



(22) Date de dépôt/Filing Date: 2019/03/27

(41) Mise à la disp. pub./Open to Public Insp.: 2019/09/27

(45) Date de délivrance/Issue Date: 2023/11/07

(30) Priorité/Priority: 2018/03/27 (EP18164161.4)

(51) Cl.Int./Int.Cl. *C10M 141/08* (2006.01),
C10M 133/08 (2006.01), *C10M 133/44* (2006.01),
C10M 135/18 (2006.01)

(72) Inventeurs/Inventors:
MATSUMOTO, SHUNSUKE, JP;
KOUNO, KUNIHIRO, JP

(73) Propriétaire/Owner:
INFINEUM INTERNATIONAL LIMITED, GB

(74) Agent: BORDEN LADNER GERVAIS LLP

(54) Titre : DERIVE DE BENZOTRIAZOLE ET COMPOSITIONS D'HUILE DE LUBRIFICATION CONTENANT DU
DITHIOCARBAMATE DE MOLYBDENE POUR REDUIRE LE FROTTEMENT ET LA CONSOMMATION DE
CARBURANT

(54) Title: BENZOTRIAZOLE DERIVATIVE AND MOLYBDENUM DITHIOCARBAMATE-CONTAINING LUBRICATING OIL
COMPOSITIONS FOR FRICTION REDUCTION AND FUEL CONSUMPTION REDUCTION

(57) Abrégé/Abstract:

The invention relates to reducing friction coefficient in automotive lubricating oil, in particular although not exclusively at lower temperature by combining molybdenum dithiocarbamate additives with benzotriazole derivative corrosion inhibitors.

ABSTRACT

The invention relates to reducing friction coefficient in automotive lubricating oil, in particular although not exclusively at lower temperature by combining molybdenum dithiocarbamate additives with benzotriazole derivative corrosion inhibitors.

**BENZOTRIAZOLE DERIVATIVE AND MOLYBDENUM DITHIOCARBAMATE-
CONTAINING LUBRICATING OIL COMPOSITIONS FOR FRICTION
REDUCTION AND FUEL CONSUMPTION REDUCTION**

5 **FIELD OF THE INVENTION**

The present invention relates to automotive engine lubricating oils, which exhibit improved friction reduction and fuel consumption reduction, especially at lower operating temperatures, in particular at engine operating temperatures below 80 °C.

BACKGROUND OF THE INVENTION

10 It is well known that molybdenum containing additives can be used in automotive engine lubricants to improve friction reduction performance. However, it has generally been found that the efficacy of such additives is not realized until the engine temperature reaches around 80 °C. Thus, when an engine is operating at temperatures below 80 °C the excellent friction reducing properties of molybdenum-containing additives is not exhibited.

15 Benzotriazole compounds have been used for many years in lubricating oil compositions as corrosion inhibitors to reduce copper corrosion.

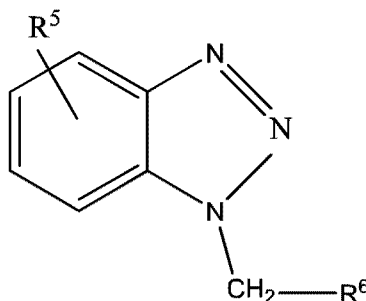
It is the object of the present invention to further improve the friction and fuel economy performance of automotive engine lubricating oils.

SUMMARY OF THE INVENTION

20 According to a first aspect the present invention provides an automotive engine lubricating oil composition comprising

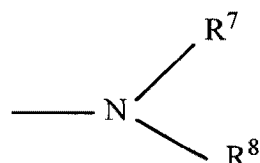
(A) a base oil of lubricating viscosity,

(B) at least one benzotriazole derivative represented by Formula (I):



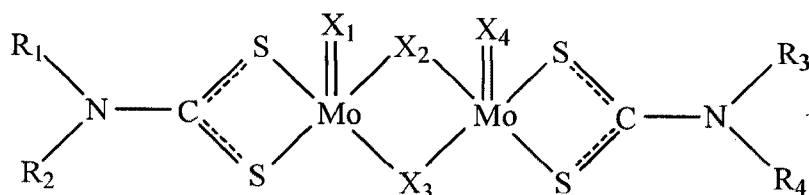
Formula (I)

wherein R⁵ is a hydrocarbyl group having 1-3 carbon atoms and R⁶ is a tertiary amine group represented by



wherein R⁷ and R⁸ are independently, linear or branched, hydrocarbyl groups having 3 to 10 carbon atoms,

(C) at least one molybdenum dithiocarbamate compound represented by either Formula (II) or Formula (III):



Formula (II)

wherein R₁ through R₄ independently denote a straight chain, branched chain or aromatic hydrocarbyl group having 1 to 24 carbon atoms; and X₁ through X₄ independently denote an oxygen atom or a sulfur atom,

Formula (III)



wherein L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil, n is from 1 to 4, k is from 4 to 7, Q is selected from the group of neutral electron donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values, and

(D) one or more additional additives chosen from metal containing or ashless detergents, ashless antioxidants, antiwear additives, corrosion inhibitors, rust inhibitors, viscosity index improvers, and dispersants,

wherein the lubricating oil composition comprises a total amount of from 100 to 2000 ppm molybdenum from components (C) and wherein the benzotriazole derivative (B) is present in the lubricating oil in an amount from 0.001 to 5 mass%.

Preferably, the base oil of lubricating viscosity (A) is present in a major amount.

5 Preferably, the automotive engine lubricating oil composition of the present invention is used to lubricate the crankcase of the engine (i.e. an automotive engine crankcase lubricant).

Suitably, the automotive engine lubricating oil composition is used to lubricate an automotive spark-ignited or automotive compression-ignited internal combustion engine, preferably an automotive spark-ignited internal combustion engine.

10 Unexpectedly, it has been found that the use of the benzotriazole compound as an additive in a lubricating oil composition which includes a molybdenum containing additive, especially a molybdenum dithiocarbamate compound, permits improved friction reduction performance, particularly boundary regime friction reduction performance, of the molybdenum containing additive when the lubricating oil composition is used to lubricate an automotive
15 engine. Furthermore, the improved friction reduction performance of the molybdenum containing compound is realized at lower engine operating temperatures i.e. when the engine is operating at temperatures below 80 °C. Accordingly, the automotive engine lubricating oil composition of the present inventions provides benefits in terms of improved friction reduction and/or improved fuel consumption reduction.

20 In accordance with a second aspect, the present invention provides a method of lubricating an automotive engine comprising lubricating the engine with a lubricating oil composition as defined in accordance with the first aspect of the present invention. Suitably, the method comprises lubricating the crankcase of the engine.

In accordance with a third aspect, the present invention provides the use, in the
25 lubrication of an automotive engine, of at least one benzotriazole derivative (B), as defined in the first aspect of the invention, as an additive in an effective minor amount, in a lubricating oil composition comprising a base oil of lubricating viscosity (A) and at least one molybdenum dithiocarbamate compound (C), as defined in the first aspect of the invention, to improve the friction reducing performance properties of the molybdenum dithiocarbamate
30 compound(s) (C) during operation of the automotive engine, wherein said molybdenum

dithiocarbamate compound(s) (C) provide the lubricating oil composition with from 100 to 2000 ppm of molybdenum.

In accordance with a fourth aspect, the present invention provides the use, in the lubrication of an automotive engine, of the combination of at least one benzotriazole derivative (B), as defined in the first aspect of the invention, and at least one molybdenum dithiocarbamate compound (C), as defined in the first aspect of the invention, as a combination of additives in an effective minor amount, in a lubricating oil composition comprising a base oil of lubricating viscosity (A), to improve friction reduction of the lubricating oil composition during operation of the automotive engine, wherein said molybdenum dithiocarbamate compound(s) (C) provide the lubricating oil composition with from 100 to 2000 ppm of molybdenum.

In accordance with a fifth aspect, the present invention provides the use, in the lubrication of an automotive engine, of the combination of at least one benzotriazole derivative (B), as defined in the first aspect of the invention, and at least one molybdenum dithiocarbamate compound (C), as defined in the first aspect of the invention, as a combination of additives in an effective minor amount, in a lubricating oil composition comprising a base oil of lubricating viscosity (A), to reduce fuel consumption of the automotive engine during operation of the engine, wherein said molybdenum dithiocarbamate compound(s) (C) provide the lubricating oil composition with from 100 to 2000 ppm of molybdenum.

