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(71) Applicant: **Afton Chemical Corporation**
Richmond, VA 23219 (US)

(72) Inventors:
• **Ryan, Helen T.**
London, W6 8NL (GB)
• **Corbett, Patricia**
Bracknell, Berkshire RG128XX (GB)

(74) Representative: **Schwabe - Sandmair - Marx**
Patentanwälte
Stuntzstraße 16
81677 München (DE)

(54) **Thermally stable zinc-free antiwear agent**

(57) There is disclosed a lubricant additive composition comprising a thermally stable, zinc-free, phosphorous-containing antiwear agent. Moreover, a lubricant composition comprising the disclosed additive composi-

tion is also disclosed. Methods for making and using the disclosed compositions are disclosed.

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Description**DESCRIPTION OF THE DISCLOSURE****Field of the Disclosure**

[0001] The present disclosure relates to a thermally stable, zinc-free antiwear agent, compositions containing same, and methods of use thereof.

Background of the Disclosure

[0002] The use of ashless and zinc-free antiwear hydraulic technology is known. However some ashless or zinc free, antiwear multigrade oils containing polyalkylmethacrylate viscosity index improvers (PMA VIIs) with very low phosphorus levels, such as between 50 and 150 ppm, have borderline failing performance in current industry pump tests, T6H20C and 35VQ25. This negative result is because the PMA VIIs compete with the thin phosphorous tribolayer in the ashless system. It is noted that this result does not occur when using ZDDP-based fluids because the tribolayer they form is thicker. One of the problems with adding more antiwear species to overcome the borderline failing pump performance is that not all the antiwear additives are thermally stable and so at the required higher levels they will contribute to sludge/ varnish formation in use. Moreover, the antiwear species break down to form acidic species that can lead to the blockage of filters.

[0003] It is a requirement of hydraulic fluids that they exhibit acceptable hydraulic performance, i.e. power transmission, as well as other important characteristics such as thermal stability, rust inhibition and antiwear performance. These latter properties are usually achieved by incorporating specific additives in a base oil. Further, to maintain good power transmission and to avoid damaging hydraulic equipment, in which they are used, hydraulic fluids should be kept meticulously clean and free of contaminants

[0004] Antiwear agents such as zinc dihydrocarbyl dithiophosphates (ZDDPs) are commonly used. One factor against use of ZDDP's as an antiwear agent in hydraulic fluids is the environmental one associated with use of zinc, and for this reason, zinc-based hydraulic fluids have been banned from some applications. It is therefore desirable to provide a zinc-free multigrade hydraulic oil with performance matching or exceeding that of a zinc-based multigrade fluid by using thermally stable antiwear additives at high phosphorus levels

[0005] What is needed is an antiwear agent for a multigrade hydraulic fluid that can provide the following properties/ solutions at high phosphorus levels: passing pump performance, acceptable varnish/sludge control, tolerance to water, thermal stability, and environmental acceptability.

SUMMARY OF THE DISCLOSURE

[0006] In accordance with the disclosure, there is disclosed a lubricant additive composition having at least one thermally stable dithiophosphate prepared by reacting a dithiophosphoric acid with an alkene and at least one polyalkyl-methacrylate viscosity index improver.

[0007] Further disclosed is a lubricant additive composition having at least one thermally stable triarylphosphate or dialkylphosphate; and at least one polyalkylmethacrylate viscosity index improver.

[0008] There is also disclosed a lubricating composition comprising a major amount of base oil, and a minor amount of the additive compositions.

[0009] Yet also disclosed is a method of controlling sludge formation in a multigrade lubricating composition, said method comprising providing a major amount of a base oil, and a minor amount of the lubricant additive compositions.

[0010] There is further disclosed a method of controlling sludge formation in a monograde lubricating composition, said method comprising providing a major amount of a base oil, and a minor amount of the lubricant additive compositions.

[0011] Also disclosed is a method of improving the thermal stability of a lubricating composition comprising formulating a lubricating oil having a major amount of a base oil and a minor amount of the lubricant additive compositions.

[0012] Additional objects and advantages of the disclosure will be set forth in part in the description which follows, and/or can be learned by practice of the disclosure. The objects and advantages of the disclosure will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims.

[0013] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the disclosure, as claimed.

