aliphatic, aromatic or substituted aromatic group, R⁹ is an aromatic or a substituted aromatic group, and R¹⁰ is H, alkyl, aryl or R¹¹S(O)_xR¹² where R¹¹ is an alkylene, alkenylene, or aralkylene group, R¹² is a higher alkyl group, or an alkenyl, aryl, or alkaryl group, and x is 0, 1 or 2. The aliphatic group R⁸ may contain from 1 to about 20 carbon atoms, and preferably contains from 6 to 12 carbon atoms. The aliphatic group is a saturated aliphatic group. Preferably, both R⁸ and R⁹ are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring

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aromatic group such as naphthyl. Aromatic groups R^8 and R^9 may be joined together with other groups such as S.

[0049] Typical aromatic amines antioxidants have alkyl substituent groups of at least about 6 carbon atoms. Examples of aliphatic groups include hexyl, heptyl, octyl, nonyl, and decyl. Generally, the aliphatic groups will not contain more than about 14 carbon atoms. The general types of amine antioxidants useful in the present compositions include diphenylamines, phenyl naphthylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more aromatic amines are also useful. Polymeric amine antioxidants can also be used. Particular examples of aromatic amine antioxidants useful in the present invention include: p,p'-dioctyldiphenylamine; t-octylphenyl-alpha-naphthylamine; phenyl-alphanaphthylamine; and p-octylphenyl-alpha-naphthylamine.

[0050] Sulfurized alkyl phenols and alkali or alkaline earth metal salts thereof also are useful antioxidants. Low sulfur peroxide decomposers are useful as antioxidants.

[0051] Another class of antioxidant used in lubricating oil compositions is 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.

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[0052] Preferred antioxidants include hindered phenols, arylamines, low sulfur peroxide decomposers and other related components. These antioxidants may be used individually by type or in combination with one another. Such additives may be used in an amount of about 0.01 to 5 weight percent, preferably about 0.01 to 1.5 weight percent.

Detergents

[0053] Detergents are commonly used in lubricating compositions. A typical detergent is an anionic material that contains a long chain oleophilic portion of the molecule and a smaller anionic or oleophobic portion of the molecule. The anionic portion of the detergent is typically derived from an organic acid such as a sulfur acid, carboxylic acid, phosphorous acid, phenol, or mixtures thereof. The counter ion is typically an alkaline earth or alkali metal.

[0054] Salts that contain a substantially stoichiometric amount of the metal are described as neutral salts and have a total base number (TBN, as measured by ASTM D2896) of from 0 to 80. Many compositions are overbased, containing large amounts of a metal base that is achieved by reacting an excess of a metal compound (a metal hydroxide or oxide, for example) with an acidic gas (such as carbon dioxide). Useful detergents can be neutral, mildly overbased, or highly overbased.

[0055] It is desirable for at least some detergent to be overbased. Overbased detergents help neutralize acidic impurities produced by the combustion process and become entrapped in the oil. Typically, the overbased material has a ratio of metallic ion to anionic portion of the detergent of about 1.05:1 to 50:1 on an equivalent basis. More preferably, the ratio is from about 4:1 to about 25:1. The resulting detergent is an overbased detergent that will typically have a TBN of

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about 150 or higher, often about 250 to 450 or more. Preferably, the overbasing cation is sodium, calcium, or magnesium. A mixture of detergents of differing TBN can be used in the present invention.

[0056] Preferred detergents include the alkali or alkaline earth metal salts of sulfates, phenates, carboxylates, phosphates, and salicylates.

[0057] Sulfonates may be prepared from sulfonic acids that are typically obtained by sulfonation of alkyl substituted aromatic hydrocarbons. Hydrocarbon examples include those obtained by alkylating benzene, toluene, xylene, naphthalene, biphenyl and their halogenated derivatives (chlorobenzene, chlorotoluene, and chloronaphthalene, for example). The alkylating agents typically have about 3 to 70 carbon atoms. The alkaryl sulfonates typically contain about 9 to about 80 carbon or more carbon atoms, more typically from about 16 to 60 carbon atoms.