Preferably, the automotive engine in the second to fifth aspects of the invention operates at temperatures below 80 °C.

Preferably, the lubricating oil composition as defined in the third, fourth and fifth aspects of the present invention further includes (D) one or more additional additives chosen from metal containing or ashless detergents, ashless antioxidants, antiwear additives, corrosion inhibitors, rust inhibitors, viscosity index improvers, and dispersants.

Suitably, the engine as defined in the second, third, fourth and fifth aspects of the present invention is a spark-ignited or compression-ignited internal combustion engine, preferably a spark-ignited internal combustion engine.

Suitably, the at least one benzotriazole derivative (B) is present, in the lubricating oil composition of the first aspect of the invention and the lubricating oil composition as defined in the second to fifth aspects of the invention, in an amount of from 0.001 to 5 mass %, preferably in an amount of 0.01 to 2 mass %, more preferably in an amount of 0.01 to 1 mass %, even more preferably in an amount of 0.01 to 0.04 mass % on an active matter basis.

Suitably, the at least one molybdenum dithiocarbamate compound (C) provides the lubricating oil composition of the first aspect of the invention, and the lubricating oil composition as defined in the second to fifth aspects of the invention, with a total amount of 100 to 2000, preferably 450 to 2000, more preferably 450 to 1200, even more preferably 450 to 900, most preferably 600 to 900, ppm molybdenum (ASTM D5185).

Suitably, the lubricating oil composition of the present invention has a sulphated ash content of less than or equal to 1.2, preferably less than or equal to 1.1, more preferably less than or equal to 1.0, mass % (ASTM D874) based on the total mass of the composition.

Preferably, the lubricating oil composition of the present invention contains low levels of phosphorus. Suitably, the lubricating oil composition contains phosphorus in an amount of less than or equal to 0.12, preferably up to 0.11, more preferably less than or equal to 0.10, even more preferably less than or equal to 0.09, even more preferably less than or equal to 0.08, most preferably less than or equal to 0.06, mass % of phosphorus (ASTM D5185) based on the total mass of the composition. Suitably, the lubricating oil composition contains phosphorus in an amount of greater than or equal to 0.01, preferably greater than or equal to 0.02, more preferably greater than or equal to 0.03, even more preferably greater than or equal to 0.05, mass % of phosphorus (ASTM D5185) based on the total mass of the composition.

Typically, the lubricating oil composition may contain low levels of sulphur. Preferably, the lubricating oil composition contains sulphur in an amount of up to 0.4, more preferably up to 0.3, even more preferably up to 0.2, mass % sulphur (ASTM D2622) based on the total mass of the composition.

Typically, a lubricating oil composition according to the present invention contains up to 0.30, more preferably up to 0.20, most preferably up to 0.15, mass % nitrogen, based on the total mass of the composition and as measured according to ASTM method D5291.

Suitably, the lubricating oil composition may have a total base number (TBN), as measured in accordance with ASTM D2896, of from 4 to 15, preferably from 5 to 12 mg KOH/g.

5 In this specification, the following words and expressions, if and when used, have the meanings given below:

“active ingredients” or “(a.i.)” refers to additive material that is not diluent or solvent; “comprising” or any cognate word specifies the presence of stated features, steps, or integers or components, but does not preclude the presence or addition of one or more other features, steps, integers, components or groups thereof. The expressions
10 “consists of”, or “consists essentially of” or cognates may be embraced within “comprises” or cognates, wherein “consists essentially of” permits inclusion of substances not materially affecting the characteristics of the composition to which it applies;

“hydrocarbyl” means a chemical group of a compound that contains hydrogen and
15 carbon atoms and that is bonded to the remainder of the compound directly via a carbon atom. The group may contain one or more atoms other than carbon and hydrogen provided they do not affect the essentially hydrocarbyl nature of the group. Those skilled in the art will be aware of suitable groups (e.g., halo, especially chloro and fluoro, amino, alkoxyl, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.).
20 Preferably, the group consists essentially of hydrogen and carbon atoms, unless specified otherwise. Preferably, the hydrocarbyl group comprises an aliphatic hydrocarbyl group. The term “hydrocarbyl” includes “alkyl”, “alkenyl”, “allyl” and “aryl” as defined herein;

“alkyl” means a C₁ to C₃₀ alkyl group which is bonded to the remainder of the
25 compound directly via a single carbon atom. Unless otherwise specified, alkyl groups may, when there are a sufficient number of carbon atoms, be linear (i.e. unbranched) or branched, be cyclic, acyclic or part cyclic/acyclic. Preferably, the alkyl group comprises a linear or branched acyclic alkyl group. Representative examples of alkyl groups include, but are not limited to, methyl, ethyl, n-propyl,
30 iso-propyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl,

hexyl, heptyl, octyl, dimethyl hexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl and triacontyl;

5 “aryl” means a C₆ to C₁₈, preferably C₆ to C₁₀, aromatic group, optionally substituted by one or more alkyl groups, halo, hydroxyl, alkoxy and amino groups, which is bonded to the remainder of the compound directly via a single carbon atom. Preferred aryl groups include phenyl and naphthyl groups and substituted derivatives thereof, especially phenyl and alkyl substituted derivatives thereof;

10 “alkenyl” means a C₂ to C₃₀, preferably a C₂ to C₁₂, group which includes at least one carbon to carbon double bond and is bonded to the remainder of the compound directly via a single carbon atom, and is otherwise defined as “alkyl”;

“alkylene” means a C₂ to C₂₀, preferably a C₂ to C₁₀, more preferably a C₂ to C₆ bivalent saturated acyclic aliphatic radical which may be linear or branched. Representative examples of alkylene include ethylene, propylene, butylene, 15 isobutylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, 1-methyl ethylene, 1-ethyl ethylene, 1-ethyl-2-methyl ethylene, 1,1-dimethyl ethylene and 1-ethyl propylene;

20 “polyol” means an alcohol which includes two or more hydroxyl functional groups (i.e. a polyhydric alcohol) but excludes a “polyalkylene glycol” (component B(ii)) which is used to form the oil-soluble or oil-dispersible polymeric friction modifier. More specifically, the term “polyol” embraces a diol, triol, tetrol, and/or related dimers or chain extended polymers of such compounds. Even more specifically, the term “polyol” embraces glycerol, neopentyl glycol, trimethylolethane, trimethylolpropane, trimethylolbutane, pentaerythritol, dipentaerythritol, 25 tripentaerythritol and sorbitol;

“polycarboxylic acid” means an organic acid, preferably a hydrocarbyl acid, which includes 2 or more carboxylic acid functional groups. The term “polycarboxylic acid” embraces di-, tri- and tetra- carboxylic acids;

“halo” or “halogen” includes fluoro, chloro, bromo and iodo;

“oil-soluble” or “oil-dispersible”, or cognate terms, used herein do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible, or are capable of being suspended in the oil in all proportions. These do mean, however, that they are, for example, soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired;

“ashless” in relation to an additive means the additive does not include a metal;

“ash-containing” in relation to an additive means the additive includes a metal;

“major amount” means in excess of 50 mass % of a composition expressed in respect of the stated component and in respect of the total mass of the composition, reckoned as active ingredient of the component;

“minor amount” means less than 50 mass % of a composition, expressed in respect of the stated additive and in respect of the total mass of the composition, reckoned as active ingredient of the additive;

“effective minor amount” in respect of an additive means an amount of such an additive in a lubricating oil composition so that the additive provides the desired technical effect;

“ppm” means parts per million by mass, based on the total mass of the lubricating oil composition;

“metal content” of the lubricating oil composition or of an additive component, for example detergent metal, molybdenum or boron content or total metal content of the lubricating oil composition (i.e. the sum of all individual metal contents), is measured by ASTM D5185;

“TBN” in relation to an additive component or of a lubricating oil composition of the present invention, means total base number (mg KOH/g) as measured by ASTM D2896;

“KV₁₀₀” means kinematic viscosity at 100°C as measured by ASTM D445;

“phosphorus content” is measured by ASTM D5185;

“sulfur content” is measured by ASTM D2622; and,

“sulfated ash content” is measured by ASTM D874.

All percentages reported are mass % on an active ingredient basis, i.e. without regard to carrier or diluent oil, unless otherwise stated.

Also, it will be understood that various components used, essential as well as optimal
5 and customary, may react under conditions of formulation, storage or use and that the invention also provides the product obtainable or obtained as a result of any such reaction.

