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(54) **ANTIWEAR CONTAINING LUBRICATING COMPOSITION**

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(57) **ABSTRACT**

The present invention relates to a lubricating composition containing a sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound and an organo-sulphide. The composition has a sulphur content of greater than 0.3 weight percent of sulphur. The invention further provides for a method of lubricating a driveline device by using a lubricating composition.

## ANTIWEAR CONTAINING LUBRICATING COMPOSITION

### FIELD OF INVENTION

**[0001]** The present invention relates to a lubricating composition containing a sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound and an organo-sulphide. The composition has a sulphur content of greater than 0.3 weight percent of sulphur. The invention further provides for a method of lubricating a driveline device by using a lubricating composition.

### BACKGROUND OF THE INVENTION

**[0002]** Driveline power transmitting devices such as gears or transmissions, especially axle fluids and manual transmission fluids (MTFs), present highly challenging technological problems and solutions for satisfying the multiple and often conflicting lubricating requirements, whilst providing durability and cleanliness. One of the important parameters influencing durability is the effectiveness of phosphorus antiwear or extreme pressure additives at providing devices with appropriate protection under various conditions of load and speed. However, many of the phosphorus antiwear or extreme pressure additives contain sulphur. Due to increasing environmental concerns, the presence of sulphur in antiwear or extreme pressure additives is becoming less desirable. In addition, many of the sulphur-containing antiwear or extreme pressure additives evolve sulphur due to numerous volatile sulphur species being present, resulting in lubricating compositions containing antiwear or extreme pressure additives having an odour, may also be detrimental to health and the environment.

**[0003]** A lubricating composition having the correct balance of phosphorus antiwear or extreme pressure additives provides driveline power transmitting devices with prolonged life and efficiency with controlled deposit formation and oxidation stability. However, many of the antiwear or extreme pressure additives employed have limited oxidative stability, form deposits or increase corrosion. In addition, many phosphorus antiwear or extreme pressure additives typically also contain sulphur, which results in a lubricating composition containing the phosphorus antiwear or extreme pressure additives are odorous.

**[0004]** Consequently, it would be desirable to provide a balanced lubricant composition to meet the needs of driveline power transmitting devices without the disadvantages of known lubricating compositions. The present invention provides such a lubricating composition.

**[0005]** U.S. Pat. No. 6,656,887 discloses lubricating oils containing at least one divalent metal salt of a thiophosphoric acid ester or a phosphoric acid ester and/or a monovalent metal salt or an ammonium salt of thiophosphoric acid or phosphoric acid. The lubricating composition has antiwear properties. The lubricating composition is especially useful for engine lubricants including those with a sulphur content of 0.3 wt % or less.

**[0006]** US Patent Application 2005/0143266 discloses a lubricating composition containing (i) phosphoric acid esters and salts thereof, (ii) metal salts of phosphoric acid esters. Examples 4 and 5 disclose a combination of a zinc salt of phosphoric acid dimethyl ester and an octadecyl phosphoric acid dimethyl ester. The lubricating compositions are suitable for internal combustion engines.

**[0007]** US Patent Application 2005/0130855 discloses a lubricating composition containing a neutral or overbased metal salicylate, 0.005 to 0.2 wt % in terms of phosphorus of a phosphorus-containing antiwear agent e.g., zinc di(n-butyl)phosphate. The lubricating composition further contains 0.3 wt % or less of sulphur. The lubricating composition is suitable for internal combustion engines.

**[0008]** US Patent Application 2005/0107269 discloses a lubricating composition containing (i) phosphorus compounds of phosphoric or thiophosphoric esters, or amine or metal salts thereof, (ii) 0.005 to 0.5 wt % in terms of phosphorus of zinc dithiophosphates, (iii) metallic detergents, (iv) ashless dispersants and (v) antioxidants. The lubricating compositions are particularly useful for internal combustion engines.

**[0009]** US Patent Application 2004/0242434 discloses a lubricating composition containing in specified ranges a triphosphate, a succinimide, a metal detergent, a phenol-based and/or amine-based antioxidant.

**[0010]** EP287 618 discloses the preparation of an oil-soluble metal containing additive derived from reacting a metal hydroxide or metal oxide with a sulphur-free phosphorus acid ester. The oil-soluble metal containing additive is suitable for lubricants, fuels and functional fluids.

**[0011]** U.S. Pat. No. 6,872,693 discloses a lubricating composition suitable for gear oils and transmission fluids that contains a mineral oil with an iodine number of less than 9. The lubricating compositions also contain a phosphorus antiwear agent. The phosphorus antiwear agent includes a phosphoric acid ester or salts thereof, a metal dithiophosphate, a phosphite, a reaction product of phosphorus acid or anhydride with an unsaturated compound.

**[0012]** U.S. Pat. No. 6,730,640 discloses a lubricating composition containing an oil-soluble zinc salt containing at least one hydrocarbyl group of at least 4 carbon atoms, wherein the zinc salt is a zinc phosphate or at least one zinc salt of a carboxylic acid having 6 to 8 carbon atoms. The lubricating composition also contains a phosphorus compound of dialkyl hydrogen phosphite, alkyl hydrogen phosphonate or phosphoric acid. The oil-soluble zinc salt is suitable for continuously variable transmissions to increase steel-on-steel dynamic coefficients of friction of the lubricating composition.

**[0013]** U.S. Pat. No. 4,431,552 discloses a lubricating composition containing a non-sulphur containing phosphate, a monothiophosphate, a dithiophosphate and an alkali-metal borate. Preferred non-sulphur containing phosphate compounds include dodecyl- or oleyl-dialkyl (C4-C8) phosphates.

**[0014]** U.S. Pat. No. 5,726,132 discloses lubricating compositions with a phosphorus-containing sulphide that has a  $-\text{P}-\text{S}-(\text{S})\text{n}-\text{P}-$  group, where  $\text{n}$  is 0 to 3, a second phosphorus compound being either a phosphorus acid or esters, salt or derivatives thereof. The composition also contains an acylated nitrogen-containing compound having a substituent with at least 10 aliphatic carbon atoms.