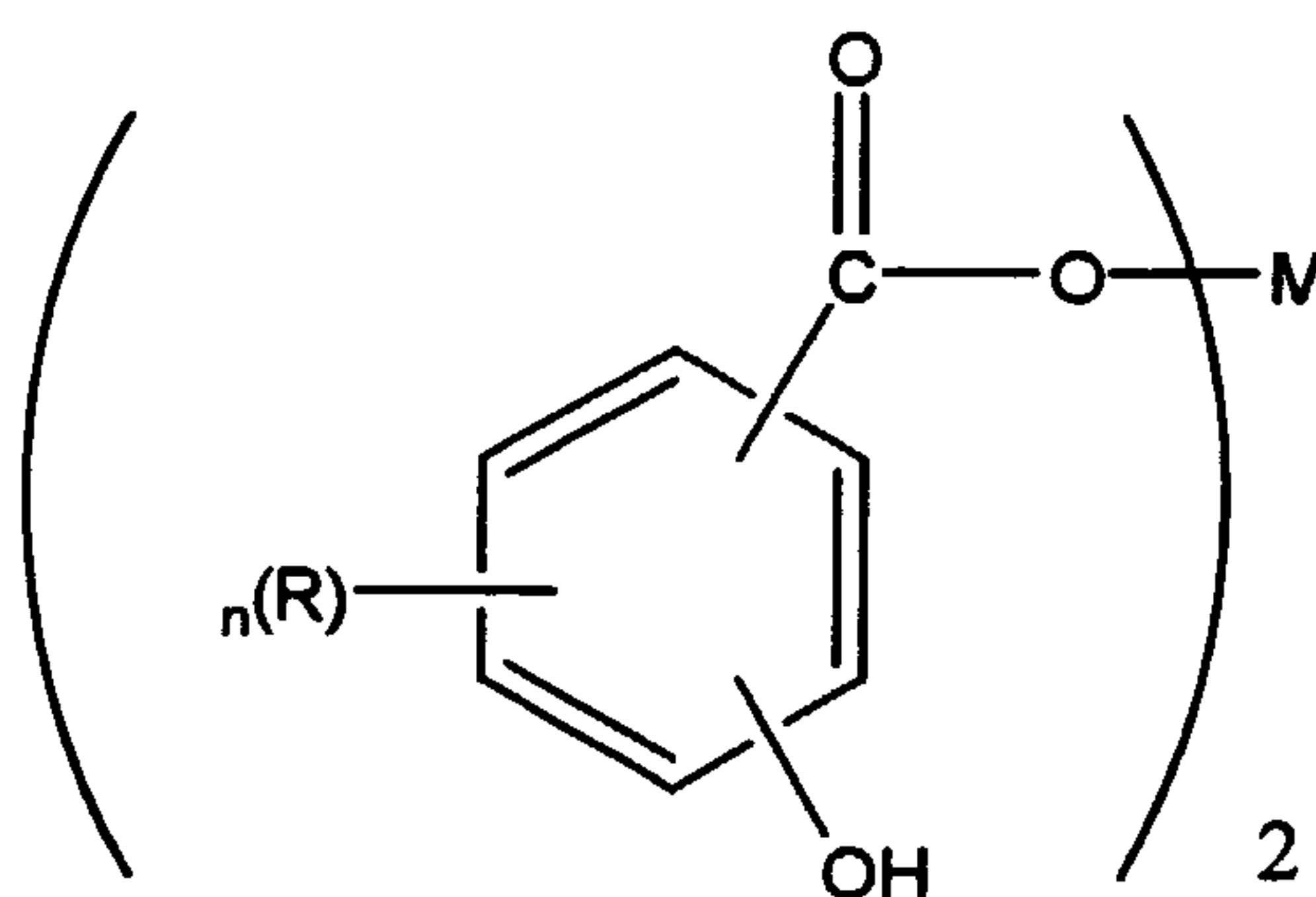
[0058] Klamann in *Lubricants and Related Products*, *op cit* discloses a number of overbased metal salts of various sulfonic acids which are useful as detergents and dispersants in lubricants. The book entitled "*Lubricant Additives*", C. V. Smallheer and R. K. Smith, published by the Lezius-Hiles Co. of Cleveland, Ohio (1967), similarly discloses a number of overbased sulfonates which are useful as dispersants/detergents.

[0059] Alkaline earth phenates are another useful class of detergent. These detergents can be made by reacting alkaline earth metal hydroxide or oxide (CaO, Ca(OH)₂, BaO, Ba(OH)₂, MgO, Mg(OH)₂, for example) with an alkyl phenol or sulfurized alkylphenol. Useful alkyl groups include straight chain or branched C₁-C₃₀ alkyl groups, preferably, C₄-C₂₀. Examples of suitable phenols include isobutylphenol, 2-ethylhexylphenol, nonylphenol, 1-ethyldecylphenol,

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and the like. It should be noted that starting alkylphenols may contain more than one alkyl substituent that are each independently straight chain or branched. When a non-sulfurized alkylphenol is used, the sulfurized product may be obtained by methods well known in the art. These methods include heating a mixture of alkylphenol and sulfurizing agent (including elemental sulfur, sulfur halides such as sulfur dichloride, and the like) and then reacting the sulfurized phenol with an alkaline earth metal base.