DESCRIPTION OF THE EMBODIMENTS

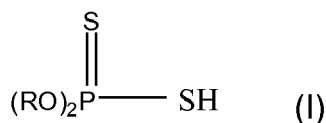
[0014] The present disclosure relates to a thermally stable, zinc-free lubricant additive composition. Moreover, there

is disclosed a lubricant composition comprising a major amount of a base oil and a minor amount of an additive composition.

[0015] By "thermally stable" herein is meant that acceptable varnish or sludge is formed in bench or pump tests that are run to evaluate functional fluids, such as hydraulic fluids. These bench tests include the Cincinnati Milacron procedure A (a thermal stability test), the Nippon oil color test at various temperatures, the ASTM D2619 hydrolytic stability test, the ASTM D4310 1000-hr TOST test, the ASTM D943 Life TOST test, the Eaton 35VQ25, a pump test, the Parker Denison T6H20C hybrid pump test, modifications of these tests, as well as non-standard industry tests.

[0016] By "zinc-free" herein is meant that no zinc has been added to the composition, but the composition can have trace levels of zinc due to contamination.

[0017] The compositions can comprise at least one thermally stable, zinc-free, antiwear agent. Suitable antiwear agents can include the reaction products of an alkene, such as a dicyclopentadiene, acrylate, or methacrylate, and a dithiophosphoric acid, and/or dicyclopentadiene dithioates. Thiophosphoric acids suitable for use in preparing the antiwear agents can have formula (I):



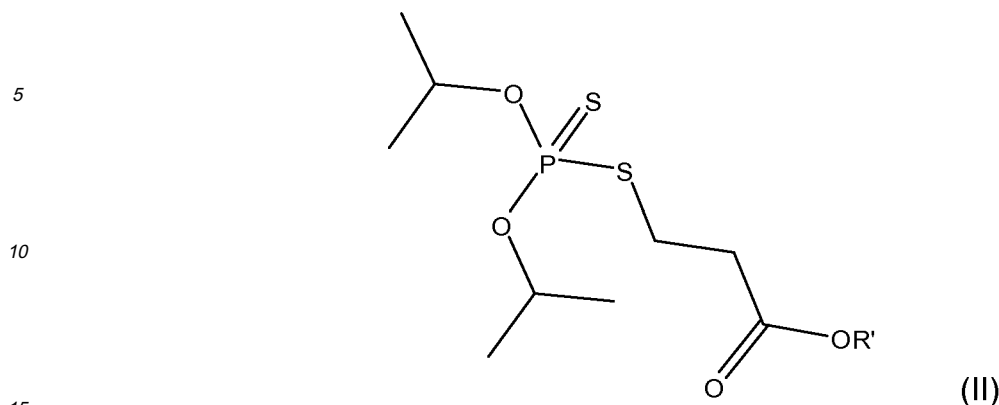
wherein R is a hydrocarbyl group having from about 2 to about 30, for example about 3 to about 18 carbon atoms. In an aspect, R comprises a mixture of hydrocarbyl groups containing from about 3 to about 18 carbon atoms.

[0018] As used herein, the term "hydrocarbyl group" or "hydrocarbyl" 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 a molecule and having a predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

- (1) 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 an alicyclic radical);
- (2) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of the description herein, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);
- (3) hetero-substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this description, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents such as pyridyl, furyl, thienyl, and imidazolyl. In general, no more than two, or as a further example, no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; in some embodiments, there may be no non-hydrocarbon substituent in the hydrocarbyl group.

[0019] The thermally stable, zinc-free antiwear agents can be prepared by mixing an alkene, for example a dicyclopentadiene, acrylate, or methacrylate, and a dithiophosphoric acid for a time and temperature sufficient to react the thioacid with the alkene. Typical reaction times range from about 30 minutes to about 6 hours, although suitable reaction conditions can readily be determined by one skilled in the art. The reaction product can be subjected to conventional post-reaction work up, including vacuum stripping and filtering.

[0020] In an embodiment, the thermally stable, zinc-free antiwear agents can be dicyclopentadiene dithioates. In another embodiment, the thermally stable, zinc free antiwear agents can be represented by formula (II):



wherein R' is a hydrocarbonyl group having from about 1 to about 6 carbon atoms.

[0021] In a further embodiment, the thermally stable, zinc-free antiwear agents can be dialkylphosphates or trialkylphosphates, such as tricresylphosphates.

