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(54) LOW VICOSITY GEAR LUBRICANTS

(57) A lubricant composition of 40 to 95 % of an oil having a kinematic viscosity at 100 °C of 3 to 7.5; 0.3 to 2 % of an amine salt of a phosphorus compound obtained by reacting phosphorus pentasulfide with one or more alcohols having 4 to about 13, or 4 to 8, or 6, carbon atoms, with an alkylene oxide, and further with phosphorus pentoxide, and salting the resulting material with one or more amines having 2 to 20 or 12 to 24 carbon atoms; and an active-sulfur containing agent in an amount to provide 0.5 to 7 % sulfur to the composition provides good wear protection to gears at a relatively low viscosity of the composition.

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Description

BACKGROUND

[0001] The disclosed technology relates to lubricants, especially for gears or bearings, having a relatively low viscosity yet having good antiwear performance by including in the lubricant a certain amine salt of a phosphorus compound (or mixtures thereof).

[0002] Moving mechanical parts generally need to be lubricated. Among surfaces or parts requiring lubrication are gears or bearings, such as those that may be found in machinery or vehicles such as in drivelines of vehicles (e.g., transmissions, gear boxes, axles, differentials). An axle assembly may typically comprise one or more gears and one or more bearings. In recent years the lubrication and transportation industry have been moving toward requiring gear oils of lower viscosity in order to provide improved efficiency and fuel economy, for instance, due to reduced fluid drag and energy loss. Lubricants of reduced viscosity, however, tend to provide reduced lubricant film thickness between the lubricated parts, and such systems thus become increasingly dependent on boundary film protection, that is, chemical protection of the surfaces provided by additive chemistry within the lubricant, as distinct from the lubrication provided by the bulk of the lubricant.

[0003] Film thickness may be described in terms of λ ratio, which is defined as the ratio of fluid film thickness to the composite surface roughness of the surfaces being lubricated $(r_1^2 + r_2^2)^{1/2}$. The λ ratio will depend on the particular surfaces involved, the pressure applied between the surfaces, and the viscosity of the lubricant, less viscous lubricants tending to provide systems having a lower λ. It is often considered that when λ is 3 or greater, full-film, or thick film, or hydrodynamic, lubrication will prevail. When λ is between 1.2 and 3, the lubrication is often referred to as mixed or thin film, and when λ is less than 1.2, boundary lubrication will prevail. That is, in the case of boundary lubrication, over a certain portion of the lubricated surface there may be direct physical contact between the surfaces (or between the chemical coatings on the surfaces) with little or no bulk lubricant separating the surfaces in those areas. It is for lubricating conditions where λ is 2 or less, 1.8 or less, or 1.5 or less, or 1.2 or less, that lubricating challenges become more severe.

[0004] The wheels of an on-highway and/or off-highway vehicle can be driven by a final drive axle unit that splits the torque received from the input shaft between the wheels by means of a gear set inside a gear housing of the final drive unit. The gears in the final drive can be of the type including but not limited to spiral bevel, hypoid, spur and helical or combination thereof. In one example the gear arrangement can be a differential gear arrangement. These gears require lubrication. Among the functions of the gear lubricant are to provide adequate protection against wear, scuffing, and micropitting and to provide for seal, rubber, and composite material capability, while providing acceptable oxidation stability and cleanliness during the service life of the gear equipment. Therefore, there is need for a gear lubricating composition having a relatively low viscosity while providing at least one of wear protection and seal, rubber and composite material capability.

[0005] U.S. Patent 3,197,405, Le Suer, July 27, 1965, discloses phosphorus- and nitrogen-containing compositions useful as additives in lubricating compositions. They may be prepared by reacting a hydroxyl-substituted triester of a phosphorothioic acid with an inorganic phosphorus reagent and neutralizing with a hydrocarbon- or hydroxy-substituted hydrocarbon amine having about 4 to about 30 carbon atoms.

[0006] U.S. Patent 8,865,633, MacPherson et al., October 21, 2014 (earlier published as US 2013/0053288, Feb. 28, 2013) discloses gear oil compositions including a major amount of a base oil having a lubricating viscosity, a polysulfide extreme pressure agent, and a reaction product of an acylated copolymer and a polyamine. An antiwear agent may be present which may include, among others, an organic ester of phosphoric acid, phosphorous acid, or an amine salt thereof. The base oil is about 55 weight percent to less than 100 weight percent bright stock base oil. In an example, the gear oil formulation had a viscosity grade of 80W-90.

[0007] The lubricating composition of the invention is suitable for lubricants in a variety of mechanical devices, including automobiles, trucks, and other equipment such as a manual transmission, an automatic transmission, an automated manual transmission, a continuously variable transmission, a dual clutch transmission, a farm tractor transmission, a transaxle, a heavy duty power-shift transmission, and wet brakes) as well as final drive axles gearing systems and gears such as an automotive gear and a farm tractor gear.

[0008] The disclosed technology solves the problem of providing wear protection for gears which are lubricated with a relatively low viscosity lubricant, and/or under a regime of $\lambda \leq 2$, by including in the lubricant an amine salt of a phosphorus compound or mixtures thereof, as described in greater detail herein.

SUMMARY

[0009] The disclosed technology provides a lubricant composition comprising: (a) an oil having a kinematic viscosity at 100 °C by ASTM D445 of 3 to 7.5 or 3.6 to 6 or 3.5 to 5 mm^2/s; (b) 0.3 to 2 percent by weight of an amine salt of a phosphorus compound, or mixtures thereof, obtained by reacting phosphorus pentasulfide with one or more alcohols having 4 to 13, or 4 to 8, or 6, carbon atoms, with an alkylene oxide, and further with phosphorus pentoxide, and salting the resulting material with one or more amines having 2 to 20 or 12 to 24 carbon atoms; and (c) a sulfurized olefin in an amount to provide about 0.5 to about 7, or about 0.5 to about 1.5, or about 1.5 to about 2, or about 3 to about 5, or about 2 to about 3, percent by weight sulfur to the composition; wherein said composition has a kinematic viscosity at 100 °C by ASTM D445 of up to 7.5, or 3.5 to 7.0, or 4 to 6.5, or 4 to 6 mm^2/s.

[0010] The disclosed technology also provides a method of lubricating a gear comprising supplying thereto the lubricant composition described herein.

DETAILED DESCRIPTION

[0011] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0012] The lubricant composition of the disclosed technology comprises as one component, an oil of lubricating viscosity. Such oils include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined, and re-refined oils and mixtures thereof. Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment. 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. Purification techniques are known in the art and include solvent extraction, secondary distillation, acid or base extraction, filtration, percolation and the like. Re-refined oils are also known as reclaimed or reprocessed oils, and are obtained by processes similar to those used to obtain refined oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0013] Natural oils useful in making the inventive lubricants include animal oils, vegetable oils (e.g., castor oil), mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types and oils derived from coal or shale or mixtures thereof.

