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(57) **Abrégé/Abstract**:

A low sulphated ash lubricating oil composition comprising an overbased magnesium salicylate detergent and an ashless alkylene bis(dihydrocarbyldithiocarbamate) which exhibits an extended drain interval.

ABSTRACT

A low sulphated ash lubricating oil composition comprising an overbased magnesium salicylate detergent and an ashless alkylene bis(dihydrocarbyldithiocarbamate) which exhibits an extended drain interval.

A LUBRICATING OIL COMPOSITION

FIELD OF THE INVENTION

The present invention relates to automotive lubricating oil compositions having low levels of sulphated ash which are suitable for extended drain interval applications. More specifically, the present invention relates to such automotive lubricating oil compositions for use in gasoline (spark-ignited) and diesel (compression-ignited) internal combustion engines, especially diesel engines, crankcase lubrication, such compositions being referred to as crankcase lubricants; and to the use of additives in such compositions for extending the drain interval of the lubricating oil composition.

In particular, although not exclusively, the present invention relates to automotive lubricating oil compositions, especially automotive lubricating oil compositions for use in heavy duty diesel (HDD) engines, having low levels of sulphated ash, and preferably low levels of phosphorus and also low levels of sulfur, which, in use, exhibit an extended time to reach the TBN/TAN cross-over point for the lubricant, thereby extending the drain interval of the lubricant.

BACKGROUND OF THE INVENTION

A crankcase lubricant is an oil used for general lubrication in an internal combustion engine where an oil sump is situated generally below the crankshaft of the engine and to which circulated oil returns. It is well known to include additives in crankcase lubricants for several purposes.

With an increasing emphasis on oil conservation and the desire for more maintenance free vehicles, there is a trend towards extending the drain interval of a crankcase lubricant without detriment to engine durability and performance. Typically, a crankcase lubricant when new has a relatively high total base number (TBN) and a relatively low total acid number (TAN). The TBN of a lubricant represents a measure of the quantity of basic components in the lubricant and provides an indication of the capacity of the lubricant to neutralize the acidic species produced in the lubricant and the acidic products of combustion which contaminate the lubricant, during use. The TAN of a lubricant represents a measure of the quantity of acidic species present in the lubricant.

More specifically, the TBN of a lubricant is the quantity of acid, expressed in terms of the equivalent number of milligrams of potassium hydroxide, that is required to neutralize the basic components present in 1 gram of the lubricant and it is expressed as mg KOH per gram of lubricant (mg/g KOH). Typically, a lubricant having a relatively high TBN has a greater capacity to neutralize the acidic species produced in the lubricant and the acidic products of combustion which contaminate the lubricant, during use, than a lubricant having a lower TBN. Usually, metal-containing or ash-forming detergents which are present in a lubricant contribute the majority of the TBN to the lubricant; the metal-containing detergents function as both detergents to reduce and remove deposits and as acid neutralizers, thereby reducing wear and corrosion and extending engine life.

The TAN of a lubricant is the number of milligrams of potassium hydroxide that are required to neutralize the acidic species present in 1 gram of the lubricant and it is expressed as mg KOH per gram of lubricant (mg/g KOH). A lubricant having a relatively high TAN is indicative of the presence of more acidic species than a lubricant having a lower TAN.

When new, the TBN of a lubricant is relatively high and its TAN is relatively low. In use, acidic species are produced in the lubricant and the lubricant becomes contaminated with acidic species of combustion. Such acidic species are neutralized by the basic components (e.g. the metal-containing detergent) in the lubricant, thereby depleting the TBN of the lubricant. The longer the lubricant is used the general trend is a decrease in TBN and an increase in TAN. The time taken, in use, to reach a point where the TBN and the TAN of the lubricant are equivalent (referred to herein as the *"TBN/TAN cross-over point"*) represents one measure for determining the useful oil change interval for the lubricant, as the lubricant no longer has the ability to neutralize acidic species produced in or which may contaminate the lubricant. Indeed, studies have shown that when TAN exceeds TBN, engine wear and/or corrosion may accelerate at abnormally high rates. Accordingly, in order to extend the drain interval of a lubricant it is desirable to extend, in use, the time taken to reach the TBN/TAN cross-over point.

Concurrent with the desire to extend the drain interval of a lubricant, there has been a continued effort to reduce the content of sulphated ash, phosphorus and sulphur in the lubricant due to both environmental concerns and to insure compatibility with pollution control devices (e.g. three-way catalytic converters and particulate traps). In Europe, a lubricant meeting the ACEA E6 SAPS (sulphated ash, phosphorus and sulphur) limitation and, in the USA, a lubricant meeting the API CJ-4 SAPS limitation, the amount of ash contributed by the detergent(s), combined with the ash contributed by the ash-containing anti-wear agents in the formulation, must be less than or equal to 1.0 mass %. The need to meet this stringent limitation on ash level and still provide adequate detergency performance typically led formulators to reduce the level of detergent overbasing. However, a reduction in the amount of overbasing typically reduces the acid neutralization capacity of the lubricant which may, in use, reduce the time taken to reach the TBN/TAN cross-over point thereby shortening the maximum drain interval of the lubricant.

Accordingly, there is a need to identify a lubricating oil composition which meets the ash constraints of the ACEA E6 and API CJ-4 specifications (i.e. a sulphated ash level of less than or equal to 1.0 mass % as determined by ASTM D874) and, in use, extends the time taken to reach the TBN/TAN cross-over point for the lubricant, thereby extending the drain interval of the lubricant.

SUMMARY OF THE INVENTION

Surprisingly, it has been found that by using a combination of an overbased magnesium salicylate detergent and an ashless alkylene bis(dihydrocarbyldithiocarbamate) additive component in a lubricating oil composition it is possible to formulate a lubricating oil composition having a low sulphated ash level of less than or equal to 1.0 mass % as determined by ASTM D874 which, in use, substantially extends the time taken to reach the TBN/TAN cross-over point for the lubricant, thereby extending the drain interval of the lubricant.

Thus, in accordance with a first aspect, the present invention provides a lubricating oil composition having a sulphated ash content of less than or equal to 1.0 mass % as determined by ASTM D874, the composition comprising or made by admixing:

(A) an oil of lubricating viscosity in a major amount;

(B) one or more oil-soluble or oil-dispersible overbased magnesium salicylate detergent(s) having a TBN of greater than or equal to 220 mg/g KOH as determined by ASTM D2896, as an additive in an effective minor amount; and,

(C) an oil-soluble or oil-dispersible ashless alkylene bis(dihydrocarbyldithiocarbamate), as an additive in an effective minor amount.

Preferably, the lubricating oil composition according to the present invention is a crankcase lubricant. Even more preferably, the lubricating composition according to the present invention is suitable for use in a heavy duty diesel engine.

According to a second aspect, the present invention provides a method of lubricating a spark-ignited or compression-ignited internal combustion engine comprising lubricating the engine with a lubricating oil composition as defined in accordance with the first aspect of the present invention.