[0060] Metal salts of carboxylic acids are also useful as detergents. These carboxylic acid detergents may be prepared by reacting a basic metal compound with at least one carboxylic acid and removing free water from the reaction product. These compounds may be overbased to produce the desired TBN level. Detergents made from salicylic acid are one preferred class of detergents derived from carboxylic acids. Useful salicylates include long chain alkyl salicylates. One useful family of compositions is of the formula



where R is a hydrogen atom or an alkyl group having 1 to about 30 carbon atoms, n is an integer from 1 to 4, and M is an alkaline earth metal. Preferred R groups are alkyl chains of at least about C₁₁, preferably C₁₃ or greater. R may be optionally substituted with substituents that do not interfere with the detergent's function. M is preferably, calcium, magnesium, or barium. More preferably, M is calcium.

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[0061] Hydrocarbyl-substituted salicylic acids may be prepared from phenols by the Kolbe reaction. See U.S. Patent No. 3,595,791 for additional information on synthesis of these compounds. The metal salts of the hydrocarbyl-substituted salicylic acids may be prepared by double decomposition of a metal salt in a polar solvent such as water or alcohol.

[0062] Alkaline earth metal phosphates are also used as detergents.

[0063] Detergents may be simple detergents or what is known as hybrid or complex detergents. The latter detergents can provide the properties of two detergents without the need to blend separate materials. See U.S. Patent No. 6,034,039 for example.

[0064] Preferred detergents include calcium phenates, calcium sulfonates, calcium salicylates, magnesium phenates, magnesium sulfonates, magnesium salicylates and other related components (including borated detergents). Typically, the total detergent concentration is about 0.01 to about 6.0 weight percent, preferably, about 0.1 to 0.4 weight percent.

Pour Point Depressants

[0065] Conventional pour point depressants (also known as lube oil flow improvers) may be added to the compositions of the present invention if desired. These pour point depressant may be added to lubricating compositions of the present invention to lower the minimum temperature at which the fluid will flow or can be poured. Examples of suitable pour point depressants include 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.

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U.S. Patent Nos. 1,815,022; 2,015,748; 2,191,498; 2,387,501; 2,655, 479; 2,666,746; 2,721,877; 2,721,878; and 3,250,715 describe useful pour point depressants and/or the preparation thereof. Such additives may be used in an amount of about 0.01 to 5 weight percent, preferably about 0.01 to 1.5 weight percent.

Corrosion Inhibitors

[0066] Corrosion inhibitors are used to reduce the degradation of metallic parts that are in contact with the lubricating oil composition. Suitable corrosion inhibitors include thiadizoles. See, for example, U.S. Patent Nos. 2,719,125; 2,719,126; and 3,087,932. Such additives may be used in an amount of about 0.01 to 5 weight percent, preferably about 0.01 to 1.5 weight percent.

Seal Compatibility Additives

[0067] 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. Additives of this type are commercially available. Such additives may be used in an amount of about 0.01 to 3 weight percent, preferably about 0.01 to 2 weight percent.

Anti-Foam Agents

[0068] Anti-foam agents may advantageously be added to lubricant compositions. These agents retard the formation of stable foams. Silicones and organic polymers are typical anti-foam agents. For example, polysiloxanes, such as

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silicon oil or polydimethyl siloxane, provide antifoam properties. Anti-foam 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 and often less than 0.1 percent.

Inhibitors and Antirust Additives

[0069] Antirust additives (or corrosion inhibitors) are additives that protect lubricated metal surfaces against chemical attack by water or other contaminants. A wide variety of these are commercially available; they are referred to also in Klamann, *op. cit.*

[0070] One type of antirust additive is a polar compound that wets the metal surface preferentially, protecting it with a film of oil. Another type of antirust additive absorbs water by incorporating it in a water-in-oil emulsion so that only the oil touches the metal surface. Yet another type of antirust 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 about 0.01 to 5 weight percent, preferably about 0.01 to 1.5 weight percent.