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

Also, it will be understood that the preferred features of each aspect of the present
10 invention are regarded as preferred features of every other aspect of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

OIL OF LUBRICATING VISCOSITY

15 The oil of lubricating viscosity (sometimes referred to as “base stock” or “base oil”) is the primary liquid constituent of a lubricant, into which additives and possibly other oils are blended, for example to produce a final lubricant (or lubricant composition). A base oil is useful for making concentrates as well as for making lubricating oil compositions therefrom, and may be selected from natural (vegetable, animal or mineral) and synthetic
20 lubricating oils and mixtures thereof.

The base stock groups are defined in the American Petroleum Institute (API) publication “Engine Oil Licensing and Certification System”, Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998. Typically, the base stock will have a viscosity preferably of 3-12, more preferably 4-10, most preferably 4.5-8,
25 mm²/s (cSt) at 100°C.

Definitions for the base stocks and base oils in this invention are the same as those found in the American Petroleum Institute (API) publication “Engine Oil Licensing and Certification System”, Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998. Said publication categorizes base stocks as follows:

- a) Group I base stocks contain less than 90 percent saturates and/or greater than 0.03 percent sulphur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1.
- b) Group II base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1.
- c) Group III base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater than or equal to 120 using the test methods specified in Table E-1.
- d) Group IV base stocks are polyalphaolefins (PAO).
- e) Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

Table E-1: Analytical Methods for Base Stock

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

Other oils of lubricating viscosity which may be included in the lubricating oil composition are detailed as follows.

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

Synthetic lubricating oils include hydrocarbon oils such as polymerized and interpolymers of olefins (e.g. polybutylenes, polypropylenes, propylene-isobutylene

copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkylbenzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenols (e.g. biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogues
5 and homologues thereof.

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

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

20 Unrefined, refined and re-refined oils can be used in the compositions of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be unrefined
25 oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art. Re-refined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already
30 used in service. Such re-refined oils are also known as reclaimed or reprocessed oils and

often are additionally processed by techniques for approval of spent additive and oil breakdown products.

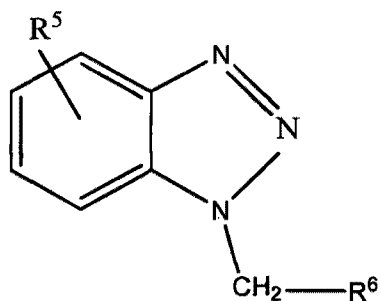
Other examples of base oil are gas-to-liquid ("GTL") base oils, i.e. the base oil may be an oil derived from Fischer-Tropsch synthesised hydrocarbons made from synthesis gas containing H₂ and CO using a Fischer-Tropsch catalyst. These hydrocarbons typically require further processing in order to be useful as a base oil. For example, they may, by methods known in the art, be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed.

Preferably, the oil of lubricating viscosity is present in an amount of greater than 55 mass %, more preferably greater than 60 mass %, even more preferably greater than 70 mass %, based on the total mass of the lubricating oil composition. Preferably, the oil of lubricating viscosity is present in an amount of less than 98 mass %, more preferably less than 95 mass %, even more preferably less than 90 mass %, based on the total mass of the lubricating oil composition.

The lubricating oil composition of each aspect of the present invention may be a multigrade oil identified by the viscometric descriptor SAE 20W-X, SAE 15W-X, SAE 10W-X, SAE 5W-X or SAE 0W-X, where X represents any one of 8, 12, 16, 20, 30, 40 and 50; the characteristics of the different viscometric grades can be found in the SAE J300 classification. In an embodiment of each aspect of the invention, independently of the other embodiments, the lubricating oil composition is in the form of an SAE 10W-X, SAE 5W-X or SAE 0W-X, preferably in the form of a SAE 0W-X or SAE 5W-X viscosity grade, wherein X represents any one of 8, 12, 16, 20 or 30. Preferably X is 8, 12, 16 or 20.

BENZOTRIAZOLE DERIVATIVE (B)

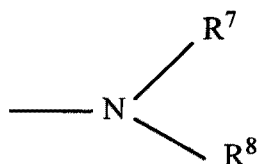
The lubricating oil composition of the present invention comprises at least one benzotriazole derivative represented by Formula (I):



Formula (I)

wherein R^5 is a hydrocarbyl group having 1-3 carbon atoms and R^6 is a tertiary amine group represented by

5

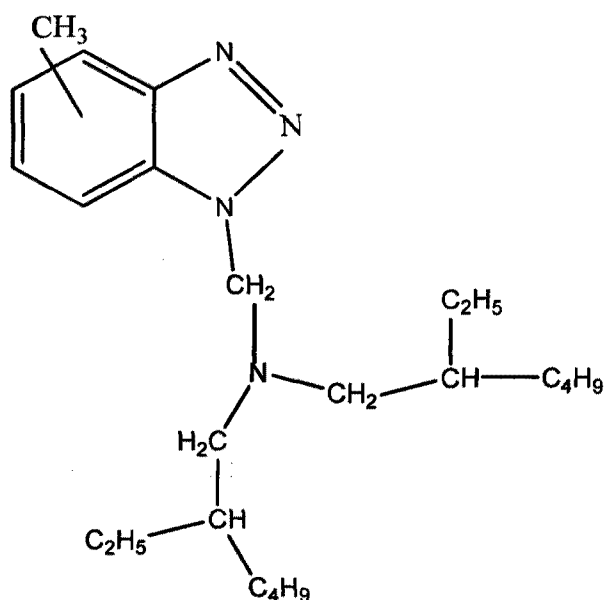


wherein R^7 and R^8 are independently, linear or branched, hydrocarbyl groups having 3 to 10 carbon atoms.

In a preferred embodiment R^5 is a methyl group. Preferably, R^7 and R^8 are both the same. In a preferred embodiment, R^7 and R^8 are hydrocarbyl groups having 6 to 8 carbon atoms.

10

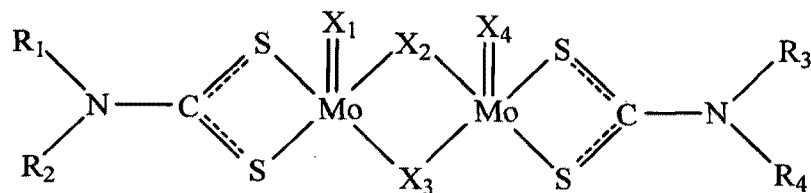
In a preferred embodiment, the benzotriazole derivative has the following structure:



Suitably the benzotriazole derivative is present in the lubricating oil composition of the present invention in an amount from 0.001 to 5 wt%, preferably in an amount of 0.01 to 2 wt% for example, in an amount of 0.01 to 1 wt% on an active matter basis. In a preferred embodiment, the benzotriazole derivative is present in the lubricating oil composition of the present invention in an amount of 0.01 to 0.04 wt% on an active matter basis.

OIL-SOLUBLE MOLYBDENUM COMPOUND (C)

Suitable dinuclear or dimeric molybdenum dialkyldithiocarbamate compounds are represented by the Formula (II):

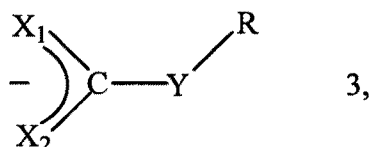
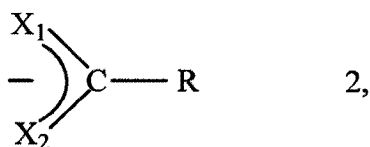


wherein R_1 through R_4 independently denote a straight chain, branched chain or aromatic hydrocarbyl group having 1 to 24 carbon atoms; and X_1 through X_4 independently denote an

oxygen atom or a sulfur atom. The four hydrocarbyl groups, R₁ through R₄, may be identical or different from one another.

Suitable tri-nuclear organo-molybdenum compounds include those of the formula Mo₃S_kL_nQ_z and mixtures thereof wherein L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 through 7, Q is selected from the group of neutral electron donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. At least 21 total carbon atoms should be present among all the ligands' organo groups, such as at least 25, at least 30, or at least 35 carbon atoms.

