



(11) **EP 1 770 155 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
04.04.2007 Bulletin 2007/14

(51) Int Cl.:
C10M 169/04 (2006.01) C10M 141/08 (2006.01)
C10N 30/00 (2006.01) C10N 40/04 (2006.01)

(21) Application number: **06121232.0**

(22) Date of filing: **25.09.2006**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI
SK TR
Designated Extension States:
AL BA HR MK YU

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(30) Priority: **03.10.2005 US 242269**

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(54) **Lubricant formulations containing extreme pressure agents with improved solubility**

(57) A method for improving the solubility of a sulfurized extreme pressure agent in a lubricant composition and improved lubricant compositions and uses therefor. The method includes pre-blending organic acid and amine components of a lubricant additive package for the lubricant composition to provide a premixture of organic acid and amine components. The premixture is combined with a sulfurized extreme pressure agent having a viscosity of less than about 5.5 centistokes at 100°

C to provide a lubricant additive package. By use of the foregoing process, a turbidity characteristic of the lubricant composition containing the additive package is lower than a turbidity characteristic of a lubricant composition that is made by combining the organic acid and amine components with the sulfurized extreme pressure agent in the absence of the premixture.

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Description**FIELD OF THE DISCLOSURE:**

5 [0001] The disclosure relates to lubricant formulations and in particular to lubricant formulations having enhanced stability and to methods for making lubricants having improved properties.

BACKGROUND AND SUMMARY:

10 [0002] Lubricants may be formulated to contain extreme pressure agents for use in particular applications. A wide variety of extreme pressure agents exist. Particularly useful extreme pressure agents are those containing sulfur. However, sulfurized extreme pressure agents are often difficult to handle, highly odiferous, expensive, or require the presence of compatibilizing components when used in lubricant formulations.

15 [0003] Accordingly, there continues to be a need for improved lubricant formulations containing extreme pressure components.

[0004] With regard to the foregoing, a method for improving the solubility of a sulfurized extreme pressure agent in a lubricant composition and improved lubricant compositions and uses therefor are provided. The method includes pre-blending organic acid and amine components of a lubricant additive package for the lubricant composition to provide a premixture of organic acid and amine components. The premixture is combined with a sulfurized extreme pressure agent having a viscosity of less than about 5.5 centistokes at 100° C to provide a lubricant additive package. By use of the foregoing process, a turbidity characteristic of the lubricant composition containing the additive package is lower than a turbidity characteristic of a lubricant composition that is made by combining the organic acid and amine components with the sulfurized extreme pressure agent in the absence of the premixture.

25 [0005] In another exemplary embodiment, there is provided a method for producing a non-hazy lubricant composition containing a sulfurized extreme pressure agent and a substantially non-polar base oil component. The sulfurized extreme pressure agent is provided by a sulfur monochloride/isobutylene adduct that is reacted with aqueous sodium hydrosulfide under conditions sufficient to provide a sulfurized isobutylene having a viscosity at 100° C no higher than about 5.5 centistokes. Organic acid and amine components of the lubricant composition are pre-blended together to provide an additive package pre-mix. The additive package pre-mix is subsequently combined with from about 50 to about 9.5 percent by weight of the sulfurized isobutylene to provide the additive composition. A base oil is treated with the additive composition to provide the non-hazy lubricant composition.

35 [0006] Another exemplary embodiment of the disclosure provides a method for making a sulfurized extreme pressure agent having characteristics that assist in the formation of a low turbidity substantially non-polar base oil containing lubricant. The method includes reacting sulfur monochloride and an olefin under conditions sufficient to provide a sulfur/olefin adduct. The sulfur/olefin adduct is mixed and reacted with an aqueous sulfur source over a period of time sufficient to provide a sulfurized extreme pressure agent in an organic phase having a viscosity of no higher than about 5.5 centistokes at 100° C. After the reaction is complete, an aqueous phase and the organic phase containing the sulfurized extreme pressure agent are separated from one another.

40 [0007] An advantage of exemplary embodiments described herein is that difficult to solubilize additive components are made more soluble in finished lubricant compositions without the need for solubilizing agents or more expensive extreme pressure agents. Accordingly, solubilizing agents may be eliminated and/or less expensive components may be substituted for more expensive components. In particular, it has been found, quite surprisingly, that combining sulfurized extreme pressure agents having a relatively low viscosity with other components of an additive concentrate for a gear lubricant after combining organic acid and amine components substantially increases the solubility of the components in a finished lubricant composition.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS:

50 [0008] 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:

- 55 (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 do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);

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(3) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, typically no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbonyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbonyl group.