[0014] Synthetic lubricating oils are useful and include hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers); poly(1-hexenes), poly(1-octenes), poly(1-decenes), and mixtures thereof; alkyl-benzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonyl¬benzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); diphenyl alkanes, alkylated diphenyl alkanes, alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof or mixtures thereof. Other synthetic lubricating oils include polyol esters (such as Priolube®3970), diesters, liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), or polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and typically may be hydroisomerized Fischer-Tropsch hydrocarbons or waxes. In one embodiment oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0015] Oils of lubricating viscosity may also be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines (2011). The five base oil groups are as follows: Group I (sulfur content >0.03 wt %, and/or <90 wt % saturates, viscosity index 80 to less than 120); Group II (sulfur content <0.03 wt %, and >90 wt % saturates, viscosity index 80 to less than120); Group III (sulfur content <0.03 wt %, and >90 wt % saturates, viscosity index ≥120); Group IV (all polyalphaolefins (PAOs)); and Group V (all others not included in Groups I, II, III, or IV). The oil of lubricating viscosity may also be an API Group II+ base oil, which term refers to a Group II base oil having a viscosity index greater than or equal to 110 and less than 120, as described in SAE publication "Design Practice: Passenger Car Automatic Transmissions", fourth Edition, AE-29, 2012, page 12-9, as well as in US 8,216,448, column 1 line 57.

[0016] The oil of lubricating viscosity may be an API Group IV oil, or mixtures thereof, i.e., a polyalphaolefin. The polyalphaolefin may be prepared by metallocene catalyzed processes or from a non-metallocene process. The oil of lubricating viscosity may comprise an API Group I, Group II, Group III, Group IV, Group V oil or mixtures thereof. Often the oil of lubricating viscosity is an API Group I, Group II, Group II+, Group III, Group IV oil or mixtures thereof. Alternatively the oil of lubricating viscosity is often an API Group II, Group II+, Group III or Group IV oil or mixtures thereof. Alternatively the oil of lubricating viscosity is often an API Group II, Group II+, Group III oil or mixtures thereof. In one embodiment, the oil of lubricating viscosity comprises a polyalphaolefin. In one embodiment, the oil of lubricating viscosity comprises a Group III oil or a Group III+ oil (where Group III+ is a subset of Group III oils, having a higher viscosity index such as ≥ 130). In one embodiment the poly alpha olefin has a kinetic viscosity at 100 °C of 3 to 7.5 (ASTM D445).

[0017] The oil of lubricating viscosity, as used in the disclosed technology, will have a kinematic viscosity at 100 °C ("KV_100") as determined by ASTM D445 of 3 to 7.5 mm^2/s or alternatively 3.3 to 6.5, or 3.6 to 6, or 3.5 to 5, mm^2/s. This viscosity value or range will be the viscosity of the entire oil of lubricating viscosity component, whether it be an oil from a single source and a single grade or a mixture of oils, but does not include any contribution to viscosity of any additives such as viscosity modifiers. In one embodiment the presence of small amounts of diluent oil which may be conventionally provided along with some of the additive components to be described later is not included in the determination of the KV_100; alternatively, if desired, the contribution of such diluent oils may be included. In either event, the KV_100 of the oil (base oil) component is less than about 7.5 mm^2/s, which is a relatively low value for a lubricant designed for use as a gear lubricant.

[0018] The KV_100 of the base oil, above, is one contributor to the KV_100 of the finished lubricant containing the additional components and additives described herein. Presence of additional components may result in an increase in the KV_100 of the finished lubricant, particularly if those components, such as polymeric components, themselves have a relatively higher KV_100. The overall KV_100 of the lubricant composition may be up to 8.5 or to 8.0 or to 7.5, such as 3.5 to 7.0 or 4 to 6.5, or 4 to 6 mm^2/s.

[0019] The amount of the oil of lubricating viscosity present is typically the balance remaining after subtracting from 100 weight percent the sum of the amount of the additives as described herein. Typical amounts include 40 to 95 percent by weight, or 45 to 90, or 50 to 80, or 55 to 75, or 58 to 70, or 60 to 65 percent by weight.

[0020] The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the lubricating composition of the invention is 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 of components of the invention to the oil of lubricating viscosity and/or to diluent oil include the ranges of 1:99 to 99:1 by weight, or 80:20 to 10:90 by weight.

[0021] Another component of the lubricant is an amine salt of a phosphorus acid ester. This material can serve as one or more of an extreme pressure agent or a wear preventing agent. The amine salt of a phosphorus acid ester includes phosphoric acid esters and salts thereof; dialkyldithiophosphoric acid esters and salts thereof; phosphites; and phosphorus-containing carboxylic esters, ethers, and amides; and mixtures thereof. In one embodiment the phosphorus compound comprises a sulfur atom in the molecule. In one embodiment the amine salt of the phosphorus compound is ashless, i.e., metal-free (prior to being mixed with other components).

[0022] The amine salt of the phosphorus acid ester may comprise any of a variety of chemical structures. In particular, a variety of structures are possible when the phosphorus acid ester compound contains one or more sulfur atoms, that is, when the phosphorus-containing acid is a thiophosphorus acid ester. The thiophosphorus acid esters may be mono- or dithiophosphorus acid esters. Thiophosphorus acid esters are also sometimes referred to as thiophosphoric acids. A thiophosphorus acid ester may be prepared by reacting a sulfur and phosphorus compound with an alcohol. Suitable phosphorus compound include phosphorus sulfides such as phosphorus pentasulfide. Suitable alcohols include those containing 4 to 13 carbon atoms, or 4 to 8, or 5 to 7, or 6 carbon atoms, including primary or secondary alcohols such as butyl, isobutyl, amyl, s-amyl, 2-ethylhexyl, hexyl, cyclohexyl, octyl, decyl and dodecyl alcohols and isomers thereof, as well as any of a variety of commercial alcohol mixtures having similar numbers of carbon atoms, e.g., 8 to 10. In one embodiment the alcohol has 6 carbon atoms; in one embodiment the alcohol comprises or is 4-methylpentan-2-ol.

[0023] In one embodiment, the thiophosphorus acid ester is a monothiophosphoric acid ester or a monothiophosphate. Monothiophosphates may be prepared by the reaction of a sulfur source with a dihydrocarbyl phosphite. The sulfur source may, for instance, be elemental sulfur, or an organosufide, such as a sulfur coupled olefin or a sulfur coupled dithiophosphate. The preparation of monothiophosphates is disclosed in U.S. Patent 4,755,311 and PCT Publication WO 87/07638, which describe monothiophosphates, sulfur sources, and the process for making monothiophosphates. Monothiophosphates may also be formed in the lubricant blend by adding a dihydrocarbyl phosphite to a lubricating composition containing a sulfur source, such as a sulfurized olefin. The phosphite may react with the sulfur source under blending conditions (i.e., temperatures from 30°C to 100°C or higher) to form the monothiophosphate salt with an amine which is present in the blend.

[0024] In certain embodiments, the phosphorus-containing acid is a dithiophosphoric acid or phosphorodithioic acid. The dithiophosphoric acid may be represented by the formula $(RO)_2PSSH$ wherein each R is independently a hydrocarbyl group containing 4 to 13 carbon atoms, such as those derived from the alcohol listed above. Examples of R include isobutyl, n-butyl, sec-butyl, the various amyl, n-hexyl, methylisobutyl carbinyl, heptyl, 2-ethylhexyl, isooctyl, nonyl, behenyl, decyl, dodecyl, and tridecyl groups. Illustrative lower alkylphenyl R groups include butylphenyl, amylphenyl, and heptylphenyl. Examples of mixtures of R groups include 1-butyl and 1-octyl; 1-pentyl and 2-ethyl-1-hexyl; isobutyl and n-hexyl; isobutyl and isoamyl; 2-propyl and 2-methyl-4-pentyl; isopropyl and sec-butyl; and isopropyl, and isooctyl.