The ligands are independently selected from the group of:

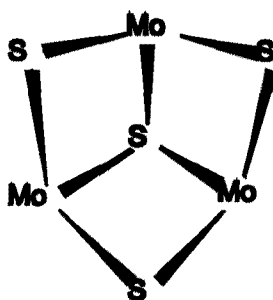


and mixtures thereof, wherein X, X₁, X₂, and Y are independently selected from the group of oxygen and sulfur, and wherein R₁, R₂, and R are independently selected from hydrogen and organo groups that may be the same or different. Preferably, the organo groups are hydrocarbyl groups such as alkyl (e.g.,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

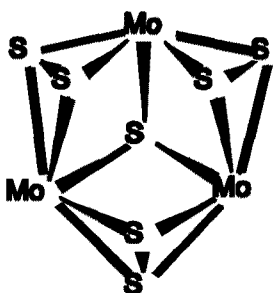
Importantly, the organo groups of the ligands have a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil. For example, the number of carbon atoms in each group will generally range between about 1 to about 100, preferably from about 1 to about 30, and more preferably between about 4 to about 20. Preferred ligands include

dialkyldithiophosphate, alkylxanthate, and dialkyldithiocarbamate, and of these dialkyldithiocarbamate is more preferred. Organic ligands containing two or more of the above functionalities are also capable of serving as ligands and binding to one or more of the cores. Those skilled in the art will realize that formation of the compounds of the present invention
5 requires selection of ligands having the appropriate charge to balance the core's charge.

Compounds having the formula $\text{Mo}_3\text{S}_k\text{L}_n\text{Q}_z$ have cationic cores surrounded by anionic ligands and are represented by structures such as



and



10

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

Oil-soluble or oil-dispersible tri-nuclear molybdenum compounds can be prepared by reacting in the appropriate liquid(s)/solvent(s) a molybdenum source such as $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13.n}(\text{H}_2\text{O})$, where n varies between 0 and 2 and includes non-stoichiometric values,

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

10 The appropriate liquid/solvent may be, for example, aqueous or organic.

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

15

The lubricating oil composition of the present invention may comprise either a dimeric or trimeric molybdenum compound or both.

The total amount of oil-soluble molybdenum dithiocarbamate compounds will depend upon the particular performance requirements of the lubricating oil composition. Suitably, the lubricating oil composition of the present invention contains a total amount of molybdenum dithiocarbamate compounds in an amount providing the composition with at least 100ppm, or at least 200ppm, or at least 300ppm, or at least 400ppm, or at least 450ppm of molybdenum (as measured according to ASTM D5185). The lubricating oil composition of all aspects of the present invention may contain the molybdenum compound in an amount providing the composition with up to 2000 ppm, or up to 1500ppm or up to 1200ppm, or up to 800 ppm of molybdenum (as measured according to ASTM D5185). In a preferred embodiment the molybdenum dithiocarbamate compound (C) provides the lubricating oil composition with from 600 to 900 ppm molybdenum.

20

25

Preferably, the dimeric molybdenum dithiocarbamate and/or the trimeric molybdenum dithiocarbamate are the sole sources of molybdenum atoms in the lubricating oil composition.

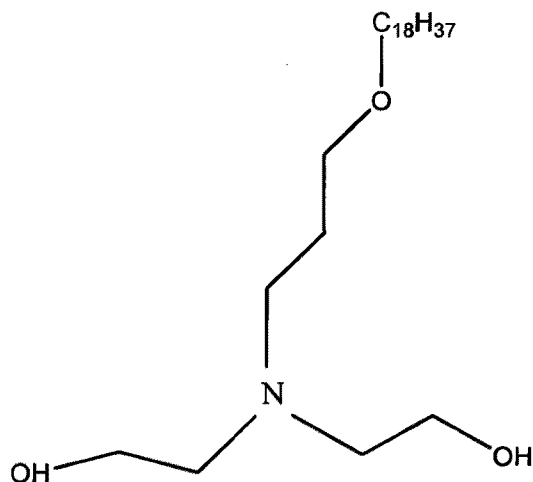
30

In a preferred embodiment the lubricating oil composition comprises both dimeric and trimeric oil soluble molybdenum dithiocarbamate.

ADDITIONAL ADDITIVES (D)

5 The lubricating oil of all aspects of the present invention may also comprise one or more additional conventional additives, including, but not limited to metal containing or ashless detergent, ashless antioxidant, antiwear additives, corrosion inhibitors, rust inhibitors, viscosity index improvers and dispersants.

10 In a preferred embodiment the lubricating oil compositions of the present invention include an aminic friction modifier having a structure according to Formula (IV) below:



Formula (IV)

15 Typically, the total amount of aminic friction modifier of Formula (IV) in the lubricating oil composition of all aspects of the present invention does not exceed 5 mass %, based on the total mass of the lubricating oil composition and preferably does not exceed 2 mass % and more preferably does not exceed 0.5 mass %. Preferably, the aminic friction modifier of Formula (IV) is present, in the lubricating oil composition of all aspects of the present invention, in an amount of from 0.1 to 1.0, more preferably 0.1 to 0.5, even more
20 preferably 0.1 to 0.3, mass %.

Dispersants are additives whose primary function is to hold solid and liquid contaminations in suspension, thereby passivating them and reducing engine deposits at the

same time as reducing sludge depositions. For example, a dispersant maintains in suspension oil-insoluble substances that result from oxidation during use of the lubricant, thus preventing sludge flocculation and precipitation or deposition on metal parts of the engine.

Dispersants are usually “ashless”, being non-metallic organic materials that form substantially no ash on combustion, in contrast to metal-containing, and hence ash-forming materials. They comprise a long hydrocarbon chain with a polar head, the polarity being derived from inclusion of e.g. an O, P, or N atom. The hydrocarbon is an oleophilic group that confers oil-solubility, having, for example 40 to 500 carbon atoms. Thus, ashless dispersants may comprise an oil-soluble polymeric backbone.

The ashless dispersant suitable for all aspects of the present invention is preferably an ashless, nitrogen-containing dispersant.

Suitable ashless dispersant may be made from polyalkenes that have been functionalised exclusively by the thermal “ene” reaction, a known reaction. Such polyalkenes are mixtures having predominantly terminal vinylidene groups, such at least 65, e.g. 70, more preferably at least 85, %. As an example, there may be mentioned a polyalkene known as highly reactive polyisobutene (HR-PIB), which is commercially available under the tradename GlissopalTM (ex BASF). US-A-4 152 499 describes the preparations of such polymers.

Alternatively, the ashless dispersant may be made from polyalkenes that have been functionalised by the so-called chlorination method, which results in a product where minor percentage of its polymer chains (e.g. less than 20%) have terminal vinylidene groups.

Preferred monounsaturated reactants that may be used to functionalize the polyalkene comprise mono- and dicarboxylic acid material, i.e., acid, anhydride, or acid ester material, including (i) monounsaturated C₄ to C₁₀ dicarboxylic acid wherein (a) the carboxyl groups are vicinyl, (i.e., located on adjacent carbon atoms) and (b) at least one, preferably both, of said adjacent carbon atoms are part of said mono unsaturation; (ii) derivatives of (i) such as anhydrides or C₁ to C₅ alcohol derived mono- or diesters of (i); (iii) monounsaturated C₃ to C₁₀ monocarboxylic acid wherein the carbon-carbon double bond is conjugated with the carboxy group, i.e., of the structure -C=C-CO-; and (iv) derivatives of (iii) such as C₁ to C₅ alcohol derived mono- or diesters of (iii). Mixtures of monounsaturated carboxylic

materials (i) - (iv) also may be used. Upon reaction with the polyalkene, the monounsaturations of the monounsaturated carboxylic reactant become saturated. Thus, for example, maleic anhydride becomes polyalkene-substituted succinic anhydride, and acrylic acid becomes polyalkene-substituted propionic acid. Exemplary of such monounsaturated carboxylic reactants are fumaric acid, itaconic acid, maleic acid, maleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, and lower alkyl (e.g., C₁ to C₄ alkyl) acid esters of the foregoing, e.g., methyl maleate, ethyl fumarate, and methyl fumarate.