According to a third aspect, the present invention provides a method of extending the time taken to reach the TBN/TAN cross-over point (i.e. extending the drain interval) of a lubricating oil composition comprising an oil of lubricating viscosity in a major amount, the method comprising admixing with the lubricating oil composition one or more oil-soluble or oil-dispersible overbased magnesium salicylate detergent(s) (B) as defined in accordance with the first aspect of the present invention, as an additive in an effective minor amount, and an oil-soluble or oil-dispersible ashless alkylene bis(dihydrocarbyldithiocarbamate) (C) as defined in accordance with the first aspect of the present invention, as an additive in an effective minor amount, and lubricating a spark-ignited or compression ignited internal combustion engine with the lubricating oil composition.

According to a fourth aspect, the present invention provides the use, in the lubrication of a spark-ignited or compression ignited internal combustion engine, of one or more oil-soluble or oil-dispersible overbased magnesium salicylate detergent(s) (B) as defined in accordance with the first aspect of the present invention, as an additive in an effective minor amount, in combination with an oil-soluble or oil-dispersible ashless alkylene bis(dihydrocarbyldithiocarbamate) (C) as defined in accordance with the first aspect of the present invention, as an additive in an effective minor amount, in a lubricating oil composition comprising an oil of lubricating viscosity in a major amount, to extend the drain interval of the lubricating oil composition during operation of the engine.

According to a fifth aspect, the present invention provides the use, in the lubrication of a spark-ignited or compression ignited internal combustion engine, of one or more oil-soluble or oil-dispersible overbased magnesium salicylate detergent(s) (B) as defined in accordance with the first aspect of the present invention, as an additive in an effective minor amount, in combination with an oil-soluble or oil-dispersible ashless alkylene bis(dihydrocarbyldithiocarbamate) (C) as defined in accordance with the first aspect of the present invention, as an additive in an effective minor amount, in a lubricating oil composition comprising an oil of lubricating viscosity in a major amount, to extend the time taken to reach the TBN/TAN cross-over point of the lubricating oil composition during operation of the engine.

Suitably, the time taken to reach the TBN/TAN cross-over point of a lubricating oil composition as defined in the third and fifth aspects of the present invention and the drain interval of a lubricating oil composition as defined in the fourth aspect of the present invention is measured by employing the extended Mack T-12 engine test procedure (ASTM D7422) and running the test until the TBN/TAN cross-over point is at least reached, as described herein, and represents the time elapsed to reach the earliest specific 25 hour sampling point at which the TBN is equivalent to TAN or, if the TBN/TAN cross-over point is not met exactly at a specific 25 hour sampling point, the time elapsed to reach the first 25 hour sampling point where the TBN has fallen below TAN.

Preferably, the time taken to reach the TBN/TAN cross-over point of a lubricating oil composition as defined in the third and fifth aspects of the present invention is greater than 400, more preferably greater than or equal to 425, most preferably greater than or equal to 450 hours as determined by employing the Mack T-12 engine test procedure (ASTM D7422) and running the test until the TBN/TAN cross-over point is reached, as described herein.

Preferably, the drain interval of a lubricating oil composition as defined in the fourth aspect of the present invention is greater than 400, more preferably greater than or equal to 425, most preferably greater than or equal to 450 hours as determined by employing the Mack T-12 engine test procedure (ASTM D7422) and running the test until the TBN/TAN cross-over point is reached, as described herein.

Preferably, the engine as defined in the second, third, fourth and fifth aspects of the present invention is a compression-ignited internal combustion engine (i.e. a diesel engine), more preferably a heavy duty diesel engine.

Preferably, the one or more overbased salicylate detergent(s) in the lubricating oil composition of the first aspect of the present invention and as defined in the second, third, fourth and fifth aspects of the present invention are the sole metal containing detergent(s) which are present in the lubricating oil composition (i.e. the only metal containing detergents which are present in the lubricating oil composition are the one or more overbased metal salicylate detergents). More preferably, the only metal containing detergents which are present in the lubricating oil composition are the one or more overbased magnesium salicylate detergents.

Preferably, the lubricating oil composition of the first aspect of the present invention and as defined in the second, third, fourth and fifth aspects of the present invention further includes an anti-oxidant, as an additive in an effective minor amount. More preferably, the anti-oxidant comprises an aminic antioxidant, preferably an aromatic amine anti-oxidant, a phenolic anti-oxidant or a combination thereof, especially an aromatic amine anti-oxidant. In a highly preferred lubricating oil composition of the first aspect of the present invention and as defined in the second, third, fourth and fifth aspects of the present invention the lubricating oil composition includes both an aromatic amine and phenolic anti-oxidant. Suitably, the anti-oxidant(s) are ashless anti-oxidant(s).

Preferably, the lubricating oil composition of the first aspect of the present invention and as defined in the second, third, fourth and fifth aspects of the present invention further includes an oil-soluble or oil-dispersible organo-molybdenum compound, as an additive in an effective minor amount. Suitably, when present, the organo-molybdenum compound provides the lubricating oil composition with at least 10 ppm of molybdenum (ASTM D5185), based on the total mass of the lubricating oil composition.

Preferably, the lubricating oil composition of the first aspect of the present invention and as defined in the second, third, fourth and fifth aspects of the present invention further includes a dihydrocarbyl dithiophosphate metal salt, as an additive component in an effective minor amount.

Preferably, the lubricating oil composition of the first aspect of the present invention and as defined in the second, third, fourth and fifth aspects of the present invention further includes one or more co-additives in an effective minor amount (e.g. 5 to 25, preferably 5 to 18, more preferably 7 to 15, mass % of the one or more co-additives), other than additive components (B) and (C), selected from ashless dispersants, metal detergents, corrosion inhibitors, antioxidants, pour point depressants, antiwear agents, friction modifiers, demulsifiers, antifoam agents and viscosity modifiers.

Preferably, the lubricating oil composition of the present invention has a sulphated ash content of less than or equal to 0.95 mass % as determined by ASTM D874.

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 mass %, preferably up to 0.11 mass %, more preferably less than or equal to 0.10 mass %, even more preferably less than or equal to 0.09 mass %, even more preferably less than or equal to 0.08 mass %, 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 0.02, preferably greater than or equal to 0.03, mass % of phosphorus (ASTM D5185) based on the total mass of the composition.