Friction modifiers

[0071] A friction modifier is any material or materials that can alter the coefficient of friction of any lubricant or fluid containing such material(s). Friction modifiers, also known as friction reducers, or lubricity agents or oiliness agents, and other such agents that change the coefficient of friction of lubricant base oils, formulated lubricant compositions, or functional fluids, may be

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effectively used in combination with the base oils or lubricant compositions of the present invention if desired. Friction modifiers that lower the coefficient of friction are particularly advantageous in combination with the base oils and lube compositions of this invention. Friction modifiers may include metal-containing compounds or materials as well as ashless compounds or materials, or mixtures thereof. Metal-containing friction modifiers may include metal salts or metal-ligand complexes where the metals may include alkali, alkaline earth, or transition group metals. Such metal-containing friction modifiers may also have low-ash characteristics. Transition metals may include Mo, Sb, Sn, Fe, Cu, Zn, and others. Ligands may include hydrocarbyl derivative of alcohols, polyols, glycerols, partial ester glycerols, thiols, carboxylates, carbamates, thiocarbamates, dithiocarbamates, phosphates, thiophosphates, dithiophosphates, amides, imides, amines, thiazoles, thiadiazoles, dithiazoles, diazoles, triazoles, and other polar molecular functional groups containing effective amounts of O, N, S, or P, individually or in combination. In particular, Mo-containing compounds can be particularly effective such as for example Mo-dithiocarbamates, Mo(DTC), Mo-dithiophosphates, Mo(DTP), Mo-amines, Mo (Am), Mo-alcoholates, Mo-alcohol-amides, etc.

[0072] Ashless friction modifiers may have also include lubricant materials that contain effective amounts of polar groups, for example hydroxyl-containing hydrocarbyl base oils, glycerides, partial glycerides, glyceride derivatives, and the like. Polar groups in friction modifiers may include hydrocarbyl groups containing effective amounts of O, N, S, or P, individually or in combination. Other friction modifiers that may be particularly effective include, for example, salts (both ash-containing and ashless derivatives) of fatty acids, fatty alcohols, fatty amides, fatty esters, hydroxyl-containing carboxylates, and comparable synthetic long-chain hydrocarbyl acids, alcohols, amides, esters, hydroxy

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carboxylates, and the like. In some instances fatty organic acids, fatty amines, and sulfurized fatty acids may be used as suitable friction modifiers.

[0073] Useful concentrations of friction modifiers may range from about 0.01 wt% to 10-15 wt% or more, often with a preferred range of about 0.1 wt% to 5 wt%. Concentrations of molybdenum containing materials are often described in terms of Mo metal concentration. Advantageous concentrations of Mo may range from about 10 ppm to 3000 ppm or more, and often with a preferred range of about 20-2000 ppm, and in some instances a more preferred range of about 30-1000 ppm. Friction modifiers of all types may be used alone or in mixtures with the materials of this invention. Often mixtures of two or more friction modifiers, or mixtures of friction modifiers(s) with alternate surface active material(s), are also desirable.

Typical Additive Amounts

[0074] When lubricating oil compositions contain one or more of the additives discussed above, the additive(s) are blended into the composition in an amount sufficient for it to perform its intended function. Typical amounts of such additives useful in the present invention are shown in the Table 1 below.

[0075] Note that many of the additives are shipped from the manufacturer and used with a certain amount of base oil solvent in the formulation. Accordingly, the weight amounts in the table below, as well as other amounts mentioned in this patent, are directed to the amount of active ingredient (that is the non-solvent or non-diluent oil portion of the ingredient). The weight percents indicated below are based on the total weight of the lubricating oil composition.

Table 1. Typical Amounts of Various Lubricant Oil Components

Compound	Approximate Weight Percent (Useful)	Approximate Weight Percent (Preferred)
Detergent	0.01-6	0.01-4
Dispersant	0.1-20	0.1-8
Friction Reducer	0.01-5	0.01-1.5
Viscosity Index Improver	0.0-40	0.01-30, more preferably 0.01 to 15
Antioxidant	0.01-5	0.01-1.5
Corrosion Inhibitor	0.01-5	0.01-1.5
Anti-wear Additive	0.01-6	0.01-4
Pour Point Depressant	0.0-5	0.01-1.5
Anti-foam Agent	0.001-3	0.001-0.15
Base Oil	Balance	balance

Experimental

[0076] The types and quantities of performance additives used in combination with the instant invention in lubricant compositions are not limited by the examples shown herein as illustrations.

[0077] Unless otherwise specified, kinematic viscosity at 40°C or 100°C is determined according to ASTM test method D 445, viscosity index is determined by ASTM test method D 2270, pour point is determined by ASTM test method D 97, and TBN by ASTM test method number D 2896.