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

The functionalised oil-soluble polyalkene is then derivatized with a nucleophilic reactant, such as an amine, amino-alcohol, alcohol, or mixture thereof, to form a corresponding derivative containing the dispersant. Useful amine compounds for derivatizing functionalized polymers comprise at least one amine and can comprise one or more additional amine or other reactive or polar groups. These amines may be hydrocarbyl amines or may be predominantly hydrocarbyl amines in which the hydrocarbyl group includes other groups, e.g., hydroxy groups, alkoxy groups, amide groups, nitriles and imidazoline groups. Particularly useful amine compounds include mono- and polyamines, e.g., polyalkene and polyoxyalkylene polyamines of 2 to 60, such as 2 to 40 (e.g., 3 to 20), total carbon atoms having 1 to 12, such as 3 to 12, preferably 3 to 9, most preferably 6 to 7, nitrogen atoms per molecule. Mixtures of amine compounds may advantageously be used. Preferred amines are aliphatic saturated amines, including, for example, 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; polyethylene amines such as diethylene triamine; triethylene tetramine; tetraethylene pentamine; and polypropyleneamines such as 1,2-propylene diamine; and di-(1,2-propylene)triamine. Such polyamine mixtures, known as PAM, are commercially available. Particularly preferred polyamine mixtures are mixtures derived by distilling the light ends from PAM products. The resulting mixtures, known as "heavy" PAM, or HPAM, are also commercially available.

The properties and attributes of both PAM and/or HPAM are described, for example, in U.S. Patent Nos. 4,938,881; 4,927,551; 5,230,714; 5,241,003; 5,565,128; 5,756,431; 5,792,730; and 5,854,186.

Other useful amine compounds include: alicyclic diamines such as 1,4-di(aminomethyl) cyclohexane and heterocyclic nitrogen compounds such as imidazolines. Another useful class of amines is the polyamido and related amido-amines as disclosed in U.S. Patent Nos. 4,857,217; 4,956,107; 4,963,275; and 5,229,022. Also usable is tris(hydroxymethyl)amino methane (TAM) as described in U.S. Patent Nos. 4,102,798; 4,113,639; 4,116,876; and UK 989,409. Dendrimers, star-like amines, and comb-structured amines may also be used. Similarly, condensed amines, as described in U.S. Patent No. 5,053,152 may be used. The functionalized polymer is reacted with the amine compound using conventional techniques as described, for example, in U.S. Patent Nos. 4,234,435 and 5,229,022, as well as in EP-A-208,560.

A dispersant of the present invention preferably comprises at least one dispersant that is derived from polyalkenyl-substituted mono- or dicarboxylic acid, anhydride or ester, which has from greater than 1.3 to 1.7, preferably from greater than 1.3 to 1.6, most preferably from greater than 1.3 to 1.5, functional groups (mono- or dicarboxylic acid producing moieties) per polyalkenyl moiety (a medium functionality dispersant). Functionality (F) can be determined according to the following formula:

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

wherein SAP is the saponification number (i.e., the number of milligrams of KOH consumed in the complete neutralization of the acid groups in one gram of the succinic-containing reaction product, as determined according to ASTM D94); M_n is the number average molecular weight of the starting olefin polymer; A.I. is the percent active ingredient of the succinic-containing reaction product (the remainder being unreacted olefin polymer, succinic anhydride and diluent); and MW is the molecular weight of the mono- or dicarboxylic acid producing moieties (e.g., 98 for maleic anhydride).

Generally, each mono- or dicarboxylic acid-producing moiety will react with a nucleophilic group (amine, alcohol, amide or ester polar moieties) and the number of

functional groups in the polyalkenyl-substituted carboxylic acylating agent will determine the number of nucleophilic groups in the finished dispersant.

The polyalkenyl moiety of the dispersant of the present invention may have a number average molecular weight of at least 900, suitably at least 1500, preferably between 1800 and 3000, such as between 2000 and 2800, more preferably from about 2100 to 2500, and most preferably from about 2200 to about 2400. The molecular weight of a dispersant is generally expressed in terms of the molecular weight of the polyalkenyl moiety; this is because the precise molecular weight range of the dispersant depends on numerous parameters including the type of polymer used to derive the dispersant, the number of functional groups, and the type of nucleophilic group employed.

Polymer molecular weight, specifically $\overline{M}_n$, can be determined by various known techniques. One convenient method is gel permeation chromatography (GPC), which additionally provides molecular weight distribution information (see W. W. Yau, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979). Another useful method for determining molecular weight, particularly for lower molecular weight polymers, is vapor pressure osmometry (see, e.g., ASTM D3592).

The polyalkenyl moiety in a dispersant of the present invention preferably has a narrow molecular weight distribution (MWD), also referred to as polydispersity, as determined by the ratio of weight average molecular weight (M_w) to number average molecular weight (M_n). Polymers having a M_w/M_n of less than 2.2, preferably less than 2.0, are most desirable. Suitable polymers have a polydispersity of from about 1.5 to 2.1, preferably from about 1.6 to about 1.8.

Suitable polyalkenes employed in the formation of the dispersants of the present invention include homopolymers, interpolymers or lower molecular weight hydrocarbons. One family of such polymers comprise polymers of ethylene and/or at least one C_3 to C_{28} alpha-olefin having the formula $H_2C=CHR^1$ wherein R^1 is a straight or branched chain alkyl radical comprising 1 to 26 carbon atoms and wherein the polymer contains carbon-to-carbon unsaturation, and a high degree of terminal ethenylidene unsaturation. Preferably, such polymers comprise interpolymers of ethylene and at least one alpha-olefin of the above

formula, wherein R¹ is alkyl of from 1 to 18 carbon atoms, and more preferably is alkyl of from 1 to 8 carbon atoms, and more preferably still of from 1 to 2 carbon atoms

Another useful class of polymers is polymers prepared by cationic polymerization of monomers such as isobutene and styrene. Common polymers from this class include polyisobutenes obtained by polymerization of a C₄ refinery stream having a butene content of 35 to 75% by wt., and an isobutene content of 30 to 60% by wt., by the thermal "ene" reaction. A preferred source of monomer for making poly-n-butenes is petroleum feedstreams such as Raffinate II. These feedstocks are disclosed in the art such as in U.S. Patent No. 4,952,739. A preferred embodiment utilizes polyisobutylene prepared from a pure isobutylene stream or a Raffinate I stream to prepare reactive isobutylene polymers with terminal vinylidene olefins as described above.

The dispersant(s) of the invention are preferably mono- or bis-succinimides.

The dispersant(s) of the present invention can be borated by conventional means, as generally taught in U.S. Patent Nos. 3,087,936, 3,254,025 and 5,430,105. Boration of the dispersant is readily accomplished by treating an acyl nitrogen-containing dispersant with a boron compound such as boron oxide, boron halide boron acids, and esters of boron acids, in an amount sufficient to provide from 0.1 to 20 atomic proportions of boron for each mole of acylated nitrogen composition.

The boron, which appears in the product as dehydrated boric acid polymers (primarily (HBO₂)₃), is believed to attach, for example, to dispersant imides and diimides as amine salts, e.g., the metaborate salt of the diimide. Boration can be carried out by adding a sufficient quantity of a boron compound, preferably boric acid, usually as a slurry, to the acyl nitrogen compound and heating with stirring at from 135C to 190, e.g., 140 to 170, °C, for from 1 to 5 hours, followed by nitrogen stripping. Alternatively, the boron treatment can be conducted by adding boric acid to a hot reaction mixture of the dicarboxylic acid material and amine, while removing water. Other post-reaction processes known in the art can also be applied.

Typically, the lubricating oil composition may contain from 1 to 20, such as 1 to 15, preferably 1 to 10, mass %, more preferably from 2 to 5 mass% dispersant.

In a preferred embodiment the lubricating oil composition of the present invention comprises from 200-500 ppm boron from a borated dispersant.

Metal-containing detergents function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with a long hydrophobic tail, with the polar head comprising a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as can be measured by ASTM D2896) of from 0 to 80 mg KOH/g. A large amount of a metal base may be incorporated by reacting excess metal compound (e.g., an oxide or hydroxide) with an acidic gas (e.g., carbon dioxide). The resulting overbased detergent comprises neutralized detergent as the outer layer of a metal base (e.g. carbonate) micelle. Such overbased detergents may have a TBN of 150 mg KOH/g or greater, and typically will have a TBN of from 250 to 450 mg KOH/g or more. In the presence of the compounds of Formula I, the amount of overbased detergent can be reduced, or detergents having reduced levels of overbasing (e.g., detergents having a TBN of 100 to 200 mg KOH/g), or neutral detergents can be employed, resulting in a corresponding reduction in the SASH content of the lubricating oil composition without a reduction in the performance thereof.

Suitably the lubricating oil composition of the present invention further comprises at least one metal-containing detergent additive.

Detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals, e.g., sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present in detergents used in a lubricating oil composition according to any aspect of the present invention. Combinations of detergents, whether overbased or neutral or both, may be used.

Sulfonates may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons. Examples

included those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl or their halogen derivatives such as chlorobenzene, chlorotoluene and chloronaphthalene. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 70 carbon atoms. The alkaryl sulfonates usually contain from about 9
5 to about 80 or more carbon atoms, preferably from about 16 to about 60 carbon atoms per alkyl substituted aromatic moiety. The oil soluble sulfonates or alkaryl sulfonic acids may be neutralized with oxides, hydroxides, alkoxides, carbonates, carboxylate, sulfides, hydrosulfides, nitrates, borates and ethers of the metal. The amount of metal compound is chosen having regard to the desired TBN of the final product but typically ranges from about
10 100 to 220 mass % (preferably at least 125 mass %) of that stoichiometrically required.

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

Carboxylate detergents, e.g., salicylates, can be prepared by reacting an aromatic carboxylic acid with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. The
20 aromatic moiety of the aromatic carboxylic acid can contain heteroatoms, such as nitrogen and oxygen. Preferably, the moiety contains only carbon atoms; more preferably the moiety contains six or more carbon atoms; for example benzene is a preferred moiety. The aromatic carboxylic acid may contain one or more aromatic moieties, such as one or more benzene rings, either fused or connected via alkylene bridges.

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

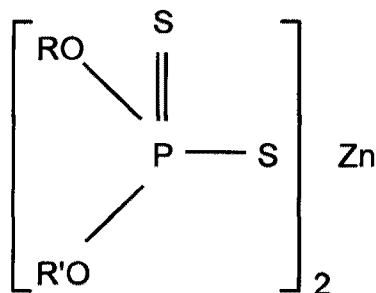
Lubricating oil compositions of the present invention preferably comprise one or more metal detergents that are neutral or overbased alkali or alkaline earth metal salicylates. Highly preferred salicylate detergents include alkaline earth metal salicylates, particularly magnesium and calcium, especially, calcium salicylates. The metal salicylate may be the sole metal-containing detergent present in the lubricating oil composition of all aspects of the present invention. Alternatively, other metal-containing detergents, such as metal sulfonates or phenates, may be present in the lubricating composition. Preferably, the salicylate detergent provides the majority of the detergent additive in the lubricating oil composition.

The total amount of metal-containing detergent additive present in the lubricating oil composition according to any aspect of the present invention is suitably in the range of 0.1-10 mass%, preferably from 0.5 to 5 mass% on an active matter basis.

Anti-wear additives reduce friction and excessive wear and are usually based on compounds containing sulfur or phosphorous or both, for example that are capable of depositing polysulfide films on the surfaces involved. Noteworthy are dihydrocarbyl dithiophosphate metal salts wherein the metal may be an alkali or alkaline earth metal, or aluminium, lead, tin, molybdenum, manganese, nickel, copper, or preferably, zinc.

Dihydrocarbyl dithiophosphate metal salts may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohols or a phenol with P_2S_5 and then neutralizing the formed DDPA with a metal compound. For example, a dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, dithiophosphoric acids can be prepared where the hydrocarbyl groups are entirely secondary in character or the hydrocarbyl groups are entirely primary in character. To make the metal salt, any basic or neutral metal compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of metal due to the use of an excess of the basic metal compound in the neutralization reaction.

The preferred zinc dihydrocarbyl dithiophosphates (ZDDP) are oil-soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



wherein R and R' may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R' groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl. In order to obtain oil solubility, the total number of carbon atoms (i.e. R and R') in the dithiophosphoric acid will generally be about 5 or greater. The zinc dihydrocarbyl dithiophosphate can therefore comprise zinc dialkyl dithiophosphates.

The ZDDP is added to the lubricating oil compositions in amounts sufficient to provide at least 500 ppm such as at least 600ppm or at least 800ppm by mass of phosphorous to the lubricating oil, based upon the total mass of the lubricating oil composition, and as measured in accordance with ASTM D5185.

The ZDDP is suitably added to the lubricating oil compositions in amounts sufficient to provide no more than 1200 ppm or, preferably no more than 1000ppm, by mass of phosphorous to the lubricating oil, based upon the total mass of the lubricating oil composition, and as measured in accordance with ASTM D5185.

Viscosity modifiers (VM) function to impart high and low temperature operability to a lubricating oil. The VM used may have that sole function, or may be multifunctional. Multifunctional viscosity modifiers that also function as dispersants are also known. Suitable viscosity modifiers are polyisobutylene, copolymers of ethylene and propylene and higher alpha-olefins, polymethacrylates, polyalkylmethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, inter polymers of styrene and acrylic esters, and partially hydrogenated copolymers of styrene/ isoprene,

styrene/butadiene, and isoprene/butadiene, as well as the partially hydrogenated homopolymers of butadiene and isoprene and isoprene/divinylbenzene. Suitable viscosity modifiers for all aspects of the present invention are copolymers of an unsaturated dicarboxylic acid and a vinyl compound, inter polymers of styrene and acrylic esters, and, most preferably, partially
5 hydrogenated copolymers of styrene/ isoprene, styrene/butadiene, and isoprene/butadiene, as well as the partially hydrogenated homopolymers of butadiene and isoprene and isoprene/divinylbenzene. The preferred partially hydrogenated copolymers of styrene/ isoprene, styrene/butadiene, and isoprene/butadiene, may be random copolymers but are preferably block copolymers. The preferred, partially hydrogenated copolymers of
10 styrene/isoprene, styrene/butadiene, and isoprene/butadiene, and partially hydrogenated homopolymers of butadiene and isoprene and isoprene/divinylbenzene viscosity modifiers may be linear polymers or star (radial) polymers.

Linear block copolymers useful in the practice of the present invention may be represented by the following general formula:



wherein:

A is a polymeric block comprising predominantly monoalkenyl aromatic hydrocarbon monomer units;

B is a polymeric block comprising predominantly conjugated diolefin monomer units;

20 x and z are, independently, a number equal to 0 or 1; and

y is a whole number ranging from 1 to about 15.

Useful tapered linear block copolymers may be represented by the following general formula:



wherein:

A is a polymeric block comprising predominantly monoalkenyl aromatic hydrocarbon monomer units;

B is a polymeric block comprising predominantly conjugated diolefin monomer units; and

30 A/B is a tapered segment containing both monoalkenyl aromatic hydrocarbon and conjugated diolefin units.

Star or radial homopolymers or random copolymers of diene(s) (e.g., isoprene and/or butadiene) may be represented, generally, by the following general formula:



wherein:

5 B and C are as previously defined; and

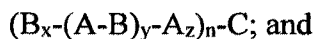
n is a number from 3 to 30;

C is the core of the radial polymer formed with a polyfunctional coupling agent;

B' is a polymeric block comprising predominantly conjugated diolefin units, which B' may be the same or different from B; and

10 n' and n'' are integers representing the number of each type of arm and the sum of n' and n'' will be a number from 3 to 30.

Star or radial block copolymers may be represented, generally, by the following general formula:



wherein:

A, B, x, y and z are as previously defined;

n is a number from 3 to 30;

C is the core of the radial polymer formed with a polyfunctional coupling agent;

20 B' is a polymeric block comprising predominantly conjugated diolefin units, which B' may be the same or different from B; and

n' and n'' are integers representing the number of each type of arm and the sum of n' and n'' will be a number from 3 to 30.

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

The lubricating oil composition according to all aspects of the present invention may comprise one or more star polymer viscosity modifier one or more linear polymer viscosity
30 modifier or a mixture of linear and star polymer viscosity modifiers.

Oil-soluble viscosity modifying polymers generally have weight average molecular weights of from 10,000 to 1,000,000, preferably 20,000 to 500,000, which may be determined by gel permeation chromatography or by light scattering.

In an embodiment of the present invention, the viscosity modifier comprises a polymethacrylate, polyalkylmethacrylate or methacrylate copolymer viscosity modifier. In a preferred embodiment, the polymethacrylate, polyalkylmethacrylate or methacrylate copolymer viscosity modifier is the only viscosity modifier in the lubricating oil composition.

Anti-oxidants, sometimes referred to as oxidation inhibitors, increase the resistance of the composition to oxidation and may work by combining with and modifying peroxides to render them harmless, by decomposing peroxides, or by rendering oxidation catalysts inert. Oxidative deterioration can be evidenced by sludge in the lubricant, varnish-like deposits on the metal surfaces, and by viscosity increase.