[0009] As used herein, the term "percent by weight", unless expressly stated otherwise, means the percentage the recited component represents to the weight of the entire composition.

[0010] Finished gear oils made according to exemplary embodiments described herein may have different primary viscosity grades which are indicated by the maximum temperature for viscosity of 150,000 cP according to ASTM D 2983 as defined in SAE J306 Automotive Gear and Lubricant Viscosity Classification. Accordingly, gear oil formulations described herein typically contain a major amount of base oil, e.g., from about 75 to about 98 percent by weight base oil, and a minor amount of functional additive or additive concentrate, e.g., from about 2 to about 25 percent by weight additive concentrate.

Base Oils

[0011] The gear oils of the compositions described herein may be based on natural or synthetic oils, or blends thereof, provided the lubricant has a suitable viscosity for use in gear oil applications. Thus, the base oils will normally have a viscosity in the range of SAE 50 to SAE 250, and more usually will range from SAE 70W to SAE 140. Suitable automotive gear oils also include multi-grade oils such as 75W-140, 80W-90, 85W-140, 85W-90, and the like.

[0012] Basestocks suitable for providing the base oils may be made using a variety of different processes including but not limited to distillation, solvent refining, hydrogen processing, oligomerization, esterification, and re-refining. API 1509 "Engine Oil Licensing and Certification System" Fourteenth Edition, December 1996 states that all basestocks are divided into five general categories:

Group I contain less than 90 wt.% saturates and/or greater than 0.03 wt.% 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 wt.% saturates and less than or equal to 0.03 wt.% 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 wt.% saturates and less than or equal to 0.03 wt.% 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.

[0013] 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.

[0014] Group IV basestocks, i.e. polyalphaolefins (PAO) include hydrogenated oligomers of an alpha-olefin, the most important methods of oligomerization being free radical processes, Ziegler catalysis, and cationic, Friedel-Crafts catalysis.

[0015] The polyalphaolefins typically have viscosities in the range of 2 to 100 cSt at 100° C, desirably 4 to 8 cSt at 100° C. They may, for example, be oligomers of branched or straight chain alpha-olefins having from 2 to 16 carbon atoms, specific examples being polypropenes, polyisobutenes, poly-1-butenes, poly-1-hexenes, poly-1-octenes and poly-1-decene. Included are homopolymers, interpolymers and mixtures.

[0016] Base oils may include a single basestock or mixtures of basestocks. In exemplary embodiments described herein, the base oil contains at least one basestock having a substantially non-polar characteristic. For example, a base oil may be a mixture of a minor amount of a Group I basestock and a major amount of a Group II, Group III, or Group IV basestock.

[0017] Some additive components are supplied in the form of solutions of active ingredient(s) in an inert diluent or solvent, such as a diluent oil or mineral oil. Unless expressly stated to the contrary, the amounts and concentrations of each additive component are expressed in terms of active additive, i.e., the amount of solvent or diluent that may be associated with such component as received is excluded.

[0018] As set forth above, a gear lubricant typically contains one or more additives. The additives may be selected from the group consisting of dispersants, corrosion inhibitors, extreme pressure additives, anti-wear additives, rust inhibitors, antioxidants, deodorizers, defoamers, demulsifiers, dyes, friction modifiers, seal swell agents, and fluorescent coloring agents. The additive package may be, although it does not have to be, a fully-formulated gear additive package, such as a package meeting the requirements for API GL-5 and/or API MT-1 and/or MIL-PRF-2105E and/or AGMA 9005-D94. The type and amount of the components present in the additive package will depend on the intended final use of the product.

Dispersant

[0019] The dispersants which may be used include at least one oil-soluble ashless dispersant having a basic nitrogen and/or at least one hydroxyl group in the molecule. Suitable dispersants include alkenyl succinimides, alkenyl succinic acid esters, alkenyl succinic ester-amides, Mannich bases, hydrocarbyl polyamines, or polymeric polyamines.