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

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

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 "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 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.). Preferably, the group consists essentially of, more preferably consists only of, hydrogen and carbon atoms, unless specified otherwise. Preferably, the hydrocarbyl group comprises an aliphatic hydrocarbyl group. The term "hydrocarbyl" includes "alkyl", "alkenyl", "alkynyl" and "aryl" as defined herein;

"alkyl" means a C_1 to C_{30}, preferably a C_1 to C_{12}, group which is bonded to the remainder of the 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, 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;

"alkenyl" means a C_2 to C_{30}, preferably a C_2 to C_{12}, 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";

"alkynyl" means a C_2 to C_{30}, preferably a C_2 to C_{12}, group which includes at least one carbon to carbon triple bond and is bonded to the remainder of the compound directly via a single carbon atom, and is otherwise defined as "alkyl";

"aryl" means a C_6 to C_{18}, preferably C_6 to C_{10}, 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 ;

"alkylene" means a C_1 to C_{20}, preferably a C_1 to C_{10}, bivalent saturated aliphatic radical which may be linear or branched. Representative examples of alkylene include methylene, ethylene, propylene, butylene, 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;

"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;

“TBN/TAN cross-over point” in relation to a lubricating oil composition means when the TBN (ASTM D4739) and TAN (ASTM D664) of the lubricating oil composition are equivalent;

“drain interval” in relation to a lubricating oil composition as used herein represents the time taken, in use, to reach the TBN/TAN cross-over point;

“to extend the drain interval” and “extend the time taken to reach the TBN/TAN cross-over point” in relation to a lubricating oil composition means extending the time taken, in use, to reach the TBN/TAN cross-over point of a lubricating oil composition by employing a combination of one or more oil-soluble or oil-dispersible overbased magnesium salicylate detergent(s) (B) as defined in accordance with the first aspect of the present invention, as an additive in an effective minor amount, in combination with an oil-soluble or oil-dispersible ashless alkylene bis(dihydrocarbyldithiocarbamate) (C) as defined in accordance with the first aspect of the present invention, as an additive in an effective minor amount, in comparison with a comparable lubricating oil composition which does not include the oil-soluble or oil-dispersible ashless alkylene bis(dihydrocarbyldithiocarbamate) (C);

“major amount” means in excess of 50 mass % of a composition;

“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 all the additives present in the composition, reckoned as active ingredient of the additive or additives;

“effective minor amount” in respect of an additive means an amount of such an additive of less than 50 mass % of the 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 magnesium content, molybdenum content or total metal content (i.e. the sum of all individual metal contents), is measured by ASTM D5185;

“TBN” in relation to an additive component or of a fresh lubricating oil composition of the present invention (i.e. unused lubricating oil composition), with the exception of measuring the TBN of a lubricating oil composition when determining the TBN/TAN cross-over point of the lubricating oil composition, means total base number as measured by ASTM D2896;

“TBN” of a lubricating oil composition when determining the TBN/TAN cross-over point of the lubricating oil composition means total base number as measured by ASTM D4739;

“TAN” means total acid number as measured by ASTM D664;

“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 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 invention are regarded as preferred features of every other aspect of the present invention. Accordingly, preferred and more preferred features of one aspect of the present invention may be independently combined with other preferred and/or more preferred features of the same aspect or different aspects of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The features of the invention relating, where appropriate, to each and all aspects of the invention, will now be described in more detail as follows:

OIL OF LUBRICATING VISCOSITY (A)

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 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, mm^2/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

Preferably, the oil of lubricating viscosity comprises greater than or equal to 10 mass %, more preferably greater than or equal to 20 mass %, even more preferably greater than or equal to 25 mass %, even more preferably greater than or equal to 30 mass %, even more preferably greater than or equal to 40 mass %, even more preferably greater than or equal to 45 mass % of a Group II or Group III base stock, based on the total mass of the oil of lubricating viscosity. Even more preferably, the oil of lubricating viscosity comprises greater than 50 mass %, preferably greater than or equal to 60 mass %, more preferably greater than or equal to 70 mass %, even more preferably greater than or equal to 80 mass %, even more preferably greater than or equal to 90 mass % of a Group II or Group III base stock, based on the total mass of the oil of lubricating viscosity. Most preferably, the oil of lubricating viscosity consists essentially of a Group II or Group III base stock. In some embodiments the oil of lubricating viscosity consists solely of Group II or Group III base stock. In the latter case it is acknowledged that additives included in the lubricating oil composition may comprise a carrier oil which is not a Group II or Group III base stock.

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 interpolymerized olefins (e.g. polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkylbenzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenols (e.g. biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogues 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, sebasic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g. butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of 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 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 C_5 to C_{12} monocarboxylic acids and polyols, and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

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 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 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 H_2 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.

The oil of lubricating viscosity may also comprise a Group I, Group IV or Group V base stocks or base oil blends of the aforementioned base stocks.

Preferably, the volatility of the oil of lubricating viscosity or oil blend, as measured by the NOACK test (ASTM D5880), is less than or equal to 16%, preferably less than or equal to 13.5%, preferably less than or equal to 12%, more preferably less than or equal to 10%, most preferably less than or equal to 8%. Preferably, the viscosity index (VI) of the oil of lubricating viscosity is at least 95, preferably at least 110, more preferably at least 120, even more preferably at least 125, most preferably from about 130 to 140.

The oil of lubricating viscosity is provided in a major amount, in combination with a minor amount of additive components (B) and (C), as defined herein and, if necessary, one or more co-additives, such as described hereinafter, constituting a lubricating oil composition. This preparation may be accomplished by adding the additives directly to the oil or by adding them in the form of a concentrate thereof to disperse or dissolve the additive. Additives may be added to the oil by any method known to those skilled in the art, either before, at the same time as, or after addition of other additives.

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 65 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.

When concentrates are used to make the lubricating oil compositions, they may for example be diluted with 3 to 100, e.g. 5 to 40, parts by mass of oil of lubricating viscosity per part by mass of the concentrate.

Preferably, the lubricating oil composition is a multigrade oil identified by the viscometric descriptor SAE 20WX, SAE 15WX, SAE 10WX, SAE 5WX or SAE 0WX, where X represents any one of 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 15 WX, SAE 10WX, SAE 5WX or SAE 0WX, wherein X represents any one of 20, 30, 40 and 50. Preferably X is 20, 30 or 40.

OVERBASED MAGNESIUM SALICYLATE DETERGENT (B)

The lubricating oil composition of the present invention requires the presence of at least one overbased magnesium salicylate detergent having a TBN of greater than or equal to 220 mg/g KOH, as measured in accordance with ASTM D2896.

A detergent is an additive that reduces formation of piston deposits, for example high-temperature varnish and lacquer deposits, in engines; it normally has acid-neutralising properties and is capable of keeping finely-divided solids in suspension. Most detergents are based on metal "soaps", that is metal salts of acidic organic compounds. Accordingly, the lubricating oil composition includes a magnesium salt of salicylic acid as the metal soap.

Detergents generally comprise a polar head with a long hydrophobic tail, the polar head comprising a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal when they are usually described as normal or neutral salts and would typically have a total base number or TBN (as may be measured by ASTM D2896) of from 0 to 80. Large amounts of a metal base can be included by reaction of an excess of a metal compound, such as an oxide or hydroxide, with an acidic gas such as carbon dioxide. The resulting overbased detergent comprises neutralised detergent as an outer layer of a metal base (e.g. carbonate) micelle. Such overbased detergents may have a TBN of 150 or greater, and typically of from 200 to 500 or more.