[0025] The dithiophosphoric acid is further reacted with an epoxide and this reaction product further reacted with a phosphorus pentoxide. The epoxide is generally an aliphatic epoxide or a styrene oxide. Examples of useful epoxides include ethylene oxide, propylene oxide, butene oxide, octene oxide, dodecene oxide, and styrene oxide. The epoxides may be aliphatic epoxides having from 2 to 12, or 3 to 6, or 3 or 4 carbon atoms. In one embodiment the alkylene oxide comprises 1,2-propylene oxide. The dithiophosphoric acids, epoxides, inorganic phosphorus reagents, and methods of reacting the same are described in U.S. Patents 3,197,405 and 3,544,465.

[0026] The following Examples P-1 and P-2 exemplify the preparation of useful phosphorus acid esters.

> Example P-1. Phosphorus pentoxide (about 64 grams) is added 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 sulfur, and an acid number of 87 (bromophenol blue).

Example P-2. A mixture of about 667 grams of phosphorus pentoxide and the reaction product of about 3514 grams of diisopropyl phosphorodithioic acid with about 986 grams of propylene oxide at about 50°C is heated at about 85°C for about 3 hours and filtered. The filtrate contains about 15.3% by weight phosphorus, about 19.6% by weight sulfur, and an acid number of 126 (bromophenol blue).

[0027] Acidic phosphoric acid esters may be reacted with ammonia or an amine, including polyamines, to form an ammonium salt. The salts may be formed separately and then the salt of the phosphorus acid ester may be added to the lubricating composition. The amines which may be suitable 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 may typically contain 2 to 30 carbon atoms, or in other embodiments 8 to 26 or 10 to 20 or 13 to 19 carbon atoms.

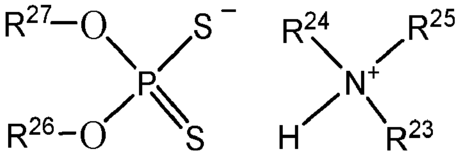
[0028] Primary amines include ethylamine, propylamine, butylamine, 2-ethylhexylamine, octylamine, and dodecylamine, as well as such fatty amines as n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine, and oleylamine. Other useful fatty amines include commercially available fatty amines such as "Armeen®" amines (products available from Akzo Chemicals, Chicago, Illinois), such as Armeen C, Armeen O, Armeen OL, Armeen T, Armeen HT, Armeen S and Armeen SD, wherein the letter designation relates to the fatty group, such as coco, oleyl, tallow, or stearyl groups.

[0029] Examples of suitable secondary amines include dimethylamine, diethylamine, dipropylamine, dibutylamine, diamylamine, dihexylamine, diheptylamine, methylethyl-amine, ethylbutylamine and ethylamylamine. The secondary amines may be cyclic amines such as piperidine, piperazine, and morpholine.

[0030] The amine may also be a tertiary-aliphatic primary amine. The aliphatic group in this case may be an alkyl group containing 2 to 30, or 6 to 26, or 8 to 24 carbon atoms. Tertiary alkyl amines include monoamines such as tert-butylamine, tert-hexyl-amine, 1-methyl-1-amino-cyclohexane, tert-octylamine, tert-decylamine, tertdodecyl-amine, tert-tetradecylamine, tert-hexadecylamine, tert-octadecylamine, tert-tetracosanyl-amine, and tert-octacosanylamine.

[0031] 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.

[0032] Suitable hydrocarbyl amine salts of dialkyldithiophosphoric acid esters of the invention may be represented by the formula:



wherein R^{26} and R^{27} are independently hydrogen or hydrocarbyl groups such as alkyl groups; for the phosphorus acid ester, at least one of R^{26} and R^{27} will be hydrocarbyl. R^{26} and R^{27} may contain 3 or 4 to 30, or 8 to 25, or 10 to 20, or 13 to 19 carbon atoms. R^{23}, R^{24}, and R^{25} can be independently hydrogen or hydrocarbyl groups, such as alkyl branched or linear alkyl chains with 1 to 30, or 4 to 24, or 6 to 20, or 10 to 16 carbon atoms. These R^{23}, R^{24}, and R^{25} groups can be branched or linear groups, and in certain embodiments at least one, or alternatively two of R^{23}, R^{24}, and R^{25} are hydrogen. Examples of alkyl groups suitable for R^{23}, R^{24}, and R^{25} include butyl, sec-butyl, isobutyl, tert-butyl, pentyl, n-hexyl, sec-hexyl, n-octyl, 2-ethylhexyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, octadecenyl, nonodecyl, eicosyl groups and mixtures thereof.

[0033] In one embodiment the hydrocarbyl amine salt of an alkylthiophosphoric acid ester is the reaction product of a C_{14} to Cis alkylated phosphoric acid with Primene 81R™ (produced and sold by Rohm & Haas) which is a mixture of C_{11} to C_{14} tertiary alkyl primary amines. Other amines which may be used include alkyl alkanol amines, dialkanolamines, trialkanolamines such as triethanolamines as well as borated amines as described hereinbelow.

[0034] The amine salt of as used as this component in the present invention may thus comprise a C_8 to C_{20} alkylamine salt of a mono- or di-alkyl phosphate ester, or mixtures thereof. It will be understood by the skilled person that the amine salt of the thiophosphrus acid ester will typically comprises a mixture of various individual chemical species. Reference herein to "an amine salt of a phosphorus compound," used in the description of component (b) herein will be understood by the skilled person to encompass mixtures of such compounds as may be prepared by the described syntheses.

[0035] The amount of the amine salt of the thiophosphorus acid ester in the lubricant can be 0.3 to 2 weight percent, or 0.4 to 1.9, or 0.5 to 1.8, or 0.7 to 1.7 weight percent. The amounts will be proportionally higher in a concentrate. The amount of said amine salt may also be an amount to contribute 0.03 to 0.2 weight percent phosphorus to the lubricant composition, or alternatively 0.08 to 0.17, or 0.11 to 0.17 weight percent.

[0036] One or more additional phosphorus compounds may also optionally be present, beside the amine salt of the thiophosphorus acid described above. They may provide a measure of additional antiwear performance, or they may be present for other functional reasons. Some of these may be amine salts of phosphorus esters, but without the sulfur component of the above-described chemistry. Examples include amine salts of dialkylphosphates such as a branched C8 amine salt of di-isooctyl phosphate; phosphites such as dibutyl phosphite, di 16- or 18-carbon alkyl- or alkylene-phosphites (that is, in which the long carbon chains may optionally contain unsaturation); an amine salt of phosphoric acid oleyl esters; and phospholipids such as lecithins, e.g., borated lecithins. The total amount of phosphorus in the lubricant composition from all sources may be 0.03 to 0.30 weight percent, or 0.03 to 0.25, or 0.03 to 0.21, or 0.05 to 0.21, or 0.08 to 0.30, or 0.08 to 0.25, or 0.08 to 0.21, or 0.10 to 0.20, or 0.12 to 0.18 weight percent.