Examples 2.1-2.4: Lubricant Wear Performance

[0078] The wear properties of lubricant oils of differing compositions are measured using Sequence IVA industry-approved engine testing (ASTM Research Report RR:D02-1473) to evaluate wear performance under severe conditions. The Sequence IVA (Nissan KA24E)* engine test measures the average wear at seven different positions along the flank of 12 cam lobes. For each cam lobe, the average wear at the seven locations are summed to determine

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the individual lobe 7-point wear. Then the 7-point wear of all 12 lobes are averaged and a final average 7-point cam lobe result is reported in microns. Lower wear numbers are beneficial and desirable. Oils with 7-point wear of $\leq 120\mu$ meet the Sequence IVA wear requirements of performance categories such as API SL and ILSAC GF-3. Test results for this invention are shown in Table 2.

[0079] Each of the above oils tested contained approximately 7% of hydrocarbyl aromatic comprising C₁₆ monoalkylated naphthalene, and is formulated with an additives package which includes detergents, inhibitors, viscosity index improvers, defoamants, supplementary dispersants, and the like.

[0080] Example 2.1 illustrates the Sequence IVA wear performance of a high wear oil exhibiting 210 microns of wear and is formulated with approximately 4.5% of a high molecular weight (derived from approximately 2500 Mn polyisobutylene) borated bissuccinimide dispersant, approximately 1.0% of an organic molybdenum compound (not containing sulfur but made from molybdenum and hydroxyl-containing nitrogen compounds), and approximately 0.5% of an auxiliary heterocyclic sulfur source. The formulation of Example 1.1 also contains 0% ZDDP which is traditionally used as an antiwear agent. This lubricant composition performs poorly on the Sequence IVA test, resulting in 210 microns of wear.

[0081] Example 2.2 illustrates the Sequence IVA wear performance of a high wear oil exhibiting 289 microns of wear and is formulated with approximately 4.5% of a high molecular weight (derived from approximately 2500 Mn polyisobutylene) borated bissuccinimide dispersant and approximately 0.35% of a molybdenum (trimer) dithiocarbamate. This formulation also contains 0% ZDDP which is traditionally used as an antiwear agent. This lubricant composi-

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tion performs poorly on the Sequence IVA test, resulting in 289 microns of wear.

[0082] Example 2.3 illustrates the Sequence IVA wear performance of an exceptionally low wear oil and exhibits a surprisingly low 44 microns of wear, well below industry accepted standards. This outstanding wear performance oil is formulated with approximately 7% of a moderate molecular (derived from approximately 1300 Mn polyisobutylene) weight borated mono- and bissuccinimide dispersant, and approximately 0.35% of a molybdenum (trimer) dithiocarbamate. In addition, this oil contains 0% ZDDP and 0% phosphorus. This lubricant composition performed surprisingly well on the Sequence IVA test, resulting in only 44 microns of wear.

[0083] Example 2.4 illustrates the Sequence IVA wear performance of a high wear oil exhibiting 134 microns of wear and is formulated with approximately 7% of a moderate molecular (derived from approximately 1300 Mn polyisobutylene) weight borated mono- and bissuccinimide dispersant and no added molybdenum. This oil also contains 0% ZDDP. This oil performs poorly on the Sequence IVA test, resulting in 134 microns of wear.

[0084] Table 1a shows another aspect of this invention. It is anticipated that wear benefits can be obtained for other combinations of moderate molecular (derived from approximately 1300 Mn polyisobutylene) weight borated mono- and bissuccinimide dispersant and molybdenum (trimer) dithiocarbamate combined with some hydrocarbyl aromatic base stock. This invention can also provide advantageous wear benefits both in hydroprocessed base stocks and Group III base stocks. Concentration ranges where benefits are expected range from 2 to 10% for the borated dispersant, 0.1 to 2% for the molybdenum (trimer) dithiocarbamate combined with hydrocarbyl aromatics ranging from 3% to 15%.

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These embodiments can be advantageously used in both hydroprocessed base stock (e.g., HDT A) and GpIII base stocks.

[0085] These above results clearly show the beneficial effect of using moderate molecular weight borated mono- and bis-succinimide dispersant and organic molybdenum compound. Additionally, beneficial effects derive from the addition of low levels of hydrocarbyl aromatic contained in the lubricants tested for wear control in the above Sequence IVA tests. It is also significant to note that excellent wear performance is obtained in the absence of ZDDP or phosphorus. This indicates that this invention can also be useful for engines that require low levels of phosphorus (e.g., about 0.05% or less) or even phosphorus-free lubricants to both protect certain emissions catalysts and provide enhanced engine performance. In addition, because ZDDP produces sulfated ash, the additive combinations embodied in this invention can be even more useful in engines that require reduced levels of sulfated ash in lubricant oils in order to protect engine exhaust after treatment devices.