The overbased magnesium salicylate detergent is preferably a C_8 to C_{30} alkyl salicylate and mixtures thereof, with C_{10} to C_{20} alkyl salicylates, particularly C_{14} to C_{18} alkyl salicylates and mixtures thereof being particularly preferred. The alkyl group(s) may be linear or branched and examples of suitable alkyl groups include: octyl; nonyl; decyl; dodecyl; pentadecyl; octadecyl; eicosyl; docosyl; tricosyl; hexacosyl; and, triacontyl. The overbased magnesium salicylate detergent, as defined herein, may also include sulfurized derivatives thereof.

The overbased magnesium salicylate may be prepared by methods well known to those skilled in the art, for example, by reacting the appropriate salicylic acid(s) with an excess of magnesium oxide or hydroxide and an acidic gas such as carbon dioxide. The salicylic acid(s) are typically prepared by carboxylation, for example by the Kolbe-Schmitt process, of phenoxides. Processes for sulfurizing the salicylic acid(s) are known to those skilled in the art.

Preferably, the overbased magnesium salicylate detergent has a TBN of at least 250, more preferably at least 300, most preferably at least 320, mg/g KOH as determined by ASTM D2896. Preferably, the overbased magnesium salicylate detergent has a TBN of less than 500, most preferably less than 450, mg/g KOH as determined by ASTM D2896.

Preferably, the overbased magnesium salicylate detergent provides the lubricating oil composition with greater than or equal to 0.05, more preferably greater than or equal to 0.06, more preferably greater than or equal to 0.07, most preferably greater than or equal to 0.10 mass % of magnesium as measured by ASTM D5185, based on the total mass of the lubricating oil composition. Preferably, the overbased magnesium salicylate detergent provides the lubricating oil composition with less than or equal to 0.50, even more preferably less than or equal to 0.40, most preferably less than or equal to 0.30, mass % of magnesium as measured by ASTM D5185, based on the total mass of the lubricating oil composition.

It will be appreciated that the overbased magnesium salicylate detergent is included in the lubricating oil composition in an amount such that total amount of sulfated ash contributed by the detergent component to the lubricant, and any other metal containing component which may be present (e.g. ZDDP), is less than or equal to 1.0, preferably less than or equal to 0.95, mass % as determined by ASTM D874. Preferably, the overbased magnesium salicylate detergent is included in the lubricating oil composition in an amount such that total amount of sulfated ash contributed by the detergent component to the lubricant, and any other metal containing component which may be present, is greater than or equal to 0.30, preferably greater than or equal to 0.40, mass % as determined by ASTM D874.

Preferably, the amount of overbased magnesium detergent provides the lubricating oil composition with greater than or equal to 5, preferably greater than or equal to 7, mmoles of magnesium salicylate soap per kilogram of the lubricating oil composition. Preferably, the amount of overbased magnesium detergent provides the lubricating oil composition with less than or equal to 20, preferably less than or equal to 15, mmoles of magnesium salicylate soap per kilogram of the lubricating oil composition. By the term "magnesium salicylate soap" we mean the amount of magnesium salicylate contributed by the overbased magnesium salicylate detergent exclusive of any overbasing material.

Preferably, the overbased magnesium salicylate detergent is present in an amount of greater than or equal to 0.1, more preferably greater than or equal to 0.2, most preferably greater than or equal to 0.5, mass % based on the total mass of the lubricating oil composition. Preferably, the overbased magnesium salicylate detergent is present in an amount of less than or equal to 15, more preferably less than or equal to 9, most preferably less than or equal to 5, mass % based on the total mass of the lubricating oil composition.

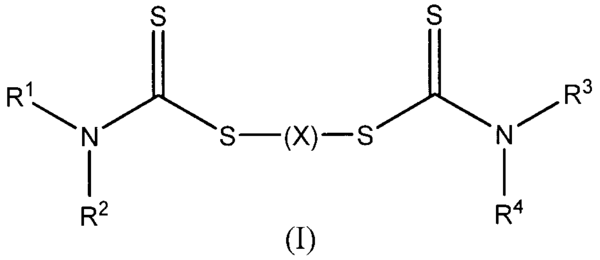
Other metal containing detergents may be present in the lubricating oil composition and include oil-soluble salts of neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates and naphthenates of a metal, particularly the alkali or alkaline earth metals, e.g. sodium, potassium, lithium, calcium and magnesium. The most commonly used metals are calcium and magnesium, which may both be present in detergents used in a lubricant, and mixtures of calcium and/or magnesium with sodium. Detergents may be used in various combinations.

According to a highly preferred aspect of the present invention, the one or more overbased magnesium salicylate detergent(s) represent the sole metal containing detergents in the lubricating oil composition.

ALKYLENE BIS(DIHYDROCARBYLDITHIOCARBAMATE) (C)

The lubricating oil composition of the present invention requires the presence of an ashless alkylene bis(dihydrocarbyldithiocarbamate).

Preferably, the ashless alkylene bis(dihydrocarbyldithiocarbamate) is a compound of formula (I):



(I)

wherein:

R^1, R^2, R^3 and R^4 each independently represent, at each occurrence when used herein, a C_1 to C_{30} hydrocarbyl group; and,

X represents a C_1 to C_{20} alkylene group.

Preferably, R^1, R^2, R^3 and R^4 each independently represent, at each occurrence when used herein, a C_1 to C_{20} hydrocarbyl group. More preferably, R^1, R^2, R^3 and R^4 each independently represent, at each occurrence when used herein, a branched or linear (i.e. unbranched) C_1 to C_{16} alkyl group or a substituted or unsubstituted aryl group. Even more preferably, R^1, R^2, R^3 and R^4 each independently represent, at each occurrence when used herein, a branched or linear C_1 to C_{16} alkyl group, a C_1 to C_{16} alkyl substituted aryl group or an unsubstituted aryl group. Even more preferably, R^1, R^2, R^3 and R^4 each independently represent, at each occurrence when used herein, a branched or linear C_1 to C_{16} alkyl group, a C_1 to C_{16} alkyl substituted phenyl group or an unsubstituted phenyl group.

It will be appreciated that when R^1, R^2, R^3 and R^4 each independently represent a substituted or unsubstituted aryl group as defined herein, then the appropriate nitrogen atom of a compound of formula I is bonded to a carbon atom of the aryl ring of the appropriate substituted or unsubstituted aryl group by a nitrogen to carbon single bond.

In a highly preferred compound of formula I, R^1, R^2, R^3 and R^4 each independently represent a branched or linear C_1 to C_{16} alkyl group, especially a branched or linear C_1 to

C_{10} alkyl group. Preferably, in such a compound of formula I each of R^1, R^2, R^3 and R^4 are identical.