**[0015]** U.S. Pat. No. 4,575,431 discloses lubricating compositions containing a mixture of phosphates being essentially free of monothiophosphates and the phosphates are (a) dihydrocarbyl hydrogen thiophosphates, (b) sulphur-free hydrocarbyl dihydrogen phosphates and (c) sulphur-free dihydrocarbyl hydrogen phosphates. The sulphur-free hydrocarbyl dihydrogen phosphates and dihydrocarbyl

hydrogen phosphates include C1-C6-alkyl dihydrogen phosphates and di-C1-C6-alkyl hydrogen phosphates.

#### SUMMARY OF THE INVENTION

[0016] In one embodiment the invention provides a lubricating composition comprising:

[0017] (a) an oil of lubricating viscosity;

[0018] (b) a phosphorus containing additive comprising:

[0019] (i) a sulphur-free metal salt of a hydrocarbyl substituted phosphorus compound; and

[0020] (ii) optionally an ammonium or metal salt of a (thio)phosphoric acid ester different from (i); and

[0021] (c) an organo-sulphide, wherein the lubricating composition has a sulphur content in the range of greater than 0.3 wt %.

[0022] In one embodiment the phosphorus containing additive comprises (i) a metal salt of a sulphur-free hydrocarbyl-substituted phosphorus compound; and (ii) an ammonium or metal salt of a phosphoric acid ester.

[0023] In one embodiment the invention provides a method of lubricating a driveline device, the method comprising supplying to the driveline device a lubricating composition comprising:

[0024] (a) an oil of lubricating viscosity;

[0025] (b) a phosphorus containing additive comprising:

[0026] (i) a sulphur-free metal salt of a hydrocarbyl substituted phosphorus compound; and

[0027] (ii) optionally an ammonium or metal salt of a (thio)phosphoric acid ester different from (i); and

[0028] (c) an organo-sulphide, wherein the lubricating composition has a sulphur content in the range of greater than 0.3 wt %, or about 0.5 wt % to about 5 wt % (or about 3 wt %), or about 0.8 wt % to about 2.5 wt %, or about 1 wt % to about 2 wt %.

[0029] In one embodiment the invention provides a method of lubricating a gear, the method comprising supplying to the gear a lubricating composition comprising:

[0030] (a) an oil of lubricating viscosity;

[0031] (b) a phosphorus containing additive comprising:

[0032] (i) a sulphur-free metal salt of a hydrocarbyl substituted phosphorus compound; and

[0033] (ii) optionally an ammonium or metal salt of a (thio)phosphoric acid ester different from (i); and

[0034] (c) an organo-sulphide, wherein the lubricating composition has a sulphur content in the range of greater than 0.3 wt %, or about 0.5 wt % to about 5 wt % (or about 3 wt %), or about 0.8 wt % to about 2.5 wt %, or about 1 wt % to about 2 wt %.

[0035] In one embodiment the lubricating compositions disclosed herein further comprise an ammonium or metal salt of a (thio)phosphoric acid ester different from (i).

[0036] In one embodiment the driveline device comprises at least one of a manual transmission or an axle gear.

#### DETAILED DESCRIPTION OF THE INVENTION

[0037] The present invention provides a lubricating composition and a method for lubricating a driveline device as disclosed above.

[0038] Unless otherwise stated, the wt % ranges quoted for the organo-sulphide, the phosphorus containing additive, and the other performance additives are quoted on an actives basis i.e., the ranges exclude the amounts of diluent oil that

is commonly used as a carrier medium for the additives. Diluent oil is commonly present in the various additives at different amounts typically ranging from about 0 wt % to about 60 wt % as is available commercially.

[0039] As used herein, the term “(thio)phosphoric acid ester” is used to describe a thiophosphoric acid ester (contains sulphur) and a phosphoric acid ester (free of sulphur).

[0040] As used herein, the term “hydrocarbyl substituent” or “hydrocarbyl group” is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

[0041] (i) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);

[0042] (ii) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulphonyl);

[0043] (iii) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulphur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thiienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

[0044] In one embodiment the lubricating composition has a sulphur content in the range of about 0.5 wt % to about 5 wt %. In one embodiment the lubricating composition has a sulphur content in the range of about 0.5 wt % to about 3 wt %. In one embodiment the lubricating composition has a sulphur content in the range of about 0.8 wt % to about 2.5 wt %. In one embodiment the lubricating composition has a sulphur content in the range of about 1 wt % to about 2 wt %.

#### Phosphorus Containing Additive

[0045] The phosphorus containing additive comprises (i) the sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound, and (ii) optionally an ammonium or metal salt of a (thio)phosphoric acid ester different from (i).

[0046] The phosphorus containing additive typically provides antiwear or extreme pressure performance in the lubricating composition.

[0047] In one embodiment the phosphorus containing additive comprises a mixture of the sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound and the ammonium or metal salt of a (thio)phosphoric acid ester different from (i).

#### Sulphur-Free Metal Salt of a Hydrocarbyl-Substituted Phosphorus Compound

[0048] The sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound is known and may be pre-

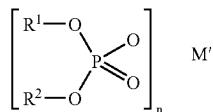
pared as is disclosed in EP 287 618, U.S. Pat. No. 2,228,658, U.S. Pat. No. 4,431,552 and U.S. Pat. No. 2,310,175.

[0049] The sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound includes a metal salt of a hydrocarbyl-substituted phosphate, a metal salt of a hydrocarbyl-substituted phosphonate, a metal salt of a hydrocarbyl-substituted phosphinate, a metal salt of a hydrocarbyl-substituted phosphite, a metal salt of a hydrocarbyl-substituted phosphonite, a metal salt of a hydrocarbyl-substituted phosphinite, or mixtures thereof.

[0050] In one embodiment the phosphorus atom of the hydrocarbyl-substituted phosphorus compound is pentavalent.

[0051] In one embodiment the sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound is a metal salt of a hydrocarbyl-substituted phosphate, a metal salt of a hydrocarbyl-substituted phosphonate, a metal salt of a hydrocarbyl-substituted phosphinate, or mixtures thereof.

[0052] In one embodiment the sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound includes compounds represented by the formula:



wherein at least one or both of  $R^1$  and  $R^2$  are hydrocarbyl groups,  $n$  is 1, 2, 3 or 4, and  $M'$  is a metal.