[0037] Component (c) is the sulfurized olefin, which may also be considered to be an active sulfur containing compound. A definition of active sulfur is that the compound meets the definition of sulfur reactive with copper powder at a temperature of 149 °C. The test method for determining active sulfur is determined in the STANDARD TEST METHOD FOR ACTIVE SULFUR IN CUTTING FLUIDS Designation: D 1662-69 (Reapproved 1979) as set forth by the American Society for Testing and Materials (ASTM).

[0038] A wide variety of sulfurized olefins can be utilized and these compounds may generally be represented by the formula RS_xR_1 wherein S represents sulfur, x is a whole number having a value of from 1 to about 10, and R and R_1 may be the same or different organic groups derived from olefins. The organic groups may be hydrocarbon groups or substituted hydrocarbon groups containing alkyl, aryl, aralkyl, alkaryl, alkanoate, thiazole, imidazole, phosphorothionate, or beta-ketoalkyl groups. The substantially hydrocarbon groups may contain other substituents such as halogen, amino, hydroxyl, mercapto, alkoxy, aryloxy, thio, nitro, sulfonic acid, carboxylic acid, or carboxylic acid ester.

[0039] Specific examples of types of sulfurized olefins include alkyl or alkenyl sulfides and polysulfides, sulfurized carboxylic acid ester olefins, sulfurized ester olefins, sulfurized olefinic oil, and mixtures thereof. The preparation of such sulfurized olefins is described in the art.

[0040] The sulfurized olefin compounds utilized in the present invention can be alkyl sulfides such as dicetyl sulfide, diparaffin wax sulfide and polysulfide, or cracked wax oleum sulfides. One method of preparing the alkyl sulfides includes the condensation of a chlorinated hydrocarbon with an inorganic sulfide whereby the chlorine atom from each of two molecules is displaced, and the free valence from each molecule is joined to a divalent sulfur atom. Generally, the reaction is conducted in the presence of elemental sulfur.

[0041] Examples of dialkenyl sulfides are described in U.S. Pat. No. 2,446,072. These sulfides can be prepared by reacting an olefinic hydrocarbon containing from 3 to 12 carbon atoms with elemental sulfur in the presence of zinc or a similar metal generally in the form of an acid salt. Examples of sulfides of this type include 6,6'-dithio-bis(5-methyl-4-nonene), 2-butenyl monosulfide and disulfide (the diisobutyl sulfides), and 2-methyl-2-butenyl monosulfide and disulfide. Certain sulfurized isobutylenes may contain 40 to 45 weight percent sulfur.

[0042] The sulfurized olefins include materials prepared by the reaction of an olefin (such as those containing 2 to 6 carbon atoms) or a lower molecular weight polyolefin derived therefrom, with a sulfur-containing compound such as sulfur, sulfur monochloride, sulfur dichloride, hydrogen sulfide, and combinations thereof.

[0043] The olefin is usually one in which each R is independently alkyl, alkenyl or aryl, or a corresponding substituted group. Monoolefinic and diolefinic compounds, particularly the former, may be used, such as terminal monoolefinic hydrocarbons. Olefinic compounds having 3 to 30, or 3 to 16, or 9 or fewer, or 8 carbon atoms may be used.

[0044] Ethylene, isobutene, propylene, and oligomers thereof are especially preferred olefinic compounds. Of these compounds, isobutylene and diisobutylene are particularly desirable because of their availability and the particularly high sulfur-containing compositions which can be prepared therefrom.

[0045] Another class of sulfurized olefins includes sulfurized aliphatic esters of an olefinic mono- or dicarboxylic acid. For example, aliphatic alcohols of from 1 to 30 carbon atoms can be used to esterify monocarboxylic acids such as acrylic acid, methacrylic acid, or 2,4-pentadienoic acid or fumaric acid, maleic acid, or muconic acid Sulfurization of these olefinic esters is conducted with elemental sulfur, sulfur monochloride and/or sulfur dichloride.

[0046] Still another class of sulfurized olefin compounds which can be utilized in the compositions of the invention are diester sulfides characterized by the general formula $ROOC(CH_2)_x\text{-}S_y\text{-}(CH_2)_xCOOR$ wherein each x is independently 2 to 5; y is 1 to 6, such as 1 to about 3; and each R is independently an alkyl group having 4 to 20 carbon atoms. The R group may be a straight chain or branched chain group that is large enough to maintain the solubility of the compositions of the invention in oil. Typical diesters include the butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, tridecyl, myristyl, pentadecyl, cetyl, heptadecyl, stearyl, lauryl, and eicosyl diesters of thiodialkanoic acids such as propionic, butanoic, pentanoic, and hexanoic acids. Of the diester sulfides, a specific example is dilauryl, 3,3'-thiodipropionate.

[0047] The amount of the sulfurized olefin may be that amount to provide 0.5 to 7, percent by weight sulfur to the composition, or 0.4 to 1.5, or 1.5 to 2, or 3 to 5, or 2 to 3 percent by weight. The actual amount of the sulfurized olefin may depend on the sulfur content thereof, as may be readily calculated. If a sulfurized olefin contains 40 weight percent sulfur, as an example, the total amounts may be 1.2 to 17 weight percent, or 1 to 3.8, or 3.8 to 5, or 7.5 to 12, or 5 to 7.5 weight percent.

[0048] A sulfurized olefin composition may be prepared as described below.

[0049] EXAMPLE S-I A sulfurized olefin is prepared by reacting sulfur, hydrogen sulfide, and diisobutylene. Thus, 128 grams of sulfur (4 moles) is charged to a jacketed high pressure reactor which is fitted with an agitator and internal cooling coil. Refrigerated brine is circulated through the coils to cool the reactor prior to the introduction of the gaseous reactants. After sealing the reactor, evacuating to a pressure of less than 0.5 kPa and cooling, 224 grams (2 moles) of diisobutylene and 34 grams (1 mole) of hydrogen sulfide are charged to the reactor.

[0050] The reactor is then heated using steam in the external jacket to a temperature of about 171 °C over about 1.5 hours. A maximum pressure of 8600 kPa is reached at about 168 °C during the heat-up step. Prior to reaching the reaction temperature, the pressure starts to decrease and continues to decrease steadily as the gaseous reactants are consumed.

[0051] After about 10 hours at a reaction temperature of about 171 °C, the pressure is approximately 2100-2200 kPa and the rate of pressure drop is about 30-70 kPa per hour. At this time the reaction is essentially complete and the unreacted hydrogen sulfide and diisobutylene are vented to a recovery system. After the pressure of the reactor has decreased to ambient, the sulfurized mixture is recovered as a liquid. The mixture is then blown with nitrogen and vacuum stripped to remove the low boiling materials including unreacted diisobutylene, mercaptans, and monosulfides. The residue is the desired sulfurized composition which will contain approximately 40% sulfur by weight.