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Table 2. Engine Wear Test Results

Example:	2.1	2.2	2.3	2.4
High MW borated bis-succinimide	4.5	4.5	0.0	0.0
Low MW borated mono & bis-succinimide	0.0	0.0	7.0	7.0
Polybutenyl succinate ester/imide mixture	2.5	2.5	0.0	0.0
Detergent/Dispersant/Inhibitor performance package	8.8	8.8	8.8	8.8
Dimercaptothiadiazole derivative	0.5	0.0	0.0	0.0
Organic molybdenum additive	1.0	0.0	0.0	0.0
Trimeric molybdenum dithiocarbamate	0.0	0.35	0.35	0.0
4 cSt PAO	Bal	Bal	Bal	Bal
Hydrocarbyl aromatic	7	7	7	7
Blend Physical Properties				
Phosphorous (calculated), ppm	0	0	0	0
Boron (calculated), ppm	104	104	665	665
Molybdenum (calculated), ppm	800	197	197	0.0
Engine Test Wear Results				
Nissan KA24E 7-Point Wear, μ	210	289	44	134

[0086] Lubricant compositions cited below are examples of the instant invention, with such compositions not limiting the invention.

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Table 3. Lubricant Compositions

Example	3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8
Low MW borated mono & bis-succinimide	2	10	2	10	2	10	2	10
Detergent/Dispersant/Inhibitor performance package	8.8	9.3	8.8	8.8	8.8	8.8	9.3	8.8
Trimeric molybdenum dithiocarbamate	0.1	0.1	1	1	0.1	0.1	1	1
Ester			5					
150N Group I Base Stock								5
Hydrocarbyl aromatic	3	3	3	3	15	15	15	15
HDT A	Bal	Bal	Bal	Bal	Bal	Bal	Bal	Bal
Blend Physical Properties								
Phosphorous (calculated), ppm	0	500	0	0	0	0	500	0
Boron (calculated), ppm	180	950	180	950	180	950	180	950
Molybdenum (calculated), ppm	56	56	560	560	56	56	560	560

Component	3.9	3.10	3.11	3.12	3.13	3.14	3.15	3.16
Low MW borated mono & bis-succinimide	2	10	2	10	2	10	2	10
Detergent/Dispersant/Inhibitor performance package	8.8	8.8	8.8	9.3	9.3	8.8	8.8	8.8
Trimeric molybdenum dithiocarbamate	0.1	0.1	1	1	0.1	0.1	1	1
Ester							2	
150N Group I Base Stock			10					
Hydrocarbyl aromatic	3	3	3	3	15	15	15	15
GpIII 4	Bal	Bal	Bal	Bal	Bal	Bal	Bal	Bal
Blend Physical Properties								
Phosphorous (calculated), ppm	0	0	0	500	500	0	0	0
Boron (calculated), ppm	180	950	180	950	180	950	180	950
Molybdenum (calculated), ppm	56	56	560	560	56	56	560	560

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Examples 4.1-4.4: Lubricant Oxidation and Corrosion Performance

[0087] Synergistic combinations of borated mono- and bis-succinimide dispersant and organic molybdenum compound improve lubricant oxidation and corrosion performance. Catalytic oxidation testing is performed using several groups of different components as detailed in Table 4. The results exemplify the superior properties of the compositions of the present invention. Various physical tests are performed on the oils. ASTM test methods for these are listed in Table 4.

[0088] The Catalytic Oxidation Test may be summarized as follows. The test lubricant composition is subjected to a stream of air which is bubbled through the composition at a rate of 5 liters per hour. Present in the composition are metals commonly used as materials of engine construction, namely:

- (a) 15.6 sq. in. of sand-blasted iron wire,
- (b) 0.78 sq. in. of polished copper wire.
- (c) 0.87 sq. in. of polished aluminum wire, and
- (d) 0.167 sq. in. of polished lead surface.

Lubricant performance is rated on the basis of prevention of oil deterioration as measured by the increase in acid formation or neutralization number (NN) and kinematic viscosity (KV) occasioned by the oxidation. The sludge formation during the oxidation is estimated visually.

[0089] In Example 4.1, approximately 8% of a moderate molecular weight (derived from approximately 1300 Mn polyisobutylene) borated mono- and bissuccinimide dispersant and approximately 0.17% of molybdenum (trimeric) dithiocarbamate is evaluated with approximately 0.2% mixed zinc dialkyl

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dithiophosphates (ZDDP) in a polyalphaolefin oil (PAO) derived from olefins comprising 1-decene and comprising an additional approximately 7% of hydrocarbyl aromatic fluid ("alkylated aromatic", primarily C₁₆ monoalkylated naphthalene). This oil performs outstandingly well, yielding an end of test viscosity increase of approximately 8.1%, and an exceptionally good and low lead loss of approximately 0.8-mg, with no (nil) sludge. This oil performs exceedingly well in high-temperature oxidative applications where wear metals or bearing metals can accelerate deleterious effects of oxidation.