[0053] The sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound includes mono- or di-hydrocarbyl-substituted phosphate. The hydrocarbyl group of the sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound includes a straight-chain or a branched alkyl group, a cyclic alkyl group, a straight-chain or a branched alkenyl group, an aryl group, or an arylalkyl group.

[0054] In one embodiment the hydrocarbyl group of the hydrocarbyl-substituted phosphorus compound is an oil soluble alkyl group. The alkyl group typically includes about 1 to about 40, or about 4 to about 40, or about 4 to about 20, or about 6 to about 16 carbon atoms.

[0055] Examples of the straight-chain or branched alkyl groups include methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl groups.

[0056] The cyclic alkyl group in one embodiment contains system about 5 to about 7 carbon atoms, and in another embodiment about 6 to about 11 carbon atoms.

[0057] Examples of the cyclic alkyl group include cyclopentyl, cyclohexyl, cycloheptyl group, methylcyclopentyl, dimethylcyclopentyl, methylethylcyclopentyl, diethylcyclopentyl, methylcyclohexyl, dimethylcyclohexyl, methyl-ethylcyclohexyl, diethylcyclohexyl, methylcycloheptyl, dimethylcycloheptyl, methylethylcycloheptyl, and diethylcycloheptyl groups.

[0058] In one embodiment the straight-chain or branched alkenyl group includes those having about 2 to about 30, or about 6 to about 20 carbon atoms. Examples of the alkenyl group include butenyl, pentenyl, hexenyl, heptenyl, octe-

nyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, and octadecenyl group.

[0059] In one embodiment the aryl group includes those having about 6 to about 18 carbon atoms. Examples of the aryl group include phenyl or naphthyl.

[0060] In one embodiment the aryl group is an arylalkyl group having about 7 to about 26 carbon atoms. Examples of the arylalkyl group include tolyl, xylol, ethylphenyl, propylphenyl, butylphenyl, pentylphenyl, hexylphenyl, heptylphenyl, octylphenyl, nonylphenyl, decylphenyl, undecylphenyl, dodecylphenyl, diethylphenyl, dibutylphenyl and dioctylphenyl.

[0061] In one embodiment the sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound is a metal salt of a mono-alkyl phosphate, and in another embodiment a metal salt of a di-alkyl phosphate.

[0062] In one embodiment the metal of the metal salt is a monovalent metal, in another embodiment the metal is divalent, and in another embodiment the metal is trivalent.

[0063] The metal of the metal salt includes aluminium, calcium, magnesium, strontium, chromium, iron, cobalt, nickel, zinc, tin, lead, manganese, silver, or mixtures thereof. In one embodiment the metal is zinc.

[0064] In one embodiment the sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound is present in the lubricating composition in the range of about 0.001 wt % to about 10 wt % of the lubricating composition. In one embodiment the sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound is present in the lubricating composition in the range of about 0.001 wt % to about 5 wt % of the lubricating composition. In one embodiment the sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound is present in the lubricating composition in the range of about 0.025 wt % to about 3 wt % of the lubricating composition.

#### Ammonium or Metal Salt of a (Thio)Phosphoric Acid Ester

[0065] The ammonium or metal salt of a (thio)phosphoric acid ester different from (i) is known.

[0066] The ammonium or metal salt of a (thio)phosphoric acid ester different from (i) includes a phosphorus-containing acid, salt, polymer or ester.

[0067] In one embodiment the oxidation state of the phosphorus atom of the ammonium or metal salt of a (thio)phosphoric acid ester different from (i) is +5.

[0068] In one embodiment the ammonium or metal salt of a (thio)phosphoric acid ester different from (i) is an ammonium or metal salt of a thiophosphoric acid ester (i.e. the phosphoric acid contains sulphur).

[0069] In one embodiment the ammonium or metal salt of a (thio)phosphoric acid ester different from (i) is an ammonium or metal salt of a phosphoric acid ester (i.e. the phosphoric acid is free of sulphur).

[0070] The ammonium or metal salt of a (thio)phosphoric acid ester different from (i) includes ash-containing (i.e. metal containing) or ashless (i.e. metal free (prior to being mixed with other components)).

[0071] In one embodiment the ammonium or metal salt of a (thio)phosphoric acid ester different from (i) comprises a metal dialkyldithiophosphate. The alkyl groups of the dialkyldithiophosphate includes linear or branched containing about 2 to about 20 carbon atoms, provided that the total number of carbons is sufficient to make the metal dialky-

Idithiophosphate oil soluble. The metal of the metal dialkylidithiophosphate typically includes monovalent or divalent metals. Examples of suitable metals include sodium, potassium, copper, calcium, magnesium, barium or zinc. In one embodiment the phosphorus-containing acid, salt or ester is a zinc dialkylidithiophosphate. Examples of a suitable zinc dialkylphosphate often referred to as ZDDP, ZDP or ZDTP) include zinc di-(2-methylpropyl) dithiophosphate, zinc di-(amyl) dithiophosphate, zinc di-(1,3dimethylbutyl) dithiophosphate, zinc di-(heptyl) dithiophosphate, zinc di-(octyl) dithiophosphate di-(2-ethylhexyl) dithiophosphate, zinc di-(nonyl) dithiophosphate, zinc di-(decyl) dithiophosphate, zinc di-(dodecyl) dithiophosphate, zinc di-(dodecylphenyl) dithiophosphate, zinc di-(heptylphenyl) dithiophosphate, or mixtures thereof.

[0072] In one embodiment the ammonium or metal salt of a (thio)phosphoric acid ester different from (i) is other than metal dialkylidithiophosphate.

[0073] The ammonium (thio)phosphoric acid ester includes ammonia and amine salts of phosphoric acid esters; dialkylidithiophosphoric acid esters; amine salts of phosphites; and amine salts of phosphorus-containing carboxylic esters, ethers, and amides; and mixtures thereof.

[0074] In one embodiment the ammonium or metal salt of a (thio)phosphoric acid ester different from (i) includes a partial amine salt-partial metal salt compounds or mixtures thereof.

[0075] Suitable amines for use as the amine salt include primary amines, secondary amines, tertiary amines, and mixtures thereof. The amines include those with at least one hydrocarbyl group, or, in certain embodiments, two or three hydrocarbyl groups. The hydrocarbyl groups includes those that contain about 2 to about 30, or about 8 to about 26, or about 10 to about 20, or about 13 to about 19 carbon atoms.