[0052] Other materials may also be present in, or may be absent from, the disclosed lubricant compositions. One such material may be a detergent which may optionally be an overbased detergent such as an overbased alkaline earth metal detergent. Detergents are typically overbased materials, otherwise referred to as overbased or superbased salts, which are generally homogeneous Newtonian systems having by a metal content in excess of that which would be present for neutralization according to the stoichiometry of the metal and the detergent anion. The amount of excess metal is commonly expressed in terms of metal ratio, that is, the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. Overbased materials are prepared by reacting an acidic material (such as carbon dioxide) with an acidic organic compound, an inert reaction medium (e.g., mineral oil), a stoichiometric excess of a metal base, and a promoter such as a phenol or alcohol. The acidic organic material will normally have a sufficient number of carbon atoms, to provide oil-solubility.

[0053] Overbased detergents may be characterized by Total Base Number (TBN, ASTM D2896), the amount of strong acid needed to neutralize all of the material's basicity, expressed as mg KOH per gram of sample. Since overbased detergents are commonly provided in a form which contains diluent oil, for the purpose of this document, TBN is to be recalculated to an oil-free basis. Some useful detergents may have a TBN of 100 to 800, or 150 to 750, or, 400 to 700.

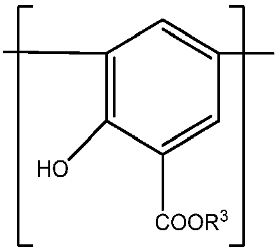
[0054] The metal compounds useful in making the basic metal salts are generally any Group 1 or Group 2 metal compounds (CAS version of the Periodic Table of the Elements). Examples include alkali metals such as sodium, potassium, lithium, copper, magnesium, calcium, barium, zinc, and cadmium. In one embodiment the metals are sodium, magnesium, or calcium. The anionic portion of the salt can be hydroxide, oxide, carbonate, borate, or nitrate.

[0055] In one embodiment the lubricant can contain an overbased sulfonate detergent. Suitable sulfonic acids include hydrocarbyl-substituted sulfonic and thiosulfonic acids, including mono- or polynuclear aromatic or cycloaliphatic compounds. In one embodiment the sulfonate detergent may be a predominantly linear alkylbenzenesulfonate detergent having a metal ratio of at least 8 as described in paragraphs [0026] to [0037] of US Patent Application 2005065045.

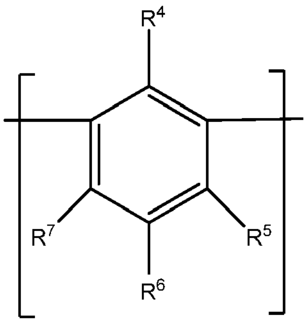
[0056] Another overbased material is an overbased phenate detergent. The phenols useful in making phenate detergents can be represented by $(R^1)_a\text{-Ar-}(OH)_b$, where R^1 is an aliphatic hydrocarbyl group of 4 to 400 or 6 to 80 or 6 to 30 or 8 to 25 or 8 to 15 carbon atoms; Ar is an aromatic group such as benzene, toluene or naphthalene; a and b are each at least one, the sum of a and b being up to the number of displaceable hydrogens on the aromatic nucleus of Ar, such as 1 to 4 or 1 to 2. Phenate detergents are also sometimes provided as sulfur-bridged species.

[0057] In one embodiment, the overbased material is an overbased saligenin detergent. Overbased saligenin detergents are commonly overbased magnesium salts which are based on saligenin derivatives. Saligenin detergents are disclosed in greater detail in U.S. Patent 6,310,009, with special reference to their methods of synthesis (Column 8 and Example 1) and preferred amounts of the various species of X and Y (Column 6).

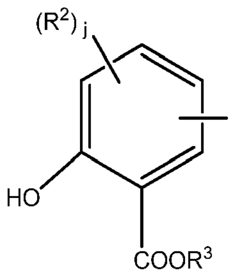
[0058] Salixarate detergents are overbased materials that can be represented by a compound comprising at least one unit of formula (I) or formula (II) and each end of the compound having a terminal group of formula (III) or (IV):



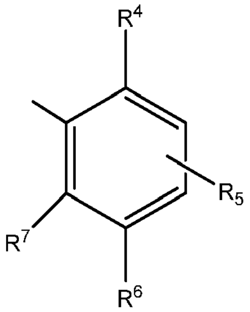
(I)



(II)



(III)



(IV)

such groups being linked by divalent bridging groups A, which may be the same or different. In formulas (I)-(IV) R^3 is hydrogen, a hydrocarbyl group, or a valence of a metal ion; R^2 is hydroxyl or a hydrocarbyl group, and j is 0, 1, or 2; R^6 is hydrogen, a hydrocarbyl group, or a hetero-substituted hydrocarbyl group; either R^4 is hydroxyl and R^5 and R^7 are independently either hydrogen, a hydrocarbyl group, or hetero-substituted hydrocarbyl group, or else R^5 and R^7 are both hydroxyl and R^4 is hydrogen, a hydrocarbyl group, or a hetero-substituted hydrocarbyl group; provided that at least one of R^4, R^5, R^6 and R^7 is hydrocarbyl containing at least 8 carbon atoms. Salixarate derivatives and methods of their preparation are described in greater detail in U.S. patent number 6,200,936 and PCT Publication WO 01/56968. It is believed that the salixarate derivatives have a predominantly linear, rather than macrocyclic, structure, although both structures are intended to be encompassed by the term "salixarate."

[0059] Glyoxylate detergents are similar overbased materials which are based on an anionic group which may be the condensation product of a hydroxyaromatic material such as a hydrocarbyl-substituted phenol with a carboxylic reactant such as glyoxylic acid or another omega-oxoalkanoic acid. Overbased glyoxylic detergents and their methods of preparation are disclosed in greater detail in U.S. Patent 6,310,011 and references cited therein.

[0060] The overbased detergent can also be an overbased salicylate, e,g., an alkali metal or alkaline earth metal salt of a substituted salicylic acid. The salicylic acids may be hydrocarbyl-substituted wherein each substituent contains an average of at least 8 carbon atoms per substituent and 1 to 3 substituents per molecule. The substituents can be polyalkene substituents. In one embodiment, the hydrocarbyl substituent group contains 7 to 300 carbon atoms and can be an alkyl group having a molecular weight of 150 to 2000. Overbased salicylate detergents and their methods of preparation are disclosed in U.S. Patents 4,719,023 and 3,372,116.

[0061] Other overbased detergents can include overbased detergents having a Mannich base structure, as disclosed in U.S. Patent 6,569,818.

[0062] In certain embodiments, the hydrocarbyl substituents on hydroxy-substituted aromatic rings in the above detergents (e.g., phenate, saligenin, salixarate, glyoxylate, or salicylate) are free of or substantially free of C_{12} aliphatic hydrocarbyl groups (e.g., less than 1%, 0.1%, or 0.01% by weight of the substituents are C_{12} aliphatic hydrocarbyl groups). In some embodiments such hydrocarbyl substituents contain at least 14 or at least 18 carbon atoms.