[0020] The alkenyl succinimides in which the succinic group contains a hydrocarbyl substituent containing at least 30 carbon atoms are described for example in U.S. Pat. Nos. 3,172,892; 3,202,678; 3,216,936; 3,219,666; 3,254,025; 3,272,746; and 4,234,435. The alkenyl succinimides may be formed by conventional methods such as by heating an alkenyl succinic anhydride, acid, acid-ester, acid halide, or lower alkyl ester with a polyamine containing at least one primary amino group. The alkenyl succinic anhydride may be made readily by heating a mixture of olefin and maleic anhydride to, for example, about 180-220° C. The olefin may be a polymer or copolymer of a lower mono-olefin such as ethylene, propylene, 1-butene, isobutene and the like and mixtures thereof. An alkenyl group source may be from polyisobutene having a gel permeation chromatography (GPC) number average molecular weight of up to 10,000 or higher, generally in the range of about 500 to about 2,500, and typically in the range of about 800 to about 1,500.

[0021] As used herein the term "succinimide" is meant to encompass the completed reaction product from reaction between one or more polyamine reactants and a hydrocarbon-substituted succinic acid or anhydride (or like succinic acylating agent), and is intended to encompass compounds wherein the product may have amide, amidine, and/or salt linkages in addition to the imide linkage of the type that results from the reaction of a primary amino group and an anhydride moiety.

[0022] The various types of ashless dispersants described above can be phosphorylated by procedures described in U.S. Pat. Nos. 3,184,411; 3,342,735; 3,403,102; 3,502,607; 3,511,780; 3,513,093; 4,615,826; 4,648,980; 4,857,214 and 5,198,133.

[0023] The dispersants may also be selected from boronated dispersants. Methods for boronating (borating) the various types of ashless dispersants described above are described in U.S. Pat. Nos. 3,087,936; 3,254,025; 3,281,428; 3,282,955; 2,284,409; 2,284,410; 3,338,832; 3,344,069; 3,533,945; 3,658,836; 3,703,536; 3,718,663; 4,455,243; and 4,652,387.

[0024] Procedures for phosphorylating and boronating ashless dispersants such as those referred to above are set forth in U.S. Pat. Nos. 4,857,214 and 5,198,133.

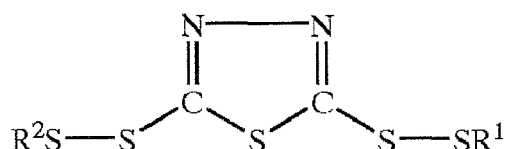
[0025] The amount of ashless dispersant, when present, on an "active ingredient basis" (i.e., excluding the weight of impurities, diluents and solvents typically associated therewith) is generally within the range of about 0.5 to about 7.5 weight percent, typically within the range of about 0.5 to 5.0 wt.%, desirably within the range of about 0.5 to about 3.0 wt.%, and more desirably within the range of about 2.0 to about 3.0 wt.%, based on the finished oil.

Corrosion Inhibitors

[0026] Copper corrosion inhibitors which may be used include thiazoles, triazoles and thiadiazoles. Examples include benzotriazole, tolyltriazole, octyltriazole, decyltriazole, dodecyltriazole, 2-mercaptobenzothiazole, 2,5-dimercapto-1,3,4-thiadiazole, 2-mercapto-5-hydrocarbylthio-1,3,4-thiadiazoles, 2-mercapto-5-hydrocarbyldithio-1,3,4-thiadiazoles, 2,5-bis(hydrocarbylthio)-1,3,4-thiadiazoles, and 2,5-bis-(hydrocarbyldithio)-1,3,4-thiadiazoles. Suitable compounds are the 1,3,4-thiadiazoles, especially the 2-hydrocarbyldithio-5-mercapto-1,3,4-dithiadiazoles and the 2,5-bis(hydrocarbyldithio)-1,3,4-thiadiazoles, and mixtures thereof, a number of which are available as articles of commerce.

[0027] Other suitable inhibitors of copper corrosion include ether amines; polyethoxylated compounds such as ethoxylated amines, ethoxylated phenols, and ethoxylated alcohols; imidazolines; and the like. See, for example, U.S. Pat. Nos. 3,663,561 and 4,097,387. Concentrations of up to about 3 wt.% in the concentrate are typical. Suitable copper corrosion inhibitors include ashless dialkyl thiadiazoles. Such ashless dialkyl thiadiazoles are available from Afton Chemical Corporation of Richmond, Virginia.