[0076] Primary amines include ethylamine, propylamine, butylamine, 2-ethylhexylamine, octylamine, and dodecylamine, as well as such fatty amines as n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine and oleyamine. Other useful fatty amines include commercially available fatty amines such as "Armeen®" amines (products available from Akzo Chemicals, Chicago, Ill.), such as Armeen C, Armeen O, Armeen O L, Armeen T, Armeen H T, Armeen S and Armeen S D, wherein the letter designation relates to the fatty group, such as coco, oleyl, tallow, or stearyl groups.

[0077] Examples of suitable secondary amines include dimethylamine, diethylamine, dipropylamine, dibutylamine, diamylamine, dihexylamine, diheptylamine, methylethylamine, ethylbutylamine and ethylamylamine. The secondary amines include cyclic amines such as piperidine, piperazine and morpholine.

[0078] In one embodiment the amine is a tertiary-aliphatic primary amine. The aliphatic group includes an alkyl group containing about 2 to about 30, or about 6 to about 26, or about 8 to about 24 carbon atoms. Examples of tertiary alkyl amines include tert-butylamine, tert-hexylamine, 1-methyl-1-amino-cyclohexane, tert-octylamine, tert-decylamine, tertdodecylamine, tert-tetradecylamine, tert-hexadecylamine, tert-octadecylamine, tert-tetracosanylamine, and tert-octacosanylamine.

[0079] In different embodiments the ammonium or metal salt of a (thio)phosphoric acid ester different from (i) comprises an amine salt of a phosphorus acid or ester amine with tertiary alkyl primary groups or mixtures thereof, wherein

the alkyl group contains mixtures of about 11 to about 14, or about 14 to about 18, or about 18 to about 22 carbon atoms.

[0080] Mixtures of amines may also be used in the invention. In one embodiment a useful mixture of amines is "Primene® 81R" and "Primene® JMT." Primene® 81R and Primene® JMT (both produced and sold by Rohm & Haas) are mixtures of C11 to C14 tertiary alkyl primary amines and C18 to C22 tertiary alkyl primary amines respectively.

[0081] In one embodiment the amine salt of a phosphorus acid or ester is the reaction product of a C14 to C18 alkylated phosphoric acid with Primene 81R™ (produced and sold by Rohm & Haas) which is a mixture of C11 to C14 tertiary alkyl primary amines.

[0082] Examples of ammonium or metal salt of a (thio)phosphoric acid ester different from (i) include the reaction product(s) of isopropyl, methyl-amyl (4-methyl-2-pentyl or mixtures thereof), 2-ethylhexyl, heptyl, octyl or nonyl dithiophosphoric acids with 2-ethylhexylamine, ethylene diamine, morpholine, or Primene 81R™, or mixtures thereof.

[0083] In one embodiment the ammonium or metal salt of a (thio)phosphoric acid ester different from (i) is a reaction product prepared from a dithiophosphoric acid is reacting with an epoxide or a glycol. This reaction product is further reacted with a phosphorus acid, anhydride, or lower ester (where "lower" signifies about 1 to about 8, or about 1 to about 6, or about 1 to about 4, or 1 to about 2 carbon atoms in the alcohol-derived portion of the ester). The epoxide includes an aliphatic epoxide or a styrene oxide. Examples of useful epoxides include ethylene oxide, propylene oxide, butene oxide, octene oxide, dodecene oxide, styrene oxide and the like. In one embodiment the epoxide is propylene oxide. The glycols include aliphatic glycols having 1 to about 12, or about 2 to about 6, or about 2 to about 3 carbon atoms. The dithiophosphoric acids, glycols, epoxides, inorganic phosphorus reagents and methods of reacting the same are described in U.S. Pat. Nos. 3,197,405 and 3,544,465. The resulting acids is then be salted with amines. An example of suitable dithiophosphoric acid is prepared by adding phosphorus pentoxide (about 64 grams) at about 58° C. over a period of about 45 minutes to about 514 grams of hydroxypropyl O,O-di(4-methyl-2-pentyl)phosphorodithioate (prepared by reacting di(4-methyl-2-pentyl)-phosphorodithioic acid with about 1.3 moles of propylene oxide at about 25° C.). The mixture is heated at about 75° C. for about 2.5 hours, mixed with a diatomaceous earth and filtered at about 70° C. The filtrate contains about 11.8% by weight phosphorus, about 15.2% by weight sulphur, and an acid number of 87 (bromophenol blue).

[0084] In one embodiment the ammonium or metal salt of a (thio)phosphoric acid ester different from (i) is a reaction product as described in Examples P-2 to P-8 of U.S. Pat. No. 6,468,946 (see column 10, line 65 to column 12, line 23). The products described in Examples P-2 to P-8 are amine salts of a phosphoric acid ester.

[0085] In one embodiment the ammonium or metal salt of a (thio)phosphoric acid ester different from (i) is present in the lubricating composition in the range of about 0 wt % to about 10 wt % of the lubricating composition. In one embodiment the ammonium or metal salt of a (thio)phosphoric acid ester different from (i) is present in the lubricating composition in the range of about 0 wt % to about 5 wt % of the lubricating composition. In one embodiment the ammonium or metal salt of a (thio)phosphoric acid ester

different from (i) is present in the lubricating composition in the range of about 0.01 wt % to about 5 wt % of the lubricating composition. In one embodiment the ammonium or metal salt of a (thio)phosphoric acid ester different from (i) is present in the lubricating composition in the range of about 0.01 wt % to about 3 wt % of the lubricating composition.

#### Organic-Sulphide

[0086] The organo-sulphide comprises at least one of a polysulphide, thiadiazole compound, or mixtures thereof.

[0087] In one embodiment the organo-sulphide is present in the lubricating composition in the range of about 0.01 wt % to about 10 wt % of the lubricating composition. In one embodiment the organo-sulphide is present in the lubricating composition in the range of about 0.1 wt % to about 8 wt % of the lubricating composition. In one embodiment the organo-sulphide is present in the lubricating composition in the range of about 0.25 wt % to about 6 wt % of the lubricating composition.