[0022] The additive composition can comprise any effective amount of the thermally stable, zinc-free antiwear agents. In particular, the additive composition can comprise from about 10% to about 45 % by weight, and for example from about 25% to about 40%, by weight of the thermally stable, zinc-free antiwear agents, relative to the total weight of the composition. In an aspect, the thermally stable, zinc-free antiwear agents can be present in a lubricant composition in an amount ranging from about 0.001 % to about 1 % by weight, for example from about 0.1 % to about 0.7% by weight relative to the total weight of the lubricant composition.

[0023] The lubricant composition can further comprise a viscosity index improver (VII). Examples of VIIs include, but are not limited to, polyalkylmethacrylate VIIs. The viscosity index improver can be supplied in the form of a solution in an inert solvent, such as a mineral oil solvent, which usually is a severely refined mineral oil. The viscosity index improver solution often will have a boiling point above 200°C., and a specific gravity of less than 1 at 25°C. On an active ingredient basis (i.e., excluding the weight of inert diluent or solvent associated with the viscosity index improver), the finished lubricant compositions of this invention can comprise in the range of about 0 to about 25 wt % of the polymeric viscosity index improver.

[0024] Suitable materials for use as a VII herein include polyalkylmethacrylate VIIs such as those available from Rohmax Additives GmbH (Darmstadt, Germany) under the trade designations: VISCOPLEX® 8-129, VISCOPLEX® 8-200, VISCOPLEX® 8-226, VISCOPLEX® 8-251, VISCOPLEX® 8-310, VISCOPLEX® 8-300, VISCOPLEX® 8-350, VISCOPLEX® 8-400, and VISCOPLEX® 8-440; from Rohm & Haas Company (Philadelphia, Pa.) under the trade designations ACRYLOID® 1277, ACRYLOID® 1265 and ACRYLOID® 1269; and from Afton Chemical Corporation (Richmond, VA) under the trade designations: HiTEC® 5708 and HiTEC® 5785H. Mixtures of the foregoing products can also be used as well as dispersant and dispersant/antioxidant VIIs. In an embodiment, the VII is a viscosity index improver such as HiTEC® 5708 or HiTEC® 5785H. Shear stable OCP VII's can also be used.

[0025] In an aspect, the additive composition is ashless. In another aspect, the additive composition is zinc free. Examples of commercially available thermally stable, zinc-free, phosphorus-containing antiwear agents include, but are not limited to, HiTEC® 511, available from Afton Chemical Corporation of Richmond, VA; Irgablube® 63, available from Ciba Specialty Chemicals Corporation of Tarrytown, NY; and Durad® 125, available from Chemtura Corporation of Middlebury, CT.

[0026] Typically, the lubricating compositions can contain a major amount of a base oil and a minor amount of the disclosed additive composition. A "major amount" is understood to mean greater than or equal to 50% by weight relative to the total weight of the lubricating composition. For example, the base oil can be present in the lubricating composition in an amount ranging from about 60 to about 99 percent by weight, and as a further example from 80 to 98 percent by weight. A "minor amount" is understood to mean less than 50% by weight, for example 0.005 to about 49 %, and as a further example from about 1 to about 30% by weight relative to the total amount of the lubricant composition.

[0027] In an aspect, the lubricating composition can comprise a phosphorous content ranging from about 100 to about 1000 parts per million, for example from about 300 to about 700 parts per million, and as a further example from about 400 to about 500 parts per million.

[0028] The lubricant compositions of this disclosure can be based on natural or synthetic oils, or blends thereof, provided the lubricant has a suitable viscosity for use in lubricant composition, such as hydraulic applications. The base oil can have a viscosity in the range of ISO 10 to ISO 460, and for example from ISO 22 to ISO 150. Suitable oils also

can have a grade of ISO 32, 46, and 68.

[0029] Mineral oils include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as other 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. Oils derived from coal or shale are also suitable.

Further, oils derived from a gas-to-liquid process are also suitable.

[0030] Non-limiting examples of synthetic oils include hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene isobutylene copolymers, etc.); polyalphaolefins such as poly(1-hexenes), poly(1-octenes), poly(1-decenes), etc. and mixtures thereof; alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, di-nonylbenzenes, di-(2-ethylhexyl)benzenes, etc.); polyphenyls (e.g., biphenyls, terphenyl, alkylated polyphenyls, etc.); alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof and the like.