[0028] Dialkyl thiadiazoles which may be used are of the general formula:



wherein R¹ is a hydrocarbyl substituent having from 6 to 18 carbon atoms; R² is a hydrocarbyl substituent having from 6 to 18 carbon atoms; and may be the same as or different from R¹. Generally, R¹ and R² are about 9-12 carbon atoms,

and typically R¹ and R² are each 9 carbon atoms.

[0029] Mixtures of dialkyl thiadiazoles of formula (I) with monoalkyl thiadiazoles may also be used within the scope of the exemplary embodiments. Such mono alkyl thiadiazoles occur when either substituent R¹ or R² is H.

5 Extreme Pressure Agents

[0030] The gear oils formulations of the disclosure may contain at least one sulfur-containing extreme pressure (EP) agent. The sulfur-containing extreme pressure agent may contain at least 25 percent by weight sulfur. The amount of said EP agent added to the gear oil is typically sufficient to provide at least 10,000 ppm sulfur, desirably from about 10,000 to about 30,000 ppm sulfur, and more desirably from about 12,000 to about 25,000 ppm sulfur in the finished gear oil formulation.

[0031] A wide variety of sulfur-containing extreme pressure or antiwear agents are available for use in the exemplary embodiments described herein. Among suitable compositions for this use are included sulfurized animal or vegetable fats or oils, sulfurized animal or vegetable fatty acid esters, fully or partially esterified esters of trivalent or pentavalent acids of phosphorus, sulfurized olefins (see for example U.S. Pat. Nos. 2,995,569; 3,673,090; 3,703,504; 3,703,505; 3,796,661; 3,873,454 4,119,549; 4,119,550; 4,147,640; 4,191,659; 4,240,958; 4,344,854; 4,472,306; and 4,711,736), dihydrocarbyl polysulfides (see for example U.S. Pat. Nos. 2,237,625; 2,237,627; 2,527,948; 2,695,316; 3,022,351; 3,308,166; 3,392,201; 4,564,709; and British 1,162,334), functionally-substituted dihydrocarbyl polysulfides (see for example U.S. Pat. No. 4,218,332), and polysulfide olefin products (see for example U.S. Pat. No. 4,795,576).

[0032] Another class of such agents is that of polysulfides composed of one or more compounds represented by the formula: R⁶-S_x-R⁷ where R⁶ and R⁷ are hydrocarbyl groups each of which may contain 3 to 18 carbon atoms and x is may be in the range of from 2 to 8, and typically in the range of from 2 to 5, especially 3. The hydrocarbyl groups can be of widely varying types such as alkyl, cycloalkyl, alkenyl, aryl, or aralkyl. Tertiary alkyl polysulfides such as di-tert-butyl trisulfide, and mixtures comprising di-tert-butyl trisulfide (e.g., a mixture composed principally or entirely of the tri, tetra-, and pentasulfides) may be used. Examples of other useful dihydrocarbyl polysulfides include the diamyl polysulfides, the dinonyl polysulfides, the didodecyl polysulfides, and the dibenzyl polysulfides.

[0033] One particularly suitable class of extreme pressure agent is made by reacting an olefin, such as isobutene, with sulfur. The product, e.g., sulfurized isobutene (SIB), notably sulfurized polyisobutylene, typically has a sulfur content of from about 10 to about 55 %, desirably from about 30 to about 50% by weight. A wide variety of other olefins or unsaturated hydrocarbons, e.g., isobutene dimer or trimer, may be used to form the sulfurized olefin extreme pressure agents. Various methods have been disclosed in the prior art for the preparation of sulfurized olefins. See, for example, U.S. Patent No. 3,471,404 to Myers; U.S. Patent No. 4,204,969 to Papay et al.; U.S. Patent No. 4,954,274 to Zaweski et al.; U.S. Patent No. 4,966,720 to DeGonia et al.; and U. S. Patent No. 3,703,504 to Horodysky, et al.

[0034] Methods for preparing sulfurized olefins, including the methods disclosed in the aforementioned patents, generally involve multiple stages. The first stage generally involves the formation of a material, typically referred to as an "adduct", in which an olefin is reacted with a sulfur halide, for example, sulfur monochloride. The adduct is then reacted with a sulfur source to provide the sulfurized olefin. The quality of a sulfurized olefin is generally measured by various physical properties, including, for example, viscosity, sulfur content, halogen content and copper corrosion test weight loss (CCT).