In an alternative highly preferred compound of formula I, R^1, R^2, R^3 and R^4 each independently represent a C_1 to C_{16} alkyl substituted aryl group or an unsubstituted aryl group, more preferably a C_1 to C_{16} alkyl substituted phenyl group or an unsubstituted phenyl group, even more preferably a C_3 to C_{16} alkyl substituted phenyl group. Preferably, in such a compound of formula I each of R^1, R^2, R^3 and R^4 are identical.

In a still further alternative highly preferred compound of formula I:

> R^1 and R^3 each independently represent a branched or linear C_1 to C_{16} alkyl group, especially a branched or linear C_1 to C_{10} alkyl group; and,
>
> R^2 and R^4 each independently represent a C_1 to C_{16} alkyl substituted aryl group or an unsubstituted aryl group, more preferably a C_1 to C_{16} alkyl substituted phenyl group or an unsubstituted phenyl group, even more preferably an unsubstituted phenyl group.

Preferably, in such a compound of formula I, R^1 and R^3 are identical, and R^2 and R^4 are identical.

Preferably, X in a compound of formula I, as defined herein, represents a C_1 to C_{10} alkylene group. More preferably, X in a compound of formula I represents $(CH_2)n$ where n is an integer from 1 to 20, preferably an integer from 1 to 10, more preferably an integer from 1 to 5, especially 1 (i.e. X represents methylene when n is 1).

Highly preferred compounds of formula I include: methylene bis(N-n-octyl-N-phenyldithiocarbamate); methylene bis(di(nonylphenyl)dithiocarbamate) – wherein each nitrogen atom of the dithiocarbamate is bonded to two phenyl rings, each of said rings are substituted with a C_9 alkyl group; and, methylene bis(dibutyldithiocarbamate). An especially preferred compound of formula I is methylene bis(dibutyldithiocarbamate).

The ashless alkylene bis(dihyrocarbyldithiocarbamates) may be prepared by methods well known to those skilled in the art. For example, an appropriate amine may be reacted with sodium hydride, the resulting product reacted with carbon disulphide, and the resulting product reacted with a dihaloalkane, e.g. iodomethane. Suitably, methylene bis(N-n-octyl-N-phenyldithiocarbamate) and methylene bis(di(nonylphenyl)dithiocarbamate) may be prepared as described in European patent application EP 2,692,840A and methylene bis(dibutyldithiocarbamate) is commercially available and sold under the trade name of Vanlube 7723 by Vanderbilt Chemicals LLC, USA.

Preferably, the ashless alkylene bis(dihydrocarbyldithiocarbamate) is present in an amount of greater than or equal to 0.1, more preferably greater than or equal to 0.2, mass %, based on the total mass of the lubricating oil composition. Preferably, the ashless alkylene bis(dihydrocarbyldithiocarbamate) is present in an amount of less than or equal to 5.0, more preferably less than or equal to 3.0, even more preferably less than or equal to 2.0, most preferably less than or equal to 1.0, mass %, based on the total mass of the lubricating oil composition.

ENGINES

The lubricating oil compositions of the invention may be used to lubricate mechanical engine components, particularly in internal combustion engines, e.g. spark-ignited or compression-ignited internal combustion engines, particularly spark-ignited or compression-ignited two- or four- stroke reciprocating engines, by adding the composition thereto. The engines may be conventional gasoline or diesel engines designed to be powered by gasoline or petroleum diesel, respectively; alternatively, the engines may be specifically modified to be powered by an alcohol based fuel or biodiesel fuel. Most preferably, the engine comprises a compression-ignited internal combustion engine, especially a heavy duty diesel engine. Preferably, the lubricating oil compositions are crankcase lubricants.

CO-ADDITIVES

Co-additives, with representative effective amounts, that may also be present, different from additive components (B) and (C), are listed below. All the values listed are stated as mass percent active ingredient in a fully formulated lubricant.

Additive	**Mass %** (Broad)	**Mass %** (Preferred)
Ashless Dispersant	0.1 – 20	1 – 8
Metal Detergents	0.1 – 15	0.2 – 9
Friction modifier	0 – 5	0 – 1.5
Corrosion Inhibitor	0 – 5	0 – 1.5
Metal Dihydrocarbyl Dithiophosphate	0 – 10	0 – 4
Anti-Oxidants	0 – 5	0.01 – 3
Pour Point Depressant	0.01 – 5	0.01 – 1.5
Anti-Foaming Agent	0 – 5	0.001 – 0.15
Supplement Anti-Wear Agents	0 – 5	0 – 2
Viscosity Modifier (1)	0 – 6	0.01 – 4
Mineral or Synthetic Base Oil	Balance	Balance

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

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 co-additives, the remainder being oil of lubricating viscosity.

Suitably, the lubricating oil composition includes one or more co-additives in a minor amount, other than additive components (B) and (C), selected from ashless dispersants, metal detergents, corrosion inhibitors, antioxidants, pour point depressants, antiwear agents, friction modifiers, demulsifiers, antifoam agents and viscosity modifiers.

The above mentioned co-additives are discussed in further detail as follows; 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.

A dispersant is an additive 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.

A preferred class of olefin polymers is constituted by polybutenes, specifically polyisobutenes (PIB) or poly-n-butenes, such as may be prepared by polymerization of a C_4 refinery stream.

Dispersants include, for example, derivatives of long chain hydrocarbon-substituted carboxylic acids, examples being derivatives of high molecular weight hydrocarbyl-substituted succinic acid. A noteworthy group of dispersants is constituted by hydrocarbon-substituted succinimides, made, for example, by reacting the above acids (or derivatives) with a nitrogen-containing compound, advantageously a polyalkylene polyamine, such as a polyethylene polyamine. Particularly preferred are the reaction products of polyalkylene polyamines with alkenyl succinic anhydrides, such as described in US-A-3,202,678; US-A-3,154,560; US-A-3,172,892; US-A-3,024,195; US-A-3,024,237, US-A-3,219,666; and US-A-3,216,936, that may be post-treated to improve their properties, such as borated (as described in US-A-3,087,936 and US-A-3,254,025) fluorinated and oxylated. For example, boration may be accomplished by treating an acyl nitrogen-containing dispersant with a boron compound selected from boron oxide, boron halides, boron acids and esters of boron acids.

Friction modifiers include glyceryl monoesters of higher fatty acids, for example, glyceryl mono-oleate; esters of long chain polycarboxylic acids with diols, for example, the butane diol ester of a dimerized unsaturated fatty acid; oxazoline compounds; and alkoxylated alkyl-substituted mono-amines, diamines and alkyl ether amines, for example, ethoxylated tallow amine and ethoxylated tallow ether amine.

Other known friction modifiers comprise oil-soluble or oil-dispersible organo-molybdenum compounds. Such organo-molybdenum friction modifiers also provide antioxidant and antiwear credits to a lubricating oil composition. Suitable oil-soluble or oil-dispersible organo-molybdenum compounds have a molybdenum-sulfur core. As examples there may be mentioned dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and mixtures thereof. Particularly preferred are molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl xanthates and alkylthioxanthates. The molybdenum compound is dinuclear or trinuclear.