[0031] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic oils that can be used. Such oils are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having an average molecular weight of about 1000, diphenyl ether of polyethylene glycol having a molecular weight of about 500-1000, diethyl ether of polypropylene glycol having a molecular weight of about 1000-1500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C₃₋₈ fatty acid esters, or the C₁₃ Oxo acid diester of tetraethylene glycol.

[0032] Another class of synthetic oils that can be used includes the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, etc.) Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl)sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid and the like.

[0033] Esters useful as synthetic oils also include those made from C₅₋₁₂ monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, tripentaerythritol, etc.

[0034] Hence, the base oil used which can be used to make the compositions as described herein can be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. Such base oil groups are as follows:

[0035] Group I contain less than 90% saturates and/or greater than 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120; Group II contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120; Group III contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 120; Group IV are polyalphaolefins (PAO); and Group V include all other basestocks not included in Group I, II, III or IV.

[0036] The test methods used in defining the above groups are ASTM D2007 for saturates; ASTM D2270 for viscosity index; and one of ASTM D2622, 4294, 4927 and 3120 for sulfur.

[0037] Group IV basestocks, i.e. polyalphaolefins (PAO) include hydrogenated oligomers of an alpha-olefin, the most important methods of oligomerisation being free radical processes, Ziegler catalysis, and cationic, Friedel-Crafts catalysis.

[0038] The polyalphaolefins typically have viscosities in the range of 2 to 100 cSt at 100°C., for example 4 to 8 cSt at 100°C. They can, for example, be oligomers of branched or straight chain alpha-olefins having from about 2 to about 30 carbon atoms, non-limiting examples include polypropenes, polyisobutenes, poly-1-butenes, poly-1-hexenes, poly-1-octenes and poly-1-decene. Included are homopolymers, interpolymers and mixtures.

[0039] Basestocks suitable for use herein can be made using a variety of different processes including but not limited to distillation, solvent refining, hydrogen processing, oligomerisation, esterification, and re-refining.

[0040] The base oil can be an oil derived from Fischer-Tropsch synthesized hydrocarbons. Fischer-Tropsch synthesized hydrocarbons can be made from synthesis gas containing H₂ and CO using a Fischer-Tropsch catalyst. Such hydrocarbons typically require further processing in order to be useful as the base oil. For example, the hydrocarbons can be hydroisomerized using processes disclosed in U.S. Pat. No. 6,103,099 or 6,180,575; hydrocracked and hydroisomerized using processes disclosed in U.S. Pat. No. 4,943,672 or 6,096,940; dewaxed using processes disclosed in U.S. Pat. No. 5,882,505; or hydroisomerized and dewaxed using processes disclosed in U.S. Pat. No. 6,013,171; 6,080,301; or 6,165,949.

[0041] Unrefined, refined and re-refined oils, either mineral or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can be used in the base oils. Unrefined oils are those obtained directly from a mineral or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from primary distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except

they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques are known to those skilled in the art such as solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, etc. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives, contaminants, and oil breakdown products.

[0042] Gas to liquid (GTL) hydrocarbons, such as gasoline fraction, kerosene fraction, and light oil fraction, can also be used as base oils.

[0043] The lubricant compositions of this disclosure can further comprise thermally unstable phosphorus-containing antiwear additives as secondary antiwear agents, so long as such additives are present in an amount that does not contribute to sludge formation, such as from about 1 to about 500 parts per million, for example from about 150 to about 300 parts per million. In an aspect, the thermally unstable antiwear additives can be thermally unstable metal-free antiwear agents. In an embodiment, the thermally unstable metal-free antiwear agent is a thermally unstable dithiophosphate prepared by reacting a dithiophosphoric acid with an alkenoic acid or an amine salt of sulfurized phosphate; and mixtures thereof.

[0044] The disclosed lubricant compositions can comprise optional additional additives known to those of ordinary skill in the art. Non-limiting examples of optional additional additives include antioxidants, dispersants, detergents, rust inhibitors, corrosion inhibitors, demulsifiers, and supplemental viscosity index improvers. The optional additional additives can be present in the disclosed compositions in any effective amount, which can readily be determined by one of ordinary skill in the art.

[0045] In an aspect, the lubricating compositions disclosed herein can be multigrade lubricating compositions. In another aspect, the lubricating compositions can be monograde lubricating compositions. In an embodiment, the lubricant compositions can be functional fluids for power transmission applications, such as a hydraulic fluid for use in hydraulic machines.