[0035] U.S. Patent No. 4,966,720, relates to sulfurized olefins useful as extreme pressure (EP) additives in lubrication oils and to a two stage reaction for their preparation. In the first stage, the reaction temperature between the olefin and sulfur monochloride is maintained from 0° to 22° C in order to make a low molecular weight adduct. In the second stage of the reaction a sulfur monochloride/aliphatic monoolefin adduct is reacted in a basic, aqueous alcoholic solution containing sodium sulfide at a temperature of from about 50° C up to reflux to form the sulfurized olefin. Conventional processes for sulfurized olefins provide products that are readily soluble in Group I base oils. However, without a compatibilizer, the sulfurized olefins are less soluble in Group II and Group III base oils.

[0036] Accordingly, a more readily soluble sulfurized olefin for Group II and Group III base oils may be formed by increasing the adduct addition rate to the aqueous sodium sulfide solution, minimizing the reaction time, and eliminating the addition of solid sulfur during the reaction. The resulting sulfurized olefin product has a viscosity of no higher than about 5.5 centistokes at 100° C, a sulfur content within the range of from about 40 to about 50 % by weight, and is readily soluble in Group II or Group III base oils. In particular, a viscosity-dependent rate of addition of the sulfur monochloride/aliphatic monoolefin adduct to the aqueous sodium sulfide is illustrated by the following table:

Table 1

Sample No.	Adduct Addition Rate (min.)	Viscosity at 100° C
1	25	4.7

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(continued)

Sample No.	Adduct Addition Rate (min.)	Viscosity at 100° C
2	45	5.21
3	60	6.23
4	75	6.56
5	90	6.91
6	120	7.33
7	135	9.27
8	240	16.25

[0037] According to the above table, adduct addition rates of less than about 60 minutes may provide sulfurized extreme pressure agents that have the desired viscosity. An exemplary process for making a sulfurized extreme pressure agent that is readily soluble in Group II and Group III base oils is proved by the following nonlimiting example.

Example 1

Adduct Preparation

[0038] Liquid sulfur monochloride (700 grams) is charged into a suitable reaction flask equipped with a stirrer, thermometer, a condenser maintained at 5 °C, and a subsurface gas sparger. Thereafter, gaseous isobutylene is bubbled into the reaction flask below the surface of the sulfur monochloride liquid while stirring to bring the temperature up to 20 °C and the reaction mixture is maintained at that temperature for the entire reaction. A total of 530 grams of isobutylene is added to the sulfur monochloride liquid. HCl evolved by the reaction of isobutylene and sulfur monochloride is removed from the off-gas by alkaline scrubbing the off-gas. The adduct thus formed is a clear amber oil that may be used to form sulfurized isobutylene in a second stage reaction step. The adduct has a specific gravity of about 1.183 ± 0.05 at 15.6 °C.

Preparation of Group II & III Soluble Sulfurized Isobutylene

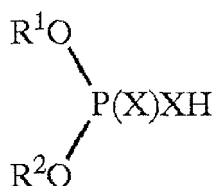
[0039] A reaction flask is charged with 175 grams water, ½ dropper of antifoam B, 325 grams of n-propanol, 13.5 grams of 50 wt.% aqueous sodium hydroxide, and 410 grams of 36 wt.% aqueous sodium hydrosulfide. The mixture is stirred at 700 rpm and heated under a nitrogen atmosphere to about 60° C at which time, 500 grams of the adduct described above is added subsurface to the mixture over a 30 minute period while gradually increasing the reaction temperature until the temperature of the reaction mass reaches to about 90 °C by the end of the adduct addition step. Upon completion of the adduct addition step, the alcohol is stripped from the reaction mixture by heating the reaction mass to 100 °C at atmospheric pressure. Following the alcohol stripping step, the pressure of the reaction flask is reduced to 23 inches of mercury while allowing the flask to cool to about 70 °C to complete the removal of the alcohol and most of the water from the reaction mass. Water (300 grams) is added to the resulting product, the product and water are stirred for 10 minutes, then allowed to settle for 15 minutes. The lower aqueous brine layer is separated by decanting this layer from the flask and the organic layer is then vacuum stripped at 28" mercury at 100 °C for 45 minutes. After filtering the stripped organic layer through a bed of diatomaceous earth, a clear yellow oil is obtained. Analysis of product made by the foregoing procedure typically has a viscosity in the range of 4.0 to 5.5 cSt. at 100°C, a sulfur content of about 44-47 weight percent, a chlorine content of less than 1 wt.%, and a copper corrosion test weight loss (CCT) of about 30-80 milligrams per 100 mL of sample.