One class of preferred oil-soluble or oil-dispersible organo-molybdenum compounds useful in all aspects of the present invention is tri-nuclear molybdenum compounds of the formula $Mo_3S_kL_nQ_z$ and mixtures thereof wherein L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compounds soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 through 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. 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.

Suitably, the oil-soluble or oil-dispersible organo-molybdenum compounds may be present in the lubricating oil composition in an amount of greater than or equal to 0.02, preferably greater than or equal to 0.05, mass % based on the total mass of the lubricating oil composition. Suitably, the oil-soluble or oil-dispersible organo-molybdenum compounds may be present in the lubricating oil composition in an amount of less than or equal to 2.0, preferably less than or equal to 1.0, even more preferably less than or equal to 0.5, mass % based on the total mass of the lubricating oil composition.

Suitably, the oil-soluble or oil-dispersible organo-molybdenum compound provides the lubricant with greater than or equal to 10, preferably greater than or equal to 20, more preferably greater than or equal to 30, ppm of molybdenum (ASTM D5185) based on the total mass of the lubricating oil composition. Suitably, oil-soluble or oil-dispersible organo-molybdenum compound provides the lubricant with less than or equal to 1500, preferably less than or equal to 1000, more preferably less than or equal to 700, ppm of molybdenum (ASTM D5185) based on the total mass of the lubricating oil composition.

Anti-oxidants are sometimes referred to as oxidation inhibitors; they 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 an oxidation catalyst inert. Oxidative deterioration can be evidenced by sludge in the lubricant, varnish-like deposits on the metal surfaces, and by viscosity growth.

They may be classified as radical scavengers (e.g. sterically hindered phenols, aromatic amines, particularly secondary aromatic amines having at least two aromatic (e.g. phenyl groups) groups attached directly to the nitrogen atom, and organo-copper salts); hydroperoxide decomposers (e.g., organosulfur and organophosphorus additives); and multifunctionals (e.g. zinc dihydrocarbyl dithiophosphates, which may also function as anti-wear additives, and organo-molybdenum compounds, which may also function as friction modifiers and anti-wear additives).

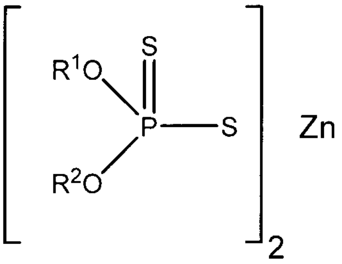
Preferably, the lubricating oil composition in all aspects of the present invention includes an anti-oxidant, more preferably an ashless anti-oxidant. More preferably, the anti-oxidant, when present, is an aromatic amine anti-oxidant, a phenolic anti-oxidant or a combination thereof, especially an aromatic amine anti-oxidant. Even more preferably, the lubricating oil composition in all aspects of the present invention includes both an aromatic amine and phenolic anti-oxidant. Accordingly, the aromatic amine and/or phenolic anti-oxidants, when present, are ashless anti-oxidants.

Suitably, the total amount of anti-oxidant (e.g. aromatic amine anti-oxidant, a phenolic anti-oxidant or a combination thereof) which may be present in the lubricating oil composition is greater than or equal to 0.05, preferably greater than or equal to 0.1, even more preferably greater than or equal to 0.2, mass % based on the total mass of the lubricating oil composition. Suitably, the total amount of anti-oxidant which may be present in the lubricating oil composition is less than or equal to 5.0, preferably less than or equal to 3.0, even more preferably less than or equal to 2.5, mass % based on the total mass of the lubricating oil composition

Anti-wear agents 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, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the 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 dihydrocarbyl dithiophosphate metal salts are zinc dihydrocarbyl dithiophosphates (ZDDPs) which are oil-soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



$$\left[(R^1O)(R^2O)P(=S)S\right]_2 Zn$$

wherein R^1 and R^2 may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and include radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R^1 and R^2 groups are alkyl groups of 2 to 8 carbon atoms, especially primary alkyl groups (i.e. R^1 and R^2 are derived from predominantly primary alcohols). Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, iso-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^1 and R^2) in the dithiophosphoric acid will generally be about 5 or greater. Preferably, the zinc dihydrocarbyl dithiophosphate comprises a zinc dialkyl dithiophosphate.

Preferably, the lubricating oil composition contains an amount of dihydrocarbyl dithiophosphate metal salt that introduces 0.02 to 0.12, more preferably 0.02 to 0.11, even more preferably 0.02 to 0.10, even more preferably 0.02 to 0.09, even more preferably 0.02

to 0.08 mass %, most preferably 0.02 to 0.06, mass % of phosphorus as measured in accordance with ASTM D5185, based on the total mass of the composition.

To limit the amount of phosphorus introduced into the lubricating oil composition to no more than 0.12 mass %, the dihydrocarbyl dithiophosphate metal salt should preferably be added to the lubricating oil compositions in amounts no greater than 1.5 mass % (a.i.), based upon the total mass of the lubricating oil composition.

Examples of ashless anti-wear agents include 1,2,3-triazoles, benzotriazoles and sulfurised fatty acid esters.

Rust and corrosion inhibitors serve to protect surfaces against rust and/or corrosion. As rust inhibitors there may be mentioned non-ionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, thiadiazoles and anionic alkyl sulfonic acids.

Pour point depressants, otherwise known as lube oil flow improvers, lower the minimum temperature at which the oil will flow or can be poured. Such additives are well known. Typical of these additive are C_8 to C_{18} dialkyl fumarate/vinyl acetate copolymers and polyalkylmethacrylates.

Additives of the polysiloxane type, for example silicone oil or polydimethyl siloxane, can provide foam control.

A small amount of a demulsifying component may be used. A preferred demulsifying component is described in EP-A-330,522. It is obtained by reacting an alkylene oxide with an adduct obtained by reaction of 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.

Viscosity modifiers (or viscosity index improvers) impart high and low temperature operability to a lubricating oil. Viscosity modifiers that also function as dispersants are also known and may be prepared as described above for ashless dispersants. In general, these dispersant viscosity modifiers are functionalised polymers (e.g. interpolymers of ethylene-propylene post grafted with an active monomer such as maleic anhydride) which are then derivatised with, for example, an alcohol or amine.

The lubricant may be formulated with or without a conventional viscosity modifier and with or without a dispersant viscosity modifier. Suitable compounds for use as viscosity modifiers are generally high molecular weight hydrocarbon polymers, including polyesters. 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.

The additives may be incorporated into an oil of lubricating viscosity (also known as a base oil) in any convenient way. Thus, each additive can be added directly to the oil by dispersing or dissolving it in the oil at the desired level of concentration. Such blending may occur at ambient temperature or at an elevated temperature. Typically an additive is available as an admixture with a base oil so that the handling thereof is easier.