[0090] In Example 4.2, approximately 8% of a moderate molecular weight (derived from approximately 1300 Mn polyisobutylene) borated mono- and bissuccinimide dispersant is evaluated with approximately 0.2% secondary zinc dialkyl dithiophosphates in a polyalphaolefin oil derived from olefins comprising 1-decene and comprising an additional approximately 7% of hydrocarbyl aromatic fluid (primarily C₁₆ monoalkylated naphthalene). This oil performed poorly, yielding an end of test viscosity increase of approximately 28.8%, and giving an exceptionally poor and high lead loss of approximately 31.5-mg, with a trace of sludge.

[0091] In Example 4.3, approximately 8% of a relatively high molecular weight (derived from approximately 2300 Mn polyisobutylene) non-borated bissuccinimide dispersant and approximately 0.17% of molybdenum (trimeric) dithiocarbamate is evaluated with approximately 0.2% secondary zinc dialkyl dithiophosphates in a polyalphaolefin oil derived from olefins comprising 1-decene and comprising an additional approximately 7% of hydrocarbyl aromatic fluid (primarily C₁₆ monoalkylated naphthalene). This oil performed poorly, yielding an end of test exceptionally poor and high lead loss of approximately 21.3 mg, with light of sludge.

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[0092] Table 5 shows lubricant compositions which are expected to demonstrate the performance benefits of this invention. It is anticipated that oxidation, sludge control, and corrosion control benefits can be obtained for other combinations of moderate molecular (derived from approximately 1300 Mn polyisobutylene) weight borated mono- and bissuccinimide dispersant, molybdenum (trimer) dithiocarbamate, and ZDDP combined with some hydrocarbyl aromatic base stock. This invention can provide oxidation, sludge control, and corrosion control benefits both in hydroprocessed base stocks (e.g., HDT A) and Group III base stocks. Concentration ranges where benefits are expected range from 2 to 10% for the borated dispersant, 0.1 to 1% for the molybdenum (trimer) dithiocarbamate, 0 to 1% ZDDP combined with hydrocarbyl aromatics ranging from 3% to 15%. These combinations can work in both hydroprocessed (e.g., HDT A) base stocks and Group III (GpIII) base stocks.

[0093] These results clearly demonstrate the synergism provided by the moderate molecular weight (derived from approximately 1300 Mn polyisobutylene) borated mono- and bissuccinimide dispersant and organic molybdenum compound [molybdenum (trimeric) dithiocarbamate]. It is also significant to note that excellent oxidation, sludge control, and corrosion performance is obtained in formulations containing low levels of ZDDP or phosphorus. This indicates that this invention can also be useful for engines that require low levels of phosphorus (e.g., about 0.05% or less) lubricants to both protect certain emissions catalysts and provide enhanced engine performance. In addition, since ZDDP produces sulfated ash, the anti-oxidation, sludge control, corrosion control system described in this invention would also be useful in engines that required reduced sulfated ash oils to protect after treatment devices.

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Table 4. Catalytic Oxidation Testing Results

<u>Example:</u>		4.1	4.2	4.3
PAO		84.6	84.8	84.6
2° ZDDP		0.2	0.2	0.2
Alkylated Aromatic		7.0	7.0	7.0
Low MW borated mono & bis-succinimide		8.0	8.0	0.0
High MW polyisobutyl bis-succinimide		0.0	0.0	8.0
Trimeric molybdenum dithiocarbamate		0.17	0.0	0.17
<u>Property</u>	<u>Test Method</u>			
Kinematic Viscosity at 100 °C	D 445	5.4	5.4	5.4
KV at 100°C after B10 Oxidation	D 455	5.9	7.0	5.0
Viscosity Increase, %		8.1	28.8	9.2
Acid Number	D 664	2.66	2.64	4.68
RBOT, min	D 2272	248	276	318
Catalytic Oxidation Test, Sludge		Nil	Trace	Light
Catalytic Oxidation Test, Lead Loss, %		0.8	31.5	21.3

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Table 5.
Other Illustrations Offering Oxidation, Sludge Control, and Corrosion Benefits

	5.1	5.2	5.3	5.4	5.5	5.6	5.7	5.8
GpIII 4	Bal			Bal			Bal	
PAO 4		Bal			Bal			
HDT A			Bal			Bal		Bal
Ester		8		2		10		3
150N Grp I	15							
Dispersant/Detergent/ Inhibitor Additive Performance Package	14	14	14	7	7	7	14	14
2° ZDDP	0	1	0	1	0	1	0	1
Alkylated Aromatic	3	3	15	15	15	3	15	15
Low MW borated mono & bis- succinimide	2	2	2	2	10	10	10	10
Trimeric molybdenum dithiocarbamate	1.0	0.1	0.1	1.0	1.0	0.1	0.1	1.0

Table 6 provides a listing of typical properties of base stocks used in formulating the oils shown in examples 2.1 through 5.8.