#### Thiadiazole Compound

[0088] Examples of a thiadiazole include 2,5-dimercapto-1,3-4-thiadiazole, 2,5-dimercapto-1,3,4-thiadiazole, or oligomers thereof, a hydrocarbyl-substituted 2,5-dimercapto-1,3-4-thiadiazole, a hydrocarbylthio-substituted 2,5-dimercapto-1,3-4-thiadiazole, or oligomers thereof. The oligomers of hydrocarbyl-substituted 2,5-dimercapto-1,3-4-thiadiazole typically form by forming a sulphur-sulphur bond between 2,5-dimercapto-1,3-4-thiadiazole units to form oligomers of two or more of said thiadiazole units.

[0089] In different embodiments the number of carbon atoms on the hydrocarbyl substituents includes ranges of about 1 to about 30, about 2 to about 20 or about 3 to about 16. In one embodiment the thiadiazole compound, e.g., hydrocarbyl-substituted mercaptothiadiazoles (as well as the unsubstituted materials), is typically substantially soluble at about 25° C. in non-polar media such as an oil of lubricating viscosity. Thus, the total number of carbon atoms in the hydrocarbyl-substituents, which tend to promote solubility, will generally be about 8 or more, or about 10 or more, or at least about 12. If there are multiple hydrocarbyl substituents, typically each substituent will contain about 8 or fewer carbon atoms. In one embodiment the thiadiazole compound, e.g., hydrocarbyl-substituted mercaptothiadiazoles (as well as the unsubstituted materials), is typically substantially insoluble at about 25° C. in non-polar media such as an oil of lubricating viscosity. Thus, the total number of carbon atoms in the hydrocarbyl-substituents, which tend to promote solubility, will generally be fewer than about 8, or about 6, or about 4. If there are multiple hydrocarbyl substituents, typically each substituent will contain about 4 or fewer carbon atoms.

[0090] By the term "substantially insoluble" it is meant that the thiadiazole compound e.g., a dimercaptothiadiazole (DMTD) compound, may typically dissolve to an extent of less than about 0.1 weight percent, or less than 0.01 or about 0.005 weight percent in oil at room temperature (about 25° C.). A suitable hydrocarbon oil of lubricating viscosity in which the solubility may be evaluated is Chevron™ RLOP 100 N oil. The specified amount of the DMTD or substituted DMTD is mixed with the oil and the solubility may be

evaluated by observing clarity versus the appearance of residual sediment after, e.g., 1 week of storage.

[0091] Examples of a suitable thiadiazole compound include at least one of a dimercaptothiadiazole, 2,5-dimercapto-[1,3,4]-thiadiazole, 3,5-dimercapto-[1,2,4]-thiadiazole, 3,4-dimercapto-[1,2,5]-thiadiazole, or 4-5-dimercapto-[1,2,3]-thiadiazole. Typically readily available materials such as 2,5-dimercapto-1,3,4-thiadiazole or a hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole or a hydrocarbylthio-substituted 2,5-dimercapto-1,3,4-thiadiazole are commonly utilised, with 2,5-dimercapto-[1,3,4]-thiadiazole most commonly utilised due to availability. In several embodiments the number of carbon atoms on the hydrocarbyl-substituent group includes about 1 to about 30, about 2 to about 25, about 4 to about 20, about 6 to about 16, or about 8 to about 10.

[0092] In one embodiment, the thiadiazole compound is the reaction product of a phenol with an aldehyde and a dimercaptothiadiazole. The phenol includes an alkyl phenol wherein the alkyl group contains at least about 6, e.g., about 6 to 24, or about 6 (or about 7) to about 12 carbon atoms. The aldehyde includes an aldehyde containing about 1 to about 7 carbon atoms or an aldehyde synthon, such as formaldehyde. In one embodiment, the aldehyde is formaldehyde or paraformaldehyde. The aldehyde, phenol and dimercaptothiadiazole are typically reacted by mixing them at a temperature up to about 150° C. such as about 50° C. to about 130° C., in molar ratios of about 0.5 to about 2 moles of phenol and about 0.5 to about 2 moles of aldehyde per mole of dimercaptothiadiazole. In one embodiment, the three reagents are reacted in equal molar amounts. The product may be described as an alkylhydroxyphenylmethylothio-substituted [1,3,4]-thiadiazole; the alkyl moiety includes, hexyl, heptyl, octyl, or nonyl.

[0093] Useful thiadiazole compounds include 2-alkyldithio-5-mercaptop-[1,3,4]-thiadiazoles, 2,5-bis(alkyldithio)-[1,3,4]-thiadiazoles, 2-alkylhydroxyphenylmethylothio-5-mercaptop-[1,3,4]-thiadiazoles, and mixtures thereof.

[0094] Examples of suitable thiadiazole compounds include 2-octyldithio-5-mercaptop-1,3,4-thiadiazole, 2-nonyldithio-5-mercaptop-1,3,4-thiadiazole, 2-dodecyldithio-5-mercaptop-1,3,4-thiadiazole, or 2,5-dimercapto-1,3,4-thiadiazole. Examples of suitable 2,5-bis(alkyldithio)-1,3,4-thiadiazoles) include 2,5-bis(tert-octyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-nonyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-decyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-undecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-dodecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-tridecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-tetradecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-pentadecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-hexadecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-heptadecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-octadecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-nonadecyldithio)-1,3,4-thiadiazole or 2,5-bis(tert-eicosyldithio)-1,3,4-thiadiazole, or oligomers thereof. In one embodiment the hydrocarbyl-substituted 2,5-dimercapto-1,3-4-thiadiazole comprises at least one of 2,5-bis(tert-octyldithio)-1,3,4-thiadiazole 2,5-bis(tert-nonyldithio)-1,3,4-thiadiazole, or 2,5-bis(tert-decyldithio)-1,3,4-thiadiazole.

[0095] In one embodiment the thiadiazole compound includes at least one of 2,5-bis(tert-octyldithio)-1,3,4-thia-

diazole, 2,5-bis(tert-nonyldithio)-1,3,4-thiadiazole, or 2,5-bis(tert-decyldithio)-1,3,4-thiadiazole.