When a plurality of additives are employed it may be desirable, although not essential, to prepare one or more additive packages (also known as additive compositions or concentrates) comprising additives and a diluent, which can be a base oil, whereby the additives, with the exception of viscosity modifiers, multifuntional viscosity modifiers and pour point depressants, can be added simultaneously to the base oil to form the lubricating oil composition. Dissolution of the additive package(s) into the oil of lubricating viscosity may be facilitated by diluent or solvents and by mixing accompanied with mild heating, but this is not essential. The additive package(s) will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration in the final formulation when the additive package(s) is/are combined with a predetermined amount of oil of lubricating viscosity. Thus, one or more detergents may be added to small amounts of base oil or other compatible solvents (such as a carrier oil or diluent oil) together with other desirable additives to form additive packages containing from 2.5 to 90, preferably from 5 to 75, most preferably from 8 to 60, mass %, based on the mass of the additive package, of additives on an active ingredient basis in the appropriate proportions. The final formulations may typically contain 5 to 40 mass % of the additive package(s), the remainder being oil of lubricating viscosity.

EXAMPLES

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

TBN/TAN Cross-Over: The Extended Mack T-12 Test

The TBN/TAN cross-over point of a lubricant is evaluated using an extended Mack T-12 engine test procedure as described in ASTM D7422; this test method is commonly referred to as the Mack T-12.

The Mack T-12 engine test procedure is a standard engine-dynamometer test for evaluating the ability of a diesel engine lubricant to control lead corrosion, oil consumption, and wear of piston rings and cylinder liners in an engine equipped with Exhaust Gas Recirculation (EGR) and running on ultra-low sulphur diesel (ULSD). The Mack T-12 test employs a Mack E-TECH V-MAC III diesel engine equipped with exhaust gas recirculation (EGR). The diesel engine is an in-line, six cylinder, four-stroke, turbocharged engine with 12 litre displacement. The standard Mack T-12 procedure is a two phase test lasting 300-hours where the engine in each phase is run at constant speed and load. The first 100-hour phase has retarded injection timing to produce soot in the oil. The second 200-hour phase is run at heavy load to promote piston ring and cylinder liner wear. The steady-state operating parameters for the two phases are set out in Table 1 of ASTM D7422. In the Mack T-12 test the engine initially includes 32.7 kg of lubricant and after the 100 hour point, i.e. after completion of Phase 1, 2.27 kg of fresh lubricant is added at every 50-hour interval. If necessary, used lubricant is removed first so that the lubricant mass is below the full mark by 2.27kg. When determining the TBN/TAN cross-over point of a lubricant, the test procedure is run for an extended time. In the extended Mack T-12 test used herein for evaluating the TBN/TAN cross-over point of a lubricant the engine is continued to run under the Phase 2 conditions until the TBN/TAN cross-over point is at least reached, more preferably for 50-hours afterwards, up to a maximum test length of 600-hours.

The initial TBN and TAN of a lubricant are measured in accordance with ASTM D4739 and D664, respectively, prior to the Mack T-12 test. During the Mack T-12 test for each lubricant, a sample of the lubricant (120 ml) is removed from the engine at 25-hours intervals throughout the test for physical and chemical analysis. The TBN (ASTM D4739) and the TAN (ASTM D664) of the lubricant sample is measured and recorded. The TBN/TAN cross-over point represents the earliest specific 25 hour sampling point at which the TBN is equivalent to TAN or, if the TBN/TAN cross-over point is not met exactly at a specific 25 hour sampling point, the first 25 hour sampling point where the TBN has fallen below TAN.

TBN/TAN Cross-Over Point Results

A series of 15W/40 multigrade lubricating oil compositions of essentially equal sulfated ash (ASTM D874) were prepared by admixing a Group II base stock with known additives, as detailed herein. Each of the Comparative lubricating oil compositions and the Inventive lubricating oil compositions included identical amounts of the following additives which are available from Infineum UK Ltd: a dispersant (4.75 mass %); a tri-nuclear organo molybdenum compound; an anti-foam; a pour point depressant; and, a viscosity modifier. Further details of the composition of each lubricant is set out below, where Lubricants A to C are comparative lubricants and lubricants 1 and 2 represent lubricants of the present invention:

Lubricant A: Overbased calcium sulphonate detergent (TBN 300 mg/g KOH); overbased magnesium sulphonate detergent (TBN 400 mg/g KOH); overbased calcium phenate detergent (TBN 140 mg/g KOH); ZDDP; aromatic amine anti-oxidant (0.50 mass %). Sulphated Ash 0.95 mass % (ASTM D874); phosphorus 0.12 mass % (ASTM D5185); sulphur 0.3 mass % (ASTM D2622).

Lubricant B: Overbased magnesium salicylate detergent (TBN 342 mg/g KOH); ZDDP; aromatic amine anti-oxidant (0.50 mass %). Sulphated Ash 0.92 mass % (ASTM D874); phosphorus 0.12 mass % (ASTM D5185); sulphur 0.3 mass % (ASTM D2622).

Lubricant C: Overbased magnesium salicylate detergent (TBN 342 mg/g KOH); ZDDP; aromatic amine anti-oxidant (1.50 mass %); phenolic anti-oxidant (1.0 mass %). Sulphated Ash 0.93 mass % (ASTM D874); phosphorus 0.12 mass % (ASTM D5185); sulphur 0.3 mass % (ASTM D2622).

Lubricant 1: Overbased magnesium salicylate detergent (TBN 342 mg/g KOH); ZDDP; aromatic amine anti-oxidant (0.50 mass %); methylene bis(dibutyldithiocarbamate) (0.40 mass %). Sulphated Ash 0.93 mass % (ASTM D874); phosphorus 0.06 mass % (ASTM D5185); sulphur 0.3 mass % (ASTM D2622); TBN 9.9 mg/g KOH (D4739) or 12.7 mg/g KOH (D2896); magnesium salicylate soap (12 mmoles); magnesium (0.2 mass %).

Lubricant 2: Overbased magnesium salicylate detergent (TBN 342 mg/g KOH); ZDDP; aromatic amine anti-oxidant (1.50 mass %); phenolic anti-oxidant (1.0 mass %); methylene bis(dibutyldithiocarbamate) (0.40 mass %). Sulphated Ash 0.93 mass % (ASTM D874); phosphorus 0.06 mass % (ASTM D5185); sulphur 0.3 mass % (ASTM D2622); TBN 9.9 mg/g KOH (D4739) or 13.9

mg/g KOH (D2896); magnesium salicylate soap (12 mmoles); magnesium (0.2 mass %).

Each of the aforementioned additives as used in Lubricants A to C and Lubricants 1 and 2, with the exception of methylene bis(dibutylditiocarbamate), are available from Infineum UK Ltd; methylene bis(dibutylditiocarbamate) is sold under the trade name of Vanlube 7723 and is available fromVanderbilt Chemicals LLC, USA.

The TBN/TAN cross-over point of each of the aforementioned lubricants was determined using the extended Mack T-12 test procedure and the results are set out in Table 1 below.