[0063] In certain embodiments an overbased alkaline earth metal detergent may optionally be present, in an amount to provide 0 to 500, or 10 to 100, or 1 to 50 parts per million of the alkaline earth metal or metals. In certain embodiments the lubricant is substantially free from overbased alkaline earth metal detergent or substantially free from all alkaline earth metal detergent, that is, the amount of the alkaline earth metal provided thereby may be less than 5 or 3 or 1 or 0.5 parts per million or may be zero parts per million.

[0064] Another material that optionally may be present, or that may be absent, is a polymeric viscosity index modifier. Viscosity modifiers (VM) and dispersant viscosity modifiers (DVM) are well known. Examples of VMs and DVMs may include polymethacrylates, polyacrylates, polyolefins, styrene-maleic ester copolymers, alpha-olefin-maleic ester copolymers, and similar polymeric substances including homopolymers, copolymers, and graft copolymers. The DVM may comprise a nitrogen-containing methacrylate polymer, for example, a nitrogen-containing methacrylate polymer derived from methyl methacrylate and dimethylaminopropyl amine.

[0065] Examples of commercially available VMs, DVMs and their chemical types may include the following: polyisobutylenes (such as Indopol™ from BP Amoco or Parapol™ from ExxonMobil); olefin copolymers (such as Lubrizol® 7060, 7065, and 7067 from Lubrizol and Lucant® polymers, including ethylene/propylene copolymers, including Lucant® HC-2000L and HC-600 also from Lubrizol); hydrogenated styrene-diene copolymers (such as Shellvis™ 40 and 50, from Shell and LZ® 7308, and 7318 from Lubrizol); styrene/maleate copolymers, which are dispersant copolymers (such as LZ® 3702 and 3715 from Lubrizol); polymethacrylates, some of which have dispersant properties (such as those in the Viscoplex™ series from RohMax, such as Viscoplex™ 0-050, the Hitec™ series of viscosity index improver from Afton, and LZ® 7702, 7706, 7727, 7720C, 8420, and VL9205F from Lubrizol); olefin-graft-polymethacrylate polymers (such as

Viscoplex™ 2-500 and 2-600 from RohMax); and hydrogenated polyisoprene star polymers (such as Shellvis™ 200 and 260, from Shell). Also included are Asteric™ polymers from Lubrizol (methacrylate polymers with radial or star architecture). Viscosity modifiers that may be used are described in U.S. Pat. Nos. 5,157,088, 5,256,752 and 5,395,539. The VMs and/or DVMs may be used in the lubricant at concentrations of 0 to 30 percent by weight, or 3 to 25, or 5 to 20, or 5 to 15 weight percent.

[0066] Additional conventional components may be used in preparing a lubricant according to the disclosed technology, for instance, those additives typically employed in a gear lubricant. Gear lubricants may typically contain any or all of the following components hereinafter described; alternatively, any one or more of the following components may optionally be omitted.

[0067] One additive is a dispersant. Dispersants are well known in the field of lubricants and include primarily what is known as ashless-type dispersants and polymeric dispersants. Ashless type dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include nitrogen-containing dispersants such as N-substituted long chain alkenyl succinimides, also known as succinimide dispersants. Succinimide dispersants are more fully described in U.S. Patents 4,234,435 and 3,172,892. Another class of ashless dispersant is high molecular weight esters, prepared by reaction of a hydrocarbyl acylating agent and a polyhydric aliphatic alcohol such as glycerol, pentaerythritol, or sorbitol. Such materials are described in more detail in U.S. Patent 3,381,022. Another class of ashless dispersant is Mannich bases. These are materials which are formed by the condensation of a higher molecular weight, alkyl substituted phenol, an alkylene polyamine, and an aldehyde such as formaldehyde and are described in more detail in U.S. Patent 3,634,515. Other dispersants include polymeric dispersant additives, which are generally hydrocarbon-based polymers which contain polar functionality to impart dispersancy characteristics to the polymer. Dispersants can also be post-treated by reaction with any of a variety of agents. Among these are urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, and phosphorus compounds. References detailing such treatment are listed in U.S. Patent 4,654,403. The amount of dispersant in the present composition can typically be 1 to 10 weight percent, or 1.5 to 9.0 percent, or 2.0 to 8.0 percent, all expressed on an oil-free basis.

[0068] Another component is an antioxidant. Antioxidants encompass phenolic antioxidants, which may comprise a butyl substituted phenol containing 2 or 3 t-butyl groups. The para position may also be occupied by a hydrocarbyl group, an ester-containing group, or a group bridging two aromatic rings. Antioxidants also include aromatic amine, such as nonylated diphenylamines or alkylated phenylnaphthylamine. Other antioxidants include sulfurized olefins, titanium compounds, and molybdenum compounds. U.S. Pat. No. 4,285,822, for instance, discloses lubricating oil compositions containing a molybdenum and sulfur containing composition. U.S. Patent Application Publication 2006-0217271 discloses a variety of titanium compounds, including titanium alkoxides and titanated dispersants, which materials may also impart improvements in deposit control and filterability. Other titanium compounds include titanium carboxylates such as neodecanoate. Typical amounts of antioxidants will, of course, depend on the specific antioxidant and its individual effectiveness, but illustrative total amounts can be 0.01 to 5 percent by weight or 0.15 to 4.5 percent or 0.2 to 4 percent. Additionally, more than one antioxidant may be present, and certain combinations of these can be synergistic in their combined overall effect.

[0069] Another additive is an antiwear agent, other than those that have been described above. Examples of antiwear agents include phosphorus-containing anti-wear/extreme pressure agents such as metal thiophosphates, phosphoric acid esters and salts thereof, phosphorus-containing carboxylic acids, esters, ethers, and amides; and phosphites. In certain embodiments a phosphorus antiwear agent may be present in an amount to deliver 0.01 to 0.2, or 0.015 to 0.15, or 0.02 to 0.1, or 0.025 to 0.08 percent phosphorus. The antiwear agent may be a zinc dialkyldithiophosphate (ZDP). For a typical ZDP, which may contain 11 percent P (calculated on an oil free basis), suitable amounts may include 0.09 to 0.82 percent. Non-phosphorus-containing anti-wear agents include borate esters (including borated epoxides), dithiocarbamate compounds, molybdenum-containing compounds, and sulfurized olefins.

[0070] Other materials that may be used as antiwear agents include tartrate esters, tartramides, and tartrimides. Examples include oleyl tartrimide (the imide formed from oleylamine and tartaric acid) and oleyl diesters (from, e.g., mixed C12-16 alcohols). Other related materials that may be useful include esters, amides, and imides of other hydroxy-carboxylic acids in general, including hydroxy-polycarboxylic acids, for instance, acids such as tartaric acid, citric acid, lactic acid, glycolic acid, hydroxy-propionic acid, hydroxyglutaric acid, and mixtures thereof. These materials may also impart additional functionality to a lubricant beyond antiwear performance. These materials are described in greater detail in US Publication 2006-0079413 and PCT publication WO2010/077630. Such derivatives of (or compounds derived from) a hydroxy-carboxylic acid, if present, may typically be present in the lubricating composition in an amount of 0.1 weight % to 5 weight %, or 0.2 weight % to 3 weight %, or greater than 0.2 weight % to 3 weight %.