[0096] In one embodiment the thiadiazole compound of the invention is present in the lubricating composition in the range of about 0 to about 10 wt % of the lubricating composition. In one embodiment the thiadiazole compound of the invention is present in the lubricating composition in the range of about 0.01 wt % to about 10 wt % of the lubricating composition. In one embodiment the thiadiazole compound of the invention is present in the lubricating composition in the range of about 0.1 wt % to about 8 wt %. In one embodiment the thiadiazole compound of the invention is present in the lubricating composition in the range of about 0.25 wt % to about 6 wt % of the lubricating composition.

#### Polysulphides

[0097] The invention comprises a polysulphide that is known in the art. As used herein the term "polysulphide" includes disulphide compounds as well as compounds that contain three or more sulphur atoms including oligomeric species that may have multiple mono- or di-sulphide linkages within the same molecule.

[0098] The polysulphide are generally characterized as having sulphur-sulphur linkages. Typically the linkages have about 2 to about 8 sulphur atoms, or about 2 to about 6 sulphur atoms, or 2 to about 4 sulphur atoms.

[0099] In one embodiment the polysulphide is a disulphide.

[0100] In one embodiment the polysulphide contains at least about 20 wt %, or at least about 30 wt % of the polysulphide molecules contain three or more sulphur atoms.

[0101] In one embodiment at least about 50 wt % of the polysulphide molecules are a mixture of tri- or tetra-sulphides. In other embodiments at least about 55 wt %, or at least about 60 wt % of the polysulphide molecules are a mixture of tri- or tetra-sulphides.

[0102] In one embodiment up to about 90 wt % of the polysulphide molecules are a mixture of tri- or tetra-sulphides. In other embodiments up to about 80 wt % of the polysulphide molecules are a mixture of tri- or tetra-sulphides.

[0103] The polysulphide in other embodiments contain about 0 wt % to about 20 wt %, or about 0.1 to about 10 wt % of a penta- or higher polysulphide.

[0104] In one embodiment the polysulphide contains less than about 30 wt % or less than about 40 wt % of a disulphide in the polysulphide.

[0105] The polysulphide typically provides about 0.5 to about 5 wt %, or about 1 to about 3 wt % of sulphur to the lubricating composition.

[0106] The polysulphide includes a sulphurised organic polysulphide from oils, fatty acids or ester, olefins or polyolefins.

[0107] Oils which may be sulfurized include natural or synthetic oils such as mineral oils, lard oil, carboxylate esters derived from aliphatic alcohols and fatty acids or aliphatic carboxylic acids (e.g., myristyl oleate and oleyl oleate), and synthetic unsaturated esters or glycerides.

[0108] Fatty acids include those that contain about 8 to about 30, or about 12 to about 24 carbon atoms. Examples of fatty acids include oleic, linoleic, linolenic, tall oil and rosin acids. Sulfurized fatty acid esters prepared from mixed

unsaturated fatty acid esters such as are obtained from animal fats and vegetable oils, including tall oil, linseed oil, soybean oil, rapeseed oil, and fish oil.

[0109] The polysulphide includes olefins derived from a wide range of alkenes. The alkenes typically have one or more double bonds. The olefins in one embodiment contain about 3 to about 30 carbon atoms. In other embodiments, olefins contain about 3 to about 16, or about 3 to about 9 carbon atoms. In one embodiment the sulphurised olefin includes an olefin derived from propylene, isobutylene, pentene or mixtures thereof.

[0110] In one embodiment the polysulphide comprises a polyolefin derived from polymerising by known techniques an olefin as described above.

[0111] In one embodiment the polysulphide includes dibutyl tetrasulphide, sulphurised methyl ester of oleic acid, sulphurised alkylphenol, sulphurised dipentene, sulphurised dicyclopentadiene, sulphurised terpene, and sulphurised Diels-Alder adducts; phosphosulphurised hydrocarbons.

[0112] In embodiment the polysulphide is present in the lubricating composition in the range of about 0.01 to about 10 wt % of the lubricating composition. In embodiment the polysulphide is present in the lubricating composition in the range of about 0.1 wt % to about 8 wt % of the lubricating composition. In embodiment the polysulphide is present in the lubricating composition in the range of or about 0.25 wt % to about 6 wt % of the lubricating composition.

#### Oils of Lubricating Viscosity

[0113] The lubricating oil composition includes natural or synthetic oils of lubricating viscosity, oil derived from hydrocracking, hydrogenation, hydrofinishing, and unrefined, refined and re-refined oils and mixtures thereof.

[0114] Natural oils include animal oils, vegetable oils, mineral oils and mixtures thereof. Synthetic oils include hydrocarbon oils, silicon-based oils, and liquid esters of phosphorus-containing acids. Synthetic oils may be produced by Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils. In one embodiment the composition of the present invention is useful when employed in a gas-to-liquid oil. Often Fischer-Tropsch hydrocarbons or waxes may be hydroisomerised.

[0115] In one embodiment the base oil comprises a poly-alphaolefin including a PAO-2, PAO-4, PAO-5, PAO-6, PAO-7 or PAO-8. The polyalphaolefin in one embodiment is prepared from dodecene and in another embodiment from decene.

[0116] In one embodiment the oil of lubricating viscosity is an ester such as an adipate.

[0117] In one embodiment the oil of lubricating viscosity is a polymer (may also be referred to as a viscosity modifier) including hydrogenated copolymers of styrene-butadiene, ethylene-propylene polymers, polyisobutenes, hydrogenated styrene-isoprene polymers, hydrogenated isoprene polymers, polymethacrylate acid esters, polyacrylate acid esters, polyalkyl styrenes, alkenyl aryl conjugated diene copolymers, polyolefins, polyalkylmethacrylates and esters of maleic anhydride-styrene copolymers. In several embodiments the polymer includes polymethacrylate acid esters, polyacrylate acid esters, polyalkylmethacrylates and esters of maleic anhydride-styrene copolymers, polyisobutenes or mixtures thereof.