[0046] By "hydraulic machine" herein is meant any pump, machine, device having a hydraulic system and in which a lubrication system can be employed to improve the functional life of the machine. The lubricant compositions disclosed herein can be used in vane-, piston-, and gear-type pumps of mobile and stationary hydraulic equipment, including in environmentally sensitive areas. Typical machines can include cars, paper machine circulating systems, dryer bearings, calendar stacks, and turbines.

[0047] A method of improving the thermal stability of a lubricating composition, said method comprising formulating the lubricating composition comprising a major amount of a base oil and a minor amount of the disclosed additive composition is disclosed.

[0048] A method of lubricating a hydraulic machine having a lubrication system, said method comprising adding to the lubrication system the disclosed lubricating composition is also disclosed.

[0049] Further, there is disclosed a method of controlling sludge formation in a lubricating composition (e.g., a multi-grade or monograde lubricating composition) comprising providing a major amount of a base oil and a minor amount of the disclosed lubricant additive composition.

EXAMPLES

[0050] Example I

[0051] A lubricating composition, such as a hydraulic fluid, was formulated with the treat rates as shown in Table 1 and subjected to the FZG test. HiTEC® 511, Irglaube 63 and Irgalube 353 are liquid ashless dithiophosphates from Afton Chemical Corporation and from Ciba Specialty Chemicals Corporation.

[0052] HiTEC® 833 is an amine salt of sulfurized phosphate and is available from Afton Chemical Corporation.

[0053] In the FZG test, two steel spur gears are rotated together with oil dip lubrication for a series of 15 minute stages. The relative torque between the gears is increased by a fixed amount after each stage and the gears are run together for a given period after which they are examined for wear or damage. The result of the test is quoted in terms of the final pass stage and the first fail stage. To be satisfactory, the pass stage must be higher than 10.

[0054] The results are shown in Table 1 below.

Table 1

Example	Treat Rate	FZG RATING
1	HiTEC® 511 (0.5%)	Pass 11
2	HiTEC® 511 (0.5%) and HiTEC® 833 (0.05%)	Pass 12
3	HiTEC® 833 at 0.05%	Pass 7

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(continued)

Example	Treat Rate	FZG RATING
4	HiTEC® 511 (0.5%) and Irgalube® 353 (0.05%)	Pass 12

[0055] In this table, the FZG result was given as a load stage result (in the stepwise phase). Examples 1 and 2 gave "pass 11" and "pass 12" results, respectively, which are satisfactory results. Example 3, on the other hand, gave an FZG result of "pass 7," which is not satisfactory. To improve the FZG performance of thermally unstable antiwear agents like HiTEC® 833 and Irgalube® 353 and to give FZG performance greater than 10 Fail and passing ump performance in multigrade formulations, an increase in treat rate of these antiwear additives would be required. However, this increase in treat rate for HiTEC® 833 and Irgalube® 353 would result in poor performance in the thermal stability tests, whereas thermally stable antiwear additives like HiTEC® 511 can be used at high treat rates to give good pump and FZG results with good thermal stability in multigrade formulations. This variation in thermal stability at higher treat is shown in the tables below.

[0056] Example II

[0057] An additive composition, such as a hydraulic fluid additive, was formulated with the treat rates as described in Table 2a below. Irgalube® 353 is the reaction product of dithiophosphoric acid and acrylic or methacrylic acid and is available from Ciba Specialty Chemicals Corporation of Tarrytown, NY. Durad® 125 is a tricresylphosphate, available from Chemtura Corporation of Middlebury, CT. The antiwear additives were added at treat level to give 500ppm of phosphorous in the finished oil approximately. All antiwear additives were tested in the same formulation containing corrosion inhibitors, rust inhibitors, detergents, dispersant and demulsifiers.

[0058] The thermal stability performance of the composition was demonstrated by results of the Cincinnati Milacron Thermal Stability Test Procedure "A" (CCMA) (see Cincinnati Milacron Lubricants Purchase Specification Approved Products Handbook, pages 3-1 to 3-3). In this test, a beaker of the lubricating composition containing copper and steel rods is heated to 135°C for 168 hours. At the end of the test, the rods are rated visually for discoloration. Appearance ratings range on a scale from 1 to 10, where the lower the numerical rating, the better the result. Additionally, the change in viscosity of the oil, the amount of sludge formed in the oil, and the weight loss of the copper and steel rods are determined. Results are provided in Table 2b below.