Examples of suitable antioxidants are selected from copper-containing antioxidants, sulfur-containing antioxidants, aromatic amine-containing antioxidants, hindered phenolic antioxidants and dithiophosphates derivative. Preferred anti-oxidants are ashless antioxidants. Preferred ashless antioxidants are ashless aromatic amine-containing antioxidants, ashless hindered phenolic antioxidants and mixtures thereof. Preferably, one or more antioxidant is present in a lubricating oil composition of all aspects of the present invention. In a preferred embodiment, a lubricating oil composition of the present invention comprises a combination of aromatic amine antioxidants and hindered phenolic antioxidant and optionally also a sulfurized olefin antioxidant.

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

In a preferred embodiment of the present invention, no copper-containing additives are present in the lubricating oil composition.

A small amount of a demulsifying component may be used. A preferred demulsifying component is described in EP 330522. It is obtained by reacting an alkylene oxide with an adduct obtained by reacting a bis-epoxide with a polyhydric alcohol. The demulsifier should be used at a level not exceeding 0.1 mass % active ingredient. A treat rate of 0.001 to 0.05 mass % active ingredient is convenient.

Pour point depressants, otherwise known as lube oil flow improvers, lower the minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Typical of those additives which improve the low temperature fluidity of the fluid are C₈ to C₁₈ dialkyl fumarate/vinyl acetate copolymers, polyalkylmethacrylates and the like.

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

Suitable additional additives and their common treat rates are discussed below. All the values listed are stated as mass percent active ingredient in a fully formulated lubricant.

10	<u>Additive</u>	<u>Mass %</u>	<u>Mass %</u>
		(Broad)	(Preferred)
	Corrosion Inhibitor	0 – 5	0 – 1.0
	Metal Dihydrocarbyl Dithiophosphate	0 – 10	0 – 4
	Anti-Oxidants	0 – 5	0.01 – 3
	Pour Point Depressant	0.01 – 5	0.01 – 1.5
15	Anti-Foaming Agent	0 – 5	0.001 – 0.15
	Viscosity Modifier (1)	0 – 10	0.01 – 4
	Mineral or Synthetic Base Oil	Balance	Balance

- (1) Viscosity modifiers are used only in multi-graded oils.

- 20 The final lubricating oil composition, typically made by blending the or each additive into the base oil, may contain from 5 to 25, preferably 5 to 18, typically 7 to 15, mass % of the additives; the remainder being oil of lubricating viscosity.

As is known in the art, some additives can provide a multiplicity of effects, for example, a single additive may act as a dispersant and as an oxidation inhibitor.

- 25 The individual additives may be incorporated into a base stock in any convenient way. Thus, each of the components can be added directly to the base stock or base oil blend by dispersing or dissolving it in the base stock or base oil blend at the desired level of concentration. Such blending may occur at ambient or elevated temperatures.

- 30 Preferably, all the additives except for the viscosity modifier and the pour point depressant are blended into a concentrate or additive package described herein as the additive

package that is subsequently blended into base stock to make the finished lubricant. The concentrate will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration in the final formulation when the concentrate is combined with a predetermined amount of a base lubricant.

5 The concentrate is preferably made in accordance with the method described in US 4,938,880. That patent describes making a pre-mix of ashless dispersant and metal detergents that is pre-blended at a temperature of at least about 100°C. Thereafter, the pre-mix is cooled to at least 85°C and the additional components are added.

10 The final crankcase lubricating oil formulation may employ from 2 to 20, preferably 4 to 18, and most preferably 5 to 17, mass % of the concentrate or additive package with the remainder being base stock.

15 The lubricating oil composition of the present invention may have a sulphated ash content of less than or equal to 1.2, preferably less than or equal to 1.1, more preferably less than or equal to 1.0, mass % (ASTM D874) based on the total mass of the composition. The lubricating oil composition of the present invention suitably has a sulphated ash content of at least 0.4, preferably at least 0.5, such as at least 0.6 mass % (ASTM D874) based on the total mass of the composition. Suitably the sulphated ash content of the lubricating oil composition is in the range of 0.4-1.2 mass%, preferably in the range of 0.6 to 1.0 mass% (ASTM D874).

20 The amount of sulfur in the lubricating oil composition will depend upon the particular application of the lubricating oil composition. The lubricating oil composition may contain sulphur in an amount of up to 0.4, such as, up to 0.35 mass % sulphur (ASTM D2622) based on the total mass of the composition. Generally the lubricating oil composition will contain at least 0.1, or even at least 0.2 mass% sulphur (ASTM D2622)
25 based on the total mass of the composition.

 Suitably, the lubricating oil composition of all aspects and embodiments of the present invention may have a total base number (TBN), as measured in accordance with ASTM D2896, of 4 to 15, preferably 4 to 10 mg KOH/g.

30

EXAMPLES

The invention will now be described in the following examples which are not intended to limit the scope of the claims hereof.

5 Example 1

The Schwingung Reibung Verschleiss “SRV”, supplied by Optimol™, is used to evaluate friction and wear properties of liquid lubricants across a broad range of applications. The test oil forms a film in between a ball and disk, the ball is engaged in a sliding or reciprocating stroke across the disk and friction between the metal-metal contact is
10 measured. This is used to evaluate the boundary regime friction characteristics of the oils. There are different specimens and configurations that can be used in SRV. In these examples the average friction was recorded at a frequency of 20 Hz and a temperature of 80 C°.

Two oils having the formulations set out in Table 1 below were tested and the average friction coefficient was recorded at each of the loads shown in Table 2 below.

15

Table 1

Additive	Oil 1	Oil 2	Oil 3	Oil 4
Additive Package ¹	10.29	10.29		
Additive Package ⁸			9.95	9.95
Dimeric Molybdenum Dithiocarbamate ²	0.70	0.70	0.80	0.80
Trimeric Molybdenum Dithiocarbamate ³	0.20	0.20		
Sulfurised ester antioxidant ⁴	0.90			
Irgamet™39 ⁵		0.01		0.01
Viscosity modifier	6.90	6.90	6.60	6.60
Group III base oil	Balance	Balance	Balance	Balance
Mo, ppm (ASTM D5185)	865	865	800	800

¹ The additive package had the same composition for Oils 1 and 2 and comprised a dispersant combination comprising non-borated and borated polyisobutenyl succinimide dispersant, a calcium salicylate detergent, a magnesium salicylate detergent, a combination of hindered phenol and diphenylamine antioxidants and zinc dialkyldithiophosphate.

² Dimeric molybdenum dithiocarbamate, Sakuralube 525.

5 ³ Trimeric molybdenum dithiocarbamate from Infineum UK Ltd.

⁴ Available from Infineum UK Ltd

⁵ 1H-benzotriazole-1-methanamine, N, N-bis(2-ethylhexyl)-ar-methyl, available from BASF

10 ⁸ The additive package had the same composition for Oils 3 and 4 and comprised a dispersant combination comprising non-borated and borated polyisobutenyl succinimide dispersant, a calcium salicylate detergent, a magnesium salicylate detergent, a combination of hindered phenol and diphenylamine antioxidants, antifoam and zinc dialkyldithiophosphate.

Table 2

Average Friction Coefficient	Oil 1	Oil 2	Oil 3	Oil 4
20N	0.154	0.125	0.133	0.119
30N	0.124	0.105	0.115	0.107
40N	0.107	0.096	0.103	0.099
50N	0.095	0.089	0.096	0.093

15 It can be seen from this data that Oils 2 and 4 containing a combination of molybdenum compound with Irgamet™ 39 exhibits significantly lower coefficient of friction than the corresponding oil without the Irgamet™ 39.

Example 2

Four more oils having the formulations set out in Table 3 below were tested and the average friction coefficient was recorded at each of the loads shown in Table 4 below.

20

Table 3

Additive	Oil 5	Oil 6	Oil 7	Oil 8
Additive Package ⁶	9.95	9.95	9.95	9.95
Dimeric Molybdenum Dithiocarbamate ²	0.80	0.80	0.80	0.80
Irgamet™39 ⁵	0.01	0.01	0.01	0.01
Viscosity Modifier	6.60	6.60	6.60	6.60

Ethoxylated amine friction modifier ⁷	0	0.10	0.20	0.30
Group III base oil	Balance	Balance	Balance	Balance
Mo, ppm (ASTM D5185)	800	800	800	800

⁶ The additive package had the same composition for all oils in Table 3 and comprised a dispersant combination comprising non-borated and borated polyisobutenyl succinimide dispersant, a calcium salicylate detergent, a magnesium salicylate detergent, a combination of hindered phenol and diphenylamine antioxidants and zinc dialkyldithiophosphate.