[0118] In one embodiment the oil of lubricating viscosity may contain a polymer (or viscosity modifier) present in

ranges of about 0 wt % to about 70 wt % of the lubricating composition. In one embodiment the oil of lubricating viscosity may contain a polymer (or viscosity modifier) present in ranges of about 5 wt % to 65 wt % of the lubricating composition. In one embodiment the oil of lubricating viscosity may contain a polymer (or viscosity modifier) present in ranges of about 10 to about 60 wt %, or about 15 to about 50 wt % of the lubricating composition. In one embodiment the lubricating composition comprises an oil of lubricating viscosity containing mixtures of a viscosity modifier and an API Group III or IV base oil. In one embodiment the lubricating composition contains a synthetic oil of lubricating viscosity.

[0119] Oils of lubricating viscosity may also be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. In one embodiment the oil of lubricating viscosity comprises an API Group I, II, III, IV, V, VI base oil, or mixtures thereof, and in another embodiment API Group II, III, IV base oil or mixtures thereof. In another embodiment the oil of lubricating viscosity is a Group III or IV base oil and in another embodiment a Group IV base oil.

[0120] The amount of the oil of lubricating viscosity present is typically the balance remaining after subtracting from about 100 wt % the sum of the amount of the phosphorus containing additive, the organo-sulphide, and the other performance additives (described below).

[0121] In one embodiment the lubricating composition is in the form of a concentrate and/or a fully formulated lubricant. If the phosphorus containing additive, the organo-sulphide, and the other performance additives are in the form of a concentrate (which may be combined with additional oil to form, in whole or in part, a finished lubricant), the ratio of the components of the lubricating composition to the oil of lubricating viscosity and/or to diluent oil include the ranges of about 1:99 to about 99:1 by weight, or about 80:20 to about 10:90 by weight.

#### Other Performance Additive

[0122] The composition of the invention optionally further includes at least one other performance additive. The other performance additives include metal deactivators, detergents, dispersants, viscosity modifiers, dispersant viscosity modifiers, antioxidants, corrosion inhibitors, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents and mixtures thereof.

[0123] The total combined amount of the other performance additive compounds present on an oil free basis may include a range of about 0 wt % to about 25 wt % of the lubricating composition. In one embodiment the other performance additive compounds present on an oil free basis may include a range of about 0.1 wt % to about 15 wt % of the lubricating composition. In one embodiment the other performance additive compounds present on an oil free basis may include a range of about 0.5 wt % to about 10 wt %, of the lubricating composition. Although one or more of the other performance additives may be present, it is common for the other performance additives to be present in different amounts relative to each other.

[0124] Antioxidants include molybdenum compounds such as molybdenum dithiocarbamates, sulphurised olefins, hindered phenols, aminic compounds (such as alkylated diphenylamines (typically di-nonyl diphenylamine, octyl diphenylamine, di-octyl diphenylamine)).

[0125] Detergents include neutral or overbased detergents, Newtonian or non-Newtonian, basic salts of alkali, alkaline earth or transition metals with one or more of a phenate, a sulphurised phenate, a sulphonate, a carboxylic acid, a phosphorus acid, a mono- and/or a di-thiophosphoric acid, a saligenin, an alkylsalicylate, and a salixarate.

[0126] Dispersants include N-substituted long chain alkenyl succinimides, as well as Mannich condensation products as well as post-treated versions thereof. Post-treated dispersants include those by reaction with urea, thiourea, dimercaptothiadiazoles, carbon disulphide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, and phosphorus compounds.

[0127] Viscosity modifiers include hydrogenated copolymers of styrene-butadiene, ethylene-propylene copolymers, polyisobutenes, hydrogenated styrene-isoprene polymers, hydrogenated isoprene polymers, polymethacrylate acid esters, polyacrylate acid esters, polyalkyl styrenes, alkenyl aryl conjugated diene copolymers, polyolefins, polyalkylmethacrylates and esters of maleic anhydride-styrene copolymers. Dispersant viscosity modifiers (often referred to as DVM) include functionalised polyolefins, for example, ethylene-propylene copolymers that have been functionalized with the reaction product of maleic anhydride and an amine, a polymethacrylate functionalised with an amine, or styrene-maleic anhydride copolymers reacted with an amine; may also be used in the composition of the invention.

[0128] Friction modifiers include fatty amines, esters such as borated glycerol esters, fatty phosphites, fatty acid amides, fatty epoxides, borated fatty epoxides, alkoxylated fatty amines, borated alkoxylated fatty amines, metal salts of fatty acids, or fatty imidazolines, condensation products of fatty acids with guanidine, aminoguanidine, urea, thiourea or derivatives thereof, condensation products of carboxylic acids and polyalkylene-polyamines.

[0129] Corrosion inhibitors include octylamine octanoate, condensation products of dodecyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine. Metal deactivators include derivatives of benzotriazoles (typically tolyltriazole), 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles or 2-alkyldithiobenzothiazoles.

[0130] Foam inhibitors include copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate. Demulsifiers include trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers. Pour point depressants include esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides. Seal swell agents include Exxon Necton-37<sup>TM</sup> (FN 1380) and Exxon Mineral Seal Oil (FN 3200).

#### INDUSTRIAL APPLICATION

[0131] The method of the invention is useful for lubricating a variety of driveline devices. The driveline device comprises at least one of a gear, a gearbox, an axle gear, a traction drive transmission, an automatic transmission or a manual transmission. In one embodiment the driveline device is a manual transmission or a gear, a gearbox, an axle gear.

[0132] The automatic transmission includes continuously variable transmissions (CVT), infinitely variable transmissions (IVT), Toroidal transmissions, continuously slipping

torque converted clutches (CSTCC), stepped automatic transmissions or dual clutch transmissions (DCT).

[0133] In one embodiment the invention provides for the use of the lubricating composition disclosed herein in gears and transmissions to impart at least one of antiwear performance, extreme pressure performance, acceptable deposit control, acceptable oxidation stability and reduced odor.

[0134] The following examples provide illustrations of the invention. These examples are non-exhaustive and are not intended to limit the scope of the invention.

## EXAMPLES

### Example 1

[0135] A gear oil lubricating composition composed of a mixture Group III and Group IV base oils. The lubricating composition further contains about 0.3 wt % of a zinc dialkylphosphate, about 0.3 wt % of an amine phosphate, about 3 wt % of a sulphurised olefin, about 0.7 wt % of other additives including a corrosion inhibitor, a dispersant, a friction modifier and an antifoam agent, and about 4.7 wt % of diluent oil. The total phosphorus content of the lubricating composition is about 0.05 wt %.