The results demonstrate that at equivalent sulphated ash levels a lubricant which includes an overbased magnesium salicylate detergent has an extended TBN/TAN cross-over point compared with a lubricant which includes a mixture of overbased sulphonate and phenate detergents; compare Lubricant B which has a TBN/TAN cross-over point of 375 hours with Lubricant A which has a TBN/TAN cross-over point of 225 hours.

Moreover, the results clearly demonstrate that, at equivalent sulphated ash levels, the combination of an overbased magnesium salicylate detergent and an alkylene bis(dihydrocarbyldithiocarbamate) additive in a lubricant further significantly extends the TBN/TAN cross-over point for a lubricant; compare Lubricant 2 of the present invention which has a TBN/TAN cross-over point of 500 hours with Lubricant C which has a TBN/TAN cross-over point of 400 hours. Accordingly, the lubricants of the present invention are suitable for extended drain intervals.

Table 1

	TBN/TAN Cross-Over Point (hours)
Lubricant A	225
Lubricant B	375
Lubricant C	400
Lubricant 1	-
Lubricant 2	500

CLAIMS

1. A lubricating oil composition having a sulphated ash content of less than or equal to 1.0 mass % as determined by ASTM D874, the composition comprising or made by admixing:

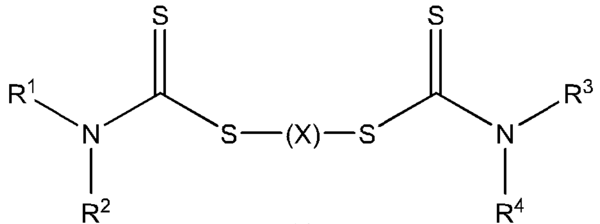
(A) an oil of lubricating viscosity present in excess of 50 mass % of the lubricating oil composition;

(B) one or more oil-soluble or oil-dispersible overbased magnesium salicylate detergent(s) having a Total Base Number (TBN) of greater than or equal to 220 to less than 500 mg/g KOH as determined by ASTM D2896, as an additive in an amount of greater than or equal to 0.1 mass % and less than or equal to 15 mass %, based on the total mass of the lubricating oil composition; and,

(C) an oil-soluble or oil-dispersible ashless alkylene bis(dihydrocarbyldithiocarbamate), as an additive, in an amount of greater than or equal to 0.1 mass % and less than or equal to 5.0 mass %, based on the total mass of the lubricating oil composition;

wherein the time taken to reach the Total Base Number/Total Acid Number (TBN/TAN) cross-over point of the lubricating oil composition is greater than 400 hours as measured in accordance with the Mack T-12 engine test procedure, ASTM D7422.

2. The lubricating oil composition as claimed in claim 1, wherein the ashless alkylene bis(dihydrocarbyldithiocarbamate) is a compound of formula (I):



(I)

wherein:

R^1, R^2, R^3 and R^4 each independently represent, at each occurrence when used herein, a C_1 to C_{30} hydrocarbyl group; and,

X represents a C_1 to C_{20} alkylene group.

3. The lubricating oil composition as claimed in claim 2, wherein R^1, R^2, R^3 and R^4 each independently represent a linear or branched C_1 to C_{16} alkyl group.

4. The lubricating oil composition as claimed in claim 2, wherein R^1, R^2, R^3 and R^4 each independently represent a C_1 to C_{16} alkyl substituted phenyl group or an unsubstituted phenyl group.

5. The lubricating oil composition as claimed in any one of claims claim 2 to 4, wherein R^1, R^2, R^3 and R^4 are identical.

6. The lubricating oil composition as claimed in claim 2, wherein R^1 and R^3 each independently represent a branched or linear C_1 to C_{16} alkyl group and R^2 and R^4 each independently represent a C_1 to C_{16} alkyl substituted phenyl group or an unsubstituted phenyl group.

7. The lubricating oil composition as claimed in any one of claims 2 to 6, wherein X represents a methylene group.

8. The lubricating oil composition as claimed in any one of claims 1 to 7, wherein the ashless alkylene bis(dihydrocarbyldithiocarbamate) is methylene bis(dibutyldithiocarbamate).

9. The lubricating oil composition as claimed in any one of claims 1 to 8, wherein the one or more overbased magnesium salicylate detergent(s) provides the lubricating oil composition with greater than or equal to 0.05 mass % of magnesium, as determined by ASTM D5185, based on the total mass of the lubricating oil composition.

10. The lubricating oil composition as claimed in any one of claims 1 to 9, wherein the one or more overbased magnesium salicylate detergent(s) are the sole metal containing detergent(s) which are present in the lubricating oil composition.

11. The lubricating oil composition as claimed in any one of claims 1 to 10, wherein the one or more overbased magnesium salicylate detergent(s) has a TBN of 300 to less than 450 mg/g KOH, as determined by ASTM D2896.

12. The lubricating oil composition as claimed in any one of claims 1 to 11, wherein the lubricating oil composition further includes at least 0.05 mass %, based on the total mass of the lubricating oil composition, of an ashless anti-oxidant selected from an aminic anti-oxidant, a phenolic anti-oxidant or a combination thereof.

13. The lubricating oil composition as claimed in any one of claims 1 to 11, wherein the lubricating oil composition further includes an oil-soluble or oil-dispersible organo-molybdenum compound which provides the lubricating oil composition with at least 10 ppm of molybdenum, as determined by ASTM D5185, based on the total mass of the lubricating oil composition.

14. The lubricating oil composition as claimed in any one of claims 1 to 13, wherein the lubricating oil composition further includes a dihydrocarbyl dithiophosphate metal salt, as an additive in an amount that introduces 0.02 to 0.12 mass % of phosphorus, as determined by ASTM D5185, based on the total mass of the composition.

15. The lubricating oil composition as claimed in any one of claims 1 to 14, wherein the lubricating oil composition contains sulphur in an amount of up to 0.4 mass % sulphur, as determined by ASTM D2622, based on the total mass of the composition.

16. A method of lubricating a spark-ignited or compression-ignited internal combustion engine comprising lubricating the engine with the lubricating oil composition as claimed in any one of claims 1 to 15.

17. Use, in lubrication of a spark-ignited or compression ignited internal combustion engine, of the of the lubricating oil composition as claimed in any one of claims 1 to 15, to extend the drain interval of the lubricating oil composition during operation of the engine.

18. The use as claimed in claim 17, wherein the drain interval represents the time taken to reach the TBN/TAN cross-over point of the lubricating oil composition during operation of the engine as measured in accordance with the Mack T-12 engine test procedure, ASTM D7422.

19. The use as claimed in claim 18, wherein the time taken to reach the TBN/TAN cross-over point of a lubricating oil composition is greater than 425 hours.

20. The lubricating oil composition as claimed in claim 1, wherein the time taken to reach the TBN/TAN cross-over point during operation of the engine as measured in accordance with the Mack T-12 engine test procedure, ASTM D7422, is greater than 400 hours.