[0071] Other additives that may optionally be used in lubricating oils include pour point depressing agents, extreme pressure agents, anti-wear agents, color stabilizers, and anti-foam agents.

[0072] The amount of each chemical component described is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, that is, on an active chemical basis, unless otherwise indicated.

However, unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade.

[0073] 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:

[0074] 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);

[0075] 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 sulfoxy);

[0076] 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 and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. Heteroatoms include sulfur, oxygen, and nitrogen. In general, no more than two, or no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; alternatively, there may be no non-hydrocarbon substituents in the hydrocarbyl group.

[0077] 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. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic or anionic sites of other molecules. The products formed thereby, including the products formed upon employing the 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 the composition prepared by admixing the components described above.

[0078] The invention herein is useful for imparting wear performance to a lubricant such as a gear lubricant formulation, which may be better understood with reference to the following examples.

EXAMPLES

[0079] Typical gear lubricant formulations are prepared in low KV_100 formulations. Details of the formulations are presented in the Table below. All amounts are on an oil-free (active chemical) basis except for the commercial anti-foam agent(s) which are reported as provided commercially (believed to contain 65-90% oil).

Ex. (ID # for reference)	1* 295	2* 296	3* 298	4 316	5 348	6 349	7 351	8 353
Poly alpha olefin oil, KV_100 = 4 mm^2/s	77.2	77.2	77.2	75.5	75.5	75.5	75.5	75.5
Amine salt of P compound[a]	-	-	-	1.66	0.83	0.50	0.65	1.25
di-C18 alkyl phosphite	0.5	0.5	0.5	0.8	0.5	0.5	0.5	0.4
di-C8 alkyl phosphate, C8 amine salt	1.3	1.3	1.5	0.8	1.0	1.0	1.0	0.4
% P in composition	0.128	0.126	0.143	0.224	0.176	0.148	0.157	0.160
Sulfurized C4 olefins (44% S)	4.2	4.6	4.2	4.1	4.1	4.1	4.1	4.0
% S in composition	1.85	2.02	1.85	1.80	1.80	1.80	1.80	1.76
KV_100 of composition	5.9	5.9	5.9	6.0	6.0	6.0	6.0	6.0
Additional components								
Ester polymer viscosity modifier	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
Corrosion inhibitors	0.7	0.7	0.7	0.65	0.65	0.65	0.65	0.65
Borated dispersant	0.67	0.67	0.67	0.72	1.00	1.00	1.00	1.00
Antifoam agents	0.07	0.07	0.07	0.02	0.02	0.02	0.02	0.02
Ester of hydroxy acid	0.08	0.11	0.11	0.08	0.08	0.08	0.10	0.10
Friction modifier(s)[c]	0.04	0.04	0.04	0.32	0.32	0.32	0.12	0.12

(continued)

Wear test results								
L-37 ring gear wear rating (ASTM D6121)	7	7	7	9/8	9	9	9	9

* a reference or comparative example
a. obtained by reacting phosphorus pentasulfide alcohol of 4-8 carbon atoms, with an alkylene oxide and further with phosphorus pentoxide, and salting the resulting material with amine having 12 to 24 carbon atoms.
b. long chain amine, amide, and/or imidazoline compounds
c. The friction modifiers are non-phosphorus-containing materials. It is known to those skilled in the art that L-37 test performance depends on the presence of phosphorus-containing component(s). The minor variations in the amount or composition of the friction modifiers will not affect the L-37 wear results.

[0080] The results show that the presence of the amine salt of the phosphorus compound provides improved wear performance compared with the other phosphorus compounds, in a low viscosity lubricant formulation.

[0081] Another series of examples were prepared in relatively low and in high viscosity formulations. The formulations are summarized in the table below:

Ex. (ID # for reference)	9* (390) Low vise.	10* (739) High visc.	11 (391) Low vise.	12* (770) High visc.
Group II base oil, 6 mm^2/s	91		91	
Group I base oil, 12 mm^2/s		77.4		77.4
Bright stock, 31 mm^2/s		13.6		13.6
Amine salt of P compound[a]			1.16	1.16
Di-C8 alkyl phosphate, C8 amine salt	0.85	0.85		
Dialkyl phosphite anti-wear agents	0.42	0.42		
Sulfurized olefin (45% S)	3.2	3.2	3.2	3.2
Borated dispersant	0.59	0.59	0.59	0.59
Other components including friction modifier, corrosion inhibitors, pour point depressant	1.54	1.54	1.86	1.86
Diluent oil	Balance to = 100%			
KV_100 of the composition	6.12	13.12	6.09	13.1

* A comparative or reference example
a. obtained by reacting phosphorus pentasulfide alcohol of 4-8 carbon atoms, with an alkylene oxide and further with phosphorus pentoxide, and salting the resulting material with amine having 12 to 24 carbon atoms.

[0082] The formulations of Examples 9-12 are subjected to the L-37 test (ASTM D6121). The results, including the pass criteria, are shown in the table below:

Test value (pass criterion)- - - - - - Ex.:	9*	10*	11	12*
Final ring gear wear (>5)	8	7	7	8
Final ring gear surface fatigue rippling (>8)	9	9	9	10
Final ring gear surface fatigue ridging (>8)	9	10	10	10
Final ring gear surface fatigue pitting/ spalling (>9.3)	9.9	9.9	9.9	9.9
Final ring gear surface fatigue scoring (>9.3)	10	10	10	10
Final pinion gear wear (>5)	6	7	7	8
Final pinion gear rippling (>8)	8.7	9.4	9.4	9

(continued)

Test value (pass criterion)- - - - - - Ex.:	9*	10*	11	12*
Final pinion gear surface ridging (>8)	7.3	8	8	10
Final pinion gear pitting/spalling merit (>9.3)	9.9	9.9	9.9	9.9
Final pinion gear scoring (>9.3)	10	10	10	10

[0083] The result show that, using the formulations of examples 9 - 12, both the compositions of the disclosed technology and the reference compositions meet all the passing criteria when used in a high viscosity formulation (10 and 12). However, in the low viscosity formulations (9 and 11), the formulation containing the amine phosphorus salt disclosed herein meets all the passing criteria, while the formulation containing the alternative phosphorus compound does not meet at least one of the passing criteria.

[0084] Each of the documents referred to above is incorporated herein by reference, including any prior applications, whether or not specifically listed above, from which priority is claimed. The mention of any document is not an admission that such document qualifies as prior art or constitutes the general knowledge of the skilled person in any jurisdiction. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as optionally modified by the word "about." It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements.

[0085] As used herein, the transitional term "comprising," which is synonymous with "including," "containing," or "characterized by," is inclusive or open-ended and does not exclude additional, un-recited elements or method steps. However, in each recitation of "comprising" herein, it is intended that the term also encompass, as alternative embodiments, the phrases "consisting essentially of' and "consisting of," where "consisting of' excludes any element or step not specified and "consisting essentially of' permits the inclusion of additional un-recited elements or steps that do not materially affect the essential or basic and novel characteristics of the composition or method under consideration. The expression "consisting of' or "consisting essentially of," when applied to an element of a claim, is intended to restrict all species of the type represented by that element, notwithstanding the presence of "comprising" elsewhere in the claim.