Table 6. Typical Properties of Base Stocks Used in Examples

*		Hydrocarbyl Aromatic	PAO 4	HDT A	GpIII 4	Ester	150N
D 445	Kinematic Viscosity at 40°C, cSt	29.3	18	22.65	15.6		32
D 445	Kinematic Viscosity at 100°C, cSt	4.7	4	4.55	3.8	5.2	5.2
D2272	Viscosity Index	75	120	116	138	131	97
D1500	ASTM Color	1.0	0	L0.5	0	0	
D2007	Saturates, wt%	na	100	97	na	na	80
D2622	Sulfur, ppm	150	0	60	0	0	200
	API Group	V	IV	II	III	V	I

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CLAIMS:

1. A method for improving the wear and oxidation performance of a lubricating oil composition comprising a base stock oil of lubricating viscosity comprising at least 20 weight percent of a base stock oil selected from the group consisting of Group II stocks, Group III stocks, Gas-to-Liquid (GTL) base stocks, synthetic base stocks and mixtures thereof, said method comprising adding to said base stock additives comprising:
 - (a) 0.1 to 3 weight percent of trimeric molybdenum dithiocarbamate; and
 - (b) 0.5 to 8 weight percent of a mixture of borated polyisobutenyl mono-succinimide and borated polyisobutenyl bis-succinimide, wherein the polyisobutenyl group has a molecular weight (Mn) of approximately 1300.
2. The method of claim 1, wherein the synthetic base stock is a polyalphaolefin.
3. The method of claim 1, wherein the base stock oil additionally comprises at least one co-base stock selected from the group consisting of hydrocarbyl aromatic and ester base stocks.
4. The method of claim 1, wherein the trimeric molybdenum dithiocarbamate compound is present in an amount of approximately 0.35 weight percent.
5. The method of claim 4, wherein the mixture of borated polyisobutenyl mono-succinimide and borated bis-succinimide compounds is present in an amount of approximately 7 weight percent.
6. The method of claim 5, wherein the base stock of lubricating oil viscosity is a Group II, Group III, or Gas-to-Liquid base stock.
7. The method of claim 1, wherein the base stock oil of lubricating viscosity comprises at least 30 weight percent of a base stock oil selected from the group consisting of Group II stocks, Group III stocks, synthetic base stocks and mixtures thereof.

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8. The method of claim 1, wherein the base stock oil of lubricating viscosity comprises at least about 80 weight percent of a base stock oil selected from the group consisting of Group II stocks, Group III stocks, synthetic base stocks and mixtures thereof.

9. The method of claim 5, wherein the base stock oil of lubricating viscosity comprises at least 50 weight percent of a base stock oil selected from the group consisting of Group II stocks, Group III stocks and mixtures thereof.

10. A method for reducing lead loss under Catalytic Oxidation Test conditions of a lubricating oil composition comprising a base stock oil of lubricating viscosity comprising at least about 20 weight percent of a base stock oil selected from the group consisting of Group II stocks, Group III stocks, Gas-to-Liquid (GTL) stocks, synthetic stocks and mixtures thereof, said method comprising adding to said base stocks additives comprising:

- (a) 0.1 to 3 weight percent of trimeric molybdenum dithiocarbamate; and
- (b) 0.5 to 8 weight percent of a mixture of borated polyisobutenyl mono-succinimide and borated polyisobutenyl bis-succinimide wherein the polyisobutenyl group has a molecular weight (Mn) of approximately 1300.

11. A method for improving viscosity increase control under high temperature oxidizing conditions of a lubricating oil composition comprising a base stock oil of lubricating viscosity comprising at least 20 weight percent of a base stock oil selected from the group consisting of Group II stocks, Group III stocks, Gas-to-Liquid (GTL) stocks, synthetic base stocks and mixtures thereof, said method comprising adding to said base stock additives comprising:

- (a) 0.1 to 3 weight percent of trimeric molybdenum dithiocarbamate; and
- (b) 0.5 to 8 weight percent of a mixture of borated polyisobutenyl mono-succinimide and borated polyisobutenyl bis-succinimide wherein the polyisobutenyl group has a molecular weight (Mn) of approximately 1300.