Table 2a

Example	Treat Rate
4	HiTEC® 511 (0.5%)
5	HiTEC® 511 (0.1 %)
6	HiTEC® 833 (0.1 %)
7	HiTEC® 833 (0.649%)
8	Irgalube® 353 (0.44%)
9	Durad® 125 (0.47%)
10	Irgalube® 63 (0.52%)

Table 2b

Property	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex.10
Sludge, mg/100mL	5.07	0.93	1.96	221.29	76.26	0.44	1.18
Copper Rod Rating	2	2	2	6	6	2	5
Copper Weight Loss, mg/100mL	0.23	-0.13	0.17	-6.18	0.8	0	0.88
Steel Rod Rating	1	1	1	3	2	1	1
Steel Weight Loss, mg/100mL	0.19	-0.27	0.11	0.49	0.54	-0.20	-0.03

[0059] In the CCMA test, Examples 7 and 8 demonstrated sludge contents of 221.29 mg and 76.26 mg, respectively, thereby demonstrating poor thermal stability. Examples 4, 5, 9, and 10, on the other hand, demonstrated sludge contents

of 5.07 mg, 0.93 mg, 0.44 mg, and 1.18 mg, respectively, thereby demonstrating good thermal stability. Additionally, Examples 7 and 8 demonstrated copper rod ratings of 6, whereas examples 4, 5, 9, and 10 demonstrated lower copper rod ratings of 2 and 5. Thus, it can be seen that the zinc-free, phosphorous-containing antiwear agents disclosed herein are thermally stable at high treat rates, as compared to thermally unstable antiwear systems at high treat rates.

[0060] The corrosion and sludge formation properties of the composition were also determined using the Nippon Oil Color Test (NOC) Test. The method is as follows: A 50mL beaker is filled with 45g of the composition. Iron and copper coil catalysts (use for ASTM D 943) are added to the beaker. The beaker is stored at 135°C for 210 hours. Thereafter, the beaker is removed and analyzed for color (ASTM D 1500) and sludge content. Low color results score less than 5.0 and acceptable sludge results are less than 10 milligrams of sludge after 210 hours of oil aging. Results are shown in Table 3 below.

Table 3

Property	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex.10
Color	3	3.5	3.5	8	7	4	2.5
Sludge content, mg	1.1	1.03	1.18	155.31	0.48	1.07	2.19

[0061] In the NOC test, Examples 4, 5, 9 and 10 demonstrated acceptable color and sludge results at high treat rates. However, although Example 6 demonstrated acceptable color and sludge at a low treat rate, the same antiwear agent demonstrated poor color and sludge results at a high treat rate. For instance, Example 7 demonstrated an unacceptable color rating of 8 and 155.31 mg of sludge, clearly exceeding the maximum sludge content. Example 8 also demonstrated a high color rating of 7 (and thus poor color results) at a high treat rate. Thus, it can be seen that the thermally stable, zinc-free, phosphorous-containing antiwear agents disclosed herein have improved corrosion properties and reduced sludge formation properties at high treat rates, as compared to thermally unstable antiwear systems at high treat rates.

[0062] The filterability of the lubricant composition was also evaluated using the ISO 13357 Filtration Test (Filtration Test). The test method is as follows: For the dry phase of the test, the sample is mixed for one minute at 30 times to the snap. For the wet phase of the test, the sample is mixed and allowed to stand for 24 hours. 350 mL of the sample is then mixed with 0.7 mL Analar water (0.2% v/v) and placed in an oven for 2 hours at 70°C. The sample is removed from the oven and stirred at 1500 rpm for 5 minutes. The sample is returned to the oven for 70 hours, removed from the oven, and placed in a dark cupboard for 24 hours. The sample is removed from the cupboard and mixed for one minute at 30 times to the snap.

[0063] Prior to filtering, a 0.8 μ m filter is preheated for 10 minutes at 70°C and wetted with the sample composition. The sample composition is filtered through the filter under positive pressures of 1 bar (ISO viscosity grades 32 and 46) and 2bar (ISO viscosity grades 68 and 100). This method is conducted in triplicate, and the results of the runs are averaged.