² Dimeric molybdenum dithiocarbamate, Sakuralube 525.

5 ⁵ 1H-benzotriazole-1-methanamine, N, N-bis(2-ethylhexyl)-ar-methyl, available from BASF

⁷ Available from Infineum UK Ltd.

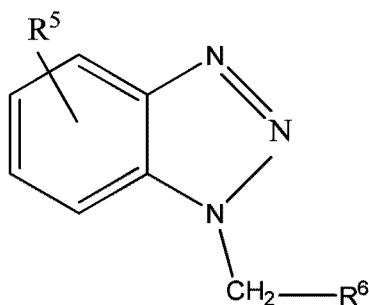
Table 4

Average Friction Coefficient	Oil 5	Oil 6	Oil 7	Oil 8
20N	0.142	0.126	0.127	0.126
30N	0.120	0.109	0.108	0.105
40N	0.107	0.099	0.096	0.094
50N	0.099	0.092	0.088	0.089

10 The data in Table 4 illustrates that addition of an ethoxylated amine friction modifier to a lubricant containing a combination of molybdenum dithiocarbamate and a benzotriazole derivative further reduced the coefficient of friction.

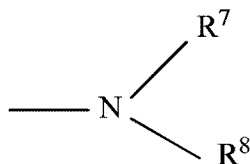
CLAIMS:

1. An automotive engine lubricating oil composition comprising
- (A) a base oil of lubricating viscosity,
- (B) at least one benzotriazole derivative represented by Formula (I):



Formula (I)

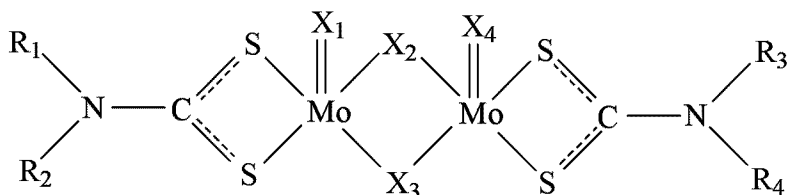
wherein R^5 is a hydrocarbyl group having 1-3 carbon atoms and R^6 is a tertiary amine group represented by



wherein R^7 and R^8 are independently hydrocarbyl groups having 3 to 10 carbon atoms,

- (C) at least one molybdenum dithiocarbamate compound represented by either Formula (II) or Formula (III):

Formula (II)



wherein R₁ through R₄ independently denote a straight chain, branched chain or aromatic hydrocarbyl group having 1 to 24 carbon atoms; and X₁ through X₄ independently denote an oxygen atom or a sulfur atom,

Formula (III)



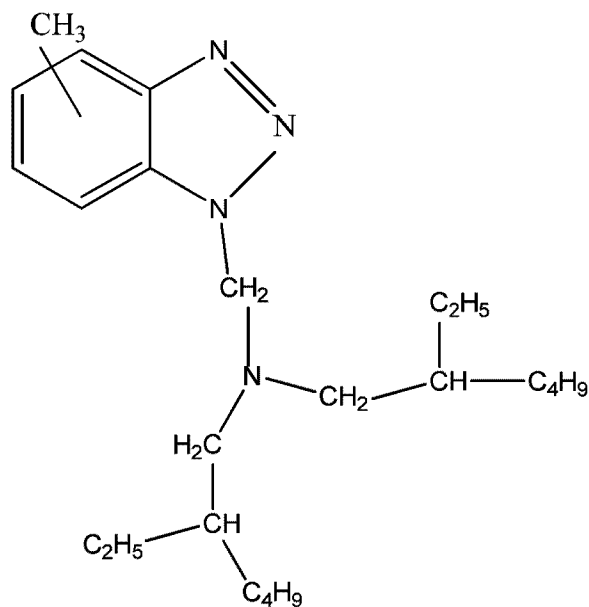
wherein L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil, n is from 1 to 4, k is from 4 to 7, Q is selected from the group of neutral electron donating compounds, and z ranges from 0 to 5 and includes non-stoichiometric values, and

(D) one or more additional additives chosen from metal containing or ashless detergents, ashless antioxidants, antiwear additives, corrosion inhibitors, rust inhibitors, viscosity index improvers, and dispersants,

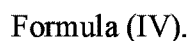
wherein the lubricating oil composition comprises a total amount of from 450 to 2000 ppm molybdenum from components (C) and wherein the benzotriazole derivative (B) is present in the lubricating oil in an amount from 0.01 to 0.04 wt% on an active matter basis.

2. The automotive engine lubricating oil composition according to claim 1, wherein the neutral electron donating compounds are water, amines, alcohols, phosphines or ethers.

3. The automotive engine lubricating oil composition according to claim 1 or 2, wherein the benzotriazole derivative (B) has the following structure:



4. The automotive engine lubricating oil composition according to any one of claims 1 to 3, wherein the molybdenum dithiocarbamate compound (C) comprises only a dimeric molybdenum dithiocarbamate of Formula (II).
5. The automotive engine lubricating oil composition according to any one of claims 1 to 3, wherein the molybdenum dithiocarbamate compound (C) comprises a mixture of dimeric molybdenum dithiocarbamate of Formula (II) and trimeric molybdenum dithiocarbamate of Formula (III).
6. The automotive engine lubricating oil composition according to any one of claims 1 to 5, wherein the molybdenum dithiocarbamate compound (C) provides the lubricating oil composition with from 600 to 900 ppm molybdenum.
7. The automotive engine lubricating oil composition according to any one of claims 1 to 6, further comprising an aminic friction modifier having a structure according to Formula (IV) below:



- 39

13. The automotive engine lubricating oil composition according to any one of claims 1 to 12, wherein the lubricating oil composition further comprises one or more oil-soluble zinc dihydrocarbyl dithiophosphates.
14. The automotive engine lubricating oil composition according to any one of claims 1 to 12, wherein the lubricating oil composition further comprises one or more oil-soluble zinc dihydrocarbyl dithiophosphates comprising only secondary alkyl groups.
15. A method of lubricating an automotive engine comprising lubricating the engine with the automotive engine lubricating oil composition as claimed in any one of claims 1 to 14.
16. Use, in lubrication of an automotive engine, of at least one benzotriazole derivative (B), as defined in claim 1 or 3, as an additive in an amount of less than 50 mass %, based on the total mass of the lubricating oil composition, in a lubricating oil composition comprising the base oil of lubricating viscosity (A) and at least one molybdenum dithiocarbamate compound (C), as defined in any one of claims 1, 2 and 4 to 6, to improve the friction reducing performance properties of the molybdenum dithiocarbamate compound(s) (C) during operation of the automotive engine, wherein said molybdenum dithiocarbamate compound(s) (C) provide the lubricating oil composition with from 100 to 2000 ppm of molybdenum.
17. Use, in lubrication of an automotive engine, of a combination of at least one benzotriazole derivative (B), as defined in claim 1 or 3, and at least one molybdenum dithiocarbamate compound (C), as defined in any one of claims 1, 2 and 4 to 6, as a combination of additives in an amount of less than 50 mass %, based on the total mass of the lubricating oil composition, in a lubricating oil composition comprising a base oil of lubricating viscosity (A), to improve friction reduction of the lubricating oil composition during operation of the automotive engine, wherein said molybdenum dithiocarbamate

compound(s) (C) provide the lubricating oil composition with from 100 to 2000 ppm of molybdenum.

18. Use, in lubrication of an automotive engine, of a combination of at least one benzotriazole derivative (B), as defined in claim 1 or 3, and at least one molybdenum dithiocarbamate compound (C), as defined in any one of claims 1, 2 and 4 to 6, as a combination of additives in an amount of less than 50 mass %, based on the total mass of the lubricating oil composition, in a lubricating oil composition comprising a base oil of lubricating viscosity (A), to reduce fuel consumption of the automotive engine during operation of the engine, wherein said molybdenum dithiocarbamate compound(s) (C) provide the lubricating oil composition with from 100 to 2000 ppm of molybdenum.

19. The use as claimed in any one of claims 16 to 18, wherein the automotive engine operates at temperatures below 80 °C.