### Example 2

[0136] A gear oil lubricating composition composed of a mixture of API Group IV base oil and a polyisobutylene. The lubricating composition further contains about 1.3 wt % of a zinc dialkylphosphate, about 0.3 wt % of an amine phosphate, about 4 wt % of a sulphurised olefin, about 1.6 wt % of other additives including a corrosion inhibitor, a dispersant, a friction modifier and an antifoam agent, and about 3 wt % of diluent oil. The total phosphorus content of the lubricating composition is about 0.14 wt %.

[0137] Test 1: Examples 1 and 2 are evaluated for corrosion on copper strips using ASTM method D130-04e1. The results obtained indicate that Example 1 has a 3B rating; and Example 2 has a 1B rating.

[0138] Test 2: Examples 1 and 2 are evaluated for the capability for load-carrying, wear, and extreme pressure properties in a hypoid axle under conditions of low-speed, high-torque operation using ASTM method D6121-05a. The results obtained are presented in the following table:

Parameter Rated	ASTM	
	D6121-05a Rating	
	Example 1	Example 2
<u>Ring Gear</u>		
Final Wear Rating	7	7
Final Surface Fatigue Rippling	10	10
Final Surface Fatigue Ridging	10	10
Final Surface Fatigue Pitting and Spalling Merit	10	9.9
Final Surface Fatigue Scoring	10	10
<u>Pinion Gear</u>		
Final Wear Rating	8	7
Final Wear Rippling	10	10
Final Wear Ridging	10	9
Final Wear Scoring	10	10
Final Pitting and Spalling Merit	10	9.8

[0139] Overall the results the lubricating composition of the invention is capable of providing acceptable gear performance whilst utilising low odor antiwear additives.

[0140] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. The products formed thereby, including the products formed upon employing lubricant composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses lubricant composition prepared by admixing the components described above.

[0141] While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

What is claimed is:

1. A lubricating composition comprising:
  - (a) an oil of lubricating viscosity;
  - (b) a phosphorus containing additive comprising:
    - (i) a sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound; and
    - (ii) optionally an ammonium or metal salt of a (thio) phosphoric acid ester different from (i); and
    - (c) an organo-sulphide, wherein the lubricating composition has a sulphur content of greater than 0.3 wt %.
2. The lubricating composition of claim 1, wherein the lubricating composition has a sulphur content of about 0.5 wt % to about 5 wt %.
3. The lubricating composition of claim 1, wherein the sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound comprises a metal salt of a hydrocarbyl-substituted phosphate, a metal salt of a hydrocarbyl-substituted phosphonate, a metal salt of a hydrocarbyl-substituted phosphinate, a metal salt of a hydrocarbyl-substituted phosphite, a metal salt of a hydrocarbyl-substituted phosphonite, a metal salt of a hydrocarbyl-substituted phosphinite, or mixtures thereof.

4. The lubricating composition of claim 3, wherein the sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound comprises a metal salt of a hydrocarbyl-substituted phosphate, a metal salt of a hydrocarbyl-substituted phosphonate, a metal salt of a hydrocarbyl-substituted phosphinate, or mixtures thereof.

5. The lubricating composition of claim 1, wherein the sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound comprises a metal salt of a mono- or di-hydrocarbyl-substituted phosphate.

6. The lubricating composition of claim 1, wherein the metal of the metal salt is selected from the group consisting of aluminium, calcium, magnesium, strontium, chromium, iron, cobalt, nickel, zinc, tin, lead, manganese, silver, and mixtures thereof.

7. The lubricating composition of claim 6, wherein the metal of the metal salt is zinc.

8. The lubricating composition of claim 1, further comprising an ammonium or metal salt of a (thio)phosphoric acid ester different from (i).

**9.** The lubricating composition of claim **1**, wherein the phosphorus containing additive comprises:

- (i) a metal salt of a sulphur-free hydrocarbyl-substituted phosphorus compound; and
- (ii) an ammonium or metal salt of a phosphoric acid ester.

**10.** The lubricating composition of claim **1**, wherein the sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound is present in the lubricating composition in a range selected from the group consisting of about 0.001 wt % to about 10 wt %, and about 0.025 wt % to about 3 wt % of the lubricating composition.

**11.** The lubricating composition of claim **1**, wherein the organo-sulphide comprises a polysulphide, thiadiazole compound, or mixtures thereof.

**12.** The lubricating composition of claim **11**, wherein the organo-sulphide comprises a polysulphide.

**13.** The lubricating composition of claim **11**, wherein the organo-sulphide comprises a thiadiazole compound.

**14.** The lubricating composition of claim **1**, wherein the organo-sulphide is present in a range selected from the group consisting of about 0.01 wt % to about 10 wt %, and about 0.25 wt % to about 6 wt % of the lubricating composition.

**15.** The lubricating composition of claim **1**, wherein the oil of lubricating viscosity comprises an API Group II, III, IV base oil, or mixtures thereof.

**16.** A lubricating composition comprising:

- (a) an oil of lubricating viscosity;
- (b) a phosphorus containing additive comprising:
  - (i) a metal salt of a sulphur-free hydrocarbyl-substituted phosphorus compound; and
  - (ii) an ammonium or metal salt of a phosphoric acid ester; and
- (c) an organo-sulphide, wherein the lubricating composition has a sulphur content in the range of greater than 0.3 wt %.

**17.** A method of lubricating a driveline device, the method comprising supplying to the driveline device a lubricating composition comprising:

- (a) an oil of lubricating viscosity;
- (b) a phosphorus containing additive comprising:
  - (i) a sulphur-free metal salt of a hydrocarbyl-substituted phosphorus compound; and
  - (ii) optionally an ammonium or metal salt of a (thio) phosphoric acid ester different from (i); and
- (c) an organo-sulphide, wherein the lubricating composition has a sulphur content of greater than 0.3 wt %.

**18.** The method of claim **17**, wherein the driveline device comprises a manual transmission or an axle gear.

**19.** The use of the lubricating composition of claim **1** in gears and transmissions to impart at least one of antiwear performance, extreme pressure performance, acceptable deposit control, acceptable oxidation stability and reduced odor.

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