[0064] Filterability is expressed as a dimensionless number which is a ratio (expressed as a percentage) between volumes (Stage 1) or flow rates (Stage 2) at specified intervals during the test. During Stage 1, filterability is calculated as a ratio (expressed as a percentage) between 240 mL and the volume of oil actually filtered at the time that 240 mL would have theoretically taken to filter with no plugging of the filter media. Good filterability indicates that the composition is unlikely to give performance problems in use, unless fine systems filters are being used.

[0065] During Stage 2, filterability is calculated as a ratio (expressed as a percentage) between the flow rate near the start of filtration (between 10 mL and 50 mL) and the flow rate near the end of filtration (between 200 mL and 300 mL). Stage 2 is considered the more severe part of the test, as it is sensitive to the presence of gels and fine silts in the lubricating composition. Good filterability indicates that the composition is unlikely to give filtration problems even in the most extreme conditions.

[0066] The minimum values to meet the ISO 13357 Filtration Test are described in Table 4 below. The results of the ISO 13357 Filtration Test are shown in Table 4a below.

Table 4

	Stage 1	Stage 2
DRY	80%	60%
WET	70%	50%

Table 4a

Property	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex.10
DRY (Stage 1)	85	85.8	91.7	88.6	65.6	91.9	85.8
DRY (Stage 2)	73.7	74.5	78.8	74.8	29	77.8	74.5
WET (Stage 1)	81.1	87.4	82.5	53.1	58.8	82.9	54.7
WET (Stage 2)	59.4	70.4	65.9	***	32.3	68.7	8.1
***Test was aborted and no result was obtained.							

[0067] As can be seen above, Examples 4, and 5 demonstrated acceptable Stage 1 and Stage 2 values during both the dry and wet phases of the Filtration Test. Examples 9 and 10 also demonstrated acceptable Stage 1 and Stage 2 results during the dry phases, and Example 9 demonstrated acceptable Stage 1 during the wet phases. These Examples thus demonstrate that lubricating compositions comprising the thermally stable, zinc-free, phosphorous-containing antiwear agents disclosed herein at both low and high treat rates are not likely to give performance problems.

[0068] However, thermally unstable antiwear systems do not give acceptable values at high treat rates, as can be seen in Examples 7 and 8. For example, Example 7 failed the wet phase, Stage 1 and Stage 2 minimum requirements. Moreover, Example 8 failed both stages of the wet and dry phases, except dry phase, Stage 1. Therefore, it can be seen that lubricating compositions comprising the thermally stable, zinc-free, phosphorous-containing antiwear agents disclosed herein at low and high treat rates are unlikely to give filtration problems, even in the most extreme conditions, as compared to thermally unstable antiwear systems.

[0069] For the purposes of this specification and appended claims, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims, are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0070] It is noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the," include plural referents unless expressly and unequivocally limited to one referent. Thus, for example, reference to "an antioxidant" includes two or more different antioxidants. As used herein, the term "include" and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be substituted or added to the listed items.

[0071] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or can be presently unforeseen can arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and as they can be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

Claims

1. A lubricant additive composition comprising

at least one thermally stable dithiophosphate prepared by reacting a dithiophosphoric acid with an alkene; and at least one polyalkylmethacrylate viscosity index improver, wherein the additive composition provides a phosphorus content ranging from about 300 to about 700 parts per million when used in a lubricating composition.

2. The additive of claim 1, wherein the alkene is a dicyclopentadiene or ethyl acrylate.

3. A method of controlling sludge formation in a multigrade lubricating composition, said method comprising providing a major amount of a base oil, and a minor amount of an additive composition comprising at least one thermally stable dithiophosphate prepared by reacting a dithiophosphoric acid with an alkene; and at least one polyalkylmethacrylate viscosity index improver, wherein the lubricating composition has a phosphorus content ranging from about 300 to about 700 parts per million.

4. The method of claim 3, wherein the lubricating composition further comprises thermally unstable metal-free antiwear agents, with the proviso that the thermally unstable metal-free antiwear agents are present in an amount that does not contribute to sludge formation.

5. The method of claim 4, wherein the metal-free antiwear agent is selected from the group consisting of thermally unstable dithiophosphates prepared by reacting a dithiophosphoric acid with an alkenoic acid, amine salts of sulfurized phosphate, and mixtures thereof.