[0086] While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention. In this regard, the scope of the invention is to be limited only by the following claims.

[0087] Various preferred features and embodiments of the present invention will now be described with reference to the following numbered paragraphs (paras).

1. A lubricant composition comprising:

(a) about 40 to about 95 percent by weight, or about 58 to about 80 percent by weight, of an oil having a kinematic viscosity at 100 °C by ASTM D445 of about 3 to about 7.5, or about 3.6 to about 6, or about 3.5 to about 5 $mm^{2/}s$;
(b) about 0.3 to about 2 percent by weight of an amine salt of a phosphorus compound, or mixtures thereof, obtained by reacting phosphorus pentasulfide with one or more alcohols having 4 to about 13, or 4 to 8, or 6, carbon atoms, with an alkylene oxide, and further with phosphorus pentoxide, and salting the resulting material with one or more amines having 2 to 20 or 12 to 24 carbon atoms; and
(c) a sulfurized olefin in an amount to provide about 0.5 to about 7, or about 0.5 to about 1.5, or about 1.5 to about 2, or about 3 to about 5, or about 2 to about 3, percent by weight sulfur to the composition;

wherein said composition has a kinematic viscosity at 100 °C by ASTM D445 of up to about 7.5, or about 3.5 to about 7.0, or about 4 to about 6.5, or about 4 to about 6 mm^2/s.

2. The lubricant composition of para 1 wherein the oil comprises a polyalpha olefin having a kinematic viscosity at 100 °C of about 3 to about 7.5.

3. The lubricant composition of para 1 wherein the oil comprises an API Group III oil or a Group III+ oil.

4. The lubricant composition of any one of paras 1 through 3 wherein the alkylene oxide comprises 1,2-propylene oxide.

5. The lubricant composition of any one of paras 1 through 4 wherein the alcohol has 6 carbon atoms.

6. The lubricant composition of any one of paras 1 through 5 wherein the alcohol is 4-methylpentan-2-ol.

7. The lubricant composition of any one of paras 1 through 6 having a phosphorus content of or about 0.02 to about 0.20, or about 0.08 to about 0.17, or about 0.11 to about 0.17, weight percent phosphorus supplied by the material of component (b).

8. The lubricant composition of any one of paras 1 to 7 wherein the total phosphorus content of the lubricant is about 0.08 to about 0.30, or about 0.08 to about 0.25, or about 0.08 to about 0.21, or about 0.10 to about 0.20, or about 0.12 to about 0.18, weight percent.

9. The lubricant composition of any one of paras 1 through 8 optionally further comprising an optionally overbased alkaline earth metal detergent in an amount to provide 0 to about 500, or 0 to about 100, or 1 to about 50 parts by million by weight alkaline earth metal.

10. The lubricant composition of any one of paras 1 through 9 being substantially free from alkaline earth metal detergent.

11. The lubricant composition of any one of paras 1 through 10 optionally comprising 0 to about 30, or about 5 to about 15, percent by weight of a polymeric viscosity index modifier.

12. A composition prepared by admixing the components of any one of paras 1 through 11.

13. A method of lubricating a gear or a bearing, comprising supplying thereto the lubricant composition of any one of paras 1 through 12.

14. The method of para 13 comprising lubricating a gear wherein the gear is located in an axle assembly.

15. The method of para 13 or para 14 comprising lubricating a gear wherein the gear is a hypoid gear.

16. The method of any one of paras 13 through 15 wherein the lubricant composition is employed in a lubricated axle assembly characterized by a λ value of less than 2.0, or 1.1 to 1.5, where λ is defined as the ratio of elastohydrodynamic film thickness of the lubricant to the composite surface roughness of the gear surface.

Claims

1. A lubricant composition comprising:

(a) about 40 to about 95 percent by weight, or about 58 to about 80 percent by weight, of an oil having a kinematic viscosity at 100 °C by ASTM D445 of about 3 to about 7.5, or about 3.6 to about 6, or about 3.5 to about 5 mm^2/s;
(b) about 0.3 to about 2 percent by weight of an amine salt of a phosphorus compound, or mixtures thereof, obtained by reacting phosphorus pentasulfide with one or more alcohols having 4 to about 13, or 4 to 8, or 6, carbon atoms, with an alkylene oxide, and further with phosphorus pentoxide, and salting the resulting material with one or more amines having 2 to 20 or 12 to 24 carbon atoms; and
(c) a sulfurized olefin in an amount to provide about 0.5 to about 7, or about 0.5 to about 1.5, or about 1.5 to about 2, or about 3 to about 5, or about 2 to about 3, percent by weight sulfur to the composition;

wherein said composition has a kinematic viscosity at 100 °C by ASTM D445 of up to about 7.5, or about 3.5 to about 7.0, or about 4 to about 6.5, or about 4 to about 6 mm^2/s.

2. The lubricant composition of claim 1 wherein the oil comprises a polyalpha olefin having a kinematic viscosity at 100 °C of about 3 to about 7.5, or wherein the oil comprises an API Group III oil or a Group III+ oil.

3. The lubricant composition of either of claims 1 and 2 wherein the alkylene oxide comprises 1,2-propylene oxide.

4. The lubricant composition of any one of claims 1 through 3 wherein the alcohol has 6 carbon atoms.

5. The lubricant composition of any one of claims 1 through 4 wherein the alcohol is 4-methylpentan-2-ol.

6. The lubricant composition of any one of claims 1 through 5 having a phosphorus content of or about 0.02 to about 0.20, or about 0.08 to about 0.17, or about 0.11 to about 0.17, weight percent phosphorus supplied by the material of component (b).

7. The lubricant composition of any one of claims 1 to 6 wherein the total phosphorus content of the lubricant is about 0.08 to about 0.30, or about 0.08 to about 0.25, or about 0.08 to about 0.21, or about 0.10 to about 0.20, or about 0.12 to about 0.18, weight percent.

8. The lubricant composition of any one of claims 1 through 7 optionally further comprising an optionally overbased alkaline earth metal detergent in an amount to provide 0 to about 500, or 0 to about 100, or 1 to about 50 parts by million by weight alkaline earth metal.

9. The lubricant composition of any one of claims 1 through 8 being substantially free from alkaline earth metal detergent.

10. The lubricant composition of any one of claims 1 through 9 optionally comprising 0 to about 30, or about 5 to about 15, percent by weight of a polymeric viscosity index modifier.

11. A composition prepared by admixing the components of any one of claims 1 through 10.

12. A method of lubricating a gear or a bearing, comprising supplying thereto the lubricant composition of any one of claims 1 through 11.

13. The method of claim 12 comprising lubricating a gear wherein the gear is located in an axle assembly.

14. The method of claim 12 or claim 13 comprising lubricating a gear wherein the gear is a hypoid gear.

15. The method of any one of claims 12 through 14 wherein the lubricant composition is employed in a lubricated axle assembly **characterized by** a λ value of less than 2.0, or 1.1 to 1.5, where λ is defined as the ratio of elastohydrodynamic film thickness of the lubricant to the composite surface roughness of the gear surface.

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EUROPEAN SEARCH REPORT

Application Number
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	30 November 2020	Greß, Tobias

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X : particularly relevant if taken alone
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