6. A method of controlling sludge formation in a monograde lubricating composition, said method comprising providing a base oil, and adding thereto at least one thermally stable dithiophosphate prepared by reacting a dithiophosphoric acid with an alkene, wherein the composition has a phosphorus content ranging from about 300 to about 700 parts per million.

7. The method of claim 6, wherein the composition further comprises thermally unstable metal-free antiwear agents, with the proviso that the thermally unstable antiwear agents are present in an amount that does not contribute to sludge formation.

8. The method of claim 7, wherein the thermally unstable metal-free antiwear agent is selected from the group consisting of thermally unstable dithiophosphates prepared by reacting a dithiophosphoric acid with an alkenoic acid, amine salts of sulfurized phosphate, and mixtures thereof.

9. A lubricant additive composition comprising

at least one thermally stable triarylphosphate or dialkylphosphate; and

at least one polyalkylmethacrylate viscosity index improver,

wherein the additive composition provides a phosphorus content ranging from about 300 to about 700 parts per million when used in a lubricating composition.

10. The additive composition of claim 9, wherein the triarylphosphate is tricresylphosphate.

11. A lubricating composition comprising:

a major amount of a base oil; and

a minor amount of the additive composition of any one of claims 1, 2, 9 or 10.

12. The lubricating composition of claim 11, wherein the base oil is chosen from a Group I, Group II, and a Group III base oil.

13. The lubricating composition of claim 11 or 12, wherein the composition is a hydraulic fluid.

14. A method of improving the thermal stability of a lubricating composition, said method comprising formulating the lubricating oil comprising a major amount of a base oil and a minor amount of the additive composition of any one of claims 1, 2, 9 or 10.

15. A method of lubricating a hydraulic machine having a lubrication system, said method comprising adding to the lubrication system the lubricating composition of any one of claims 11 to 13.



EUROPEAN SEARCH REPORT

Application Number
EP 09 15 9430

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 0 531 585 A (ETHYL PETROLEUM ADDITIVES LTD [GB]) 17 March 1993 (1993-03-17) * page 28, line 55 - page 29, line 29; examples 1,3-7 *	1-8, 11-15	INV. C10M137/04 C10M137/10 C10M161/00
X	WO 00/11122 A (SHELL INT RESEARCH [NL]; BABA YOSHIHARU [JP]; HANYUDA KIYOSHI [JP]) 2 March 2000 (2000-03-02) * page 1, line 1 - line 11; claims 2,8,9; examples 4,5; tables 1,2,4 * * page 12, line 7 - page 13, line 18 * * page 23, line 3 - line 12 *	1-8, 11-15	ADD. C10N40/08 C10N30/06 C10N30/08 C10N30/04
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X	US 5 561 104 A (MIYAGAWA TORU [JP]; HIRATA SHIGEAKI [JP]; OKADA MITSUO [JP]) 1 October 1996 (1996-10-01) * claims 1,12; example 4; table 1 *	9,11-15	TECHNICAL FIELDS SEARCHED (IPC) C10M
X	US 2008/058235 A1 (TAKIGAWA KATSUYA [JP] ET AL) 6 March 2008 (2008-03-06) * paragraph [0379] - paragraph [0413]; example 1; table 1 * * paragraph [0449] - paragraph [0511]; example 1; table 1 * * paragraph [0656] - paragraph [0690]; example 6; table 3 *	9-15	
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 20 November 2009	Examiner Pöllmann, Klaus
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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EPO FORM 1503 03.82 (P04C01)



Application Number

EP 09 15 9430

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).



**LACK OF UNITY OF INVENTION
SHEET B**

Application Number

EP 09 15 9430

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 1-8 and 11-15 (as far as referring to 1,2)

A lubricant additive composition comprising at least a reaction product of dithiophosphoric acid with an alkene that provides sufficient phosphorous to add 300 to 700 ppm phosphorous to a lubricating composition and optionally a polyalkylmethacrylate. They also disclose a method for controlling sludge formation with this lubricant additive composition.

2. claims: 9, 10 and 11-15 (as far as referring to claims 9,10)

A lubricant additive composition comprising at least triarylphosphate or dilaurylphosphate and at least a polyalkylmethacrylate that provides sufficient phosphorous to add 300 to 700 ppm phosphorous to a lubricating composition as well as a method for improving thermal stability of a lubricating composition.

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 09 15 9430

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

20-11-2009

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