Anti-Wear Agents

[0040] For purposes of this disclosure a component which contains both phosphorus and sulfur in its chemical structure is deemed a phosphorus-containing antiwear and/or extreme pressure agent rather than a sulfur-containing antiwear and/or extreme pressure agent. Suitable phosphorus-containing anti-wear agents which may be used include oil-soluble amine salts of a phosphoric acid ester, such as those taught in U.S. Pat. Nos. 5,354,484 and 5,763,372; and reaction products of dicyclopentadiene and a thiophosphoric acid.

[0041] The amine salts of a phosphoric acid ester may be prepared by reacting a phosphoric acid ester with ammonia or a basic nitrogen compound, such as an amine. The salts may be formed separately, and then the salt of the phosphoric acid ester may be added to the lubricating composition.

[0042] The phosphoric acid esters useful in preparing the amine salts may be characterized by the formula



wherein R^1 is hydrogen or a hydrocarbyl group, R^2 is a hydrocarbyl group, and both X groups are either O or S.

[0043] The hydroxy compound used in the preparation of the phosphoric acid esters are characterized by the formula ROH wherein R is a hydrocarbyl group. The hydroxy compound reacted with the phosphorus compound may comprise a mixture of hydroxy compounds of the formula ROH wherein the hydrocarbyl group R contains from about 1 to 30 carbon atoms. It is highly desirable, that the amine salt of the substituted phosphoric acid ester ultimately prepared is soluble in the lubricating compositions described herein. Generally, the R group will contain at least 2 carbon atoms, typically 3 to 30 carbon atoms.

[0044] The R group may be aliphatic or aromatic such as alkyl, aryl, alkaryl, aralkyl and alicyclic hydrocarbon groups. Examples of useful hydroxy compounds of the formula ROH includes, for example, ethyl alcohol, iso-propyl alcohol, amyl alcohol, hexyl alcohol, 2-ethyl-hexyl alcohol, nonyl alcohol, dodecyl alcohol, stearyl alcohol, amyl phenol, octyl phenol, nonyl phenol, methyl cyclohexanol, alkylated naphthol, etc.

[0045] Suitable alcohols, ROH, are aliphatic alcohols and more particularly, primary aliphatic alcohols containing at least about 4 carbon atoms. Accordingly, examples of the monohydric alcohols ROH which are useful include, amyl alcohol, 1-octanol, 1-decanol, 1-dodecanol, 1-tetradecanol, 1-hexadecanol, 1-octadecanol, oleyl alcohol, linoleyl alcohol, linolenyl alcohol, phytol, myricyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol and behenyl alcohol. Commercial alcohols (including mixtures) are contemplated herein.

[0046] The amine salts of the present may be prepared by reaction of the above-described phosphoric acid esters with at least one amino compound which may be a primary or secondary amino compound. The amines which are reacted with the phosphoric acid esters to form the amine salts are primary hydrocarbyl amines having the general formula

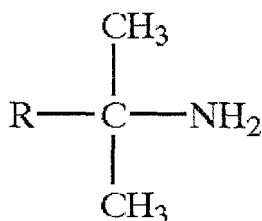


wherein R' is a hydrocarbyl group containing up to about 150 carbon atoms and will more often be an aliphatic hydrocarbyl group containing from about 4 to about 30 carbon atoms.

[0047] In one exemplary embodiment, the hydrocarbyl amines which are useful in preparing the amine salts are primary hydrocarbyl amines containing from about 4 to about 30 carbon atoms in the hydrocarbyl group, and typically from about 8 to about 20 carbon atoms in the hydrocarbyl group. The hydrocarbyl group may be saturated or unsaturated. Representative examples of primary saturated amines are those known as aliphatic primary fatty amines. Typical fatty amines include alkyl amines such as n-hexylamine, n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-pentadecylamine, n-hexadecylamine, n-octadecylamine (stearyl amine), etc. Unsaturated primary amines include, dodecylamine, myristoleylamine, palmitoleylamine, oleylamine and linoleylamine.

[0048] In another exemplary embodiment, the amine salts are those derived from tertiary-aliphatic primary amines having at least about 4 carbon atoms in the alkyl group. For the most part, they are derived from alkyl amines having a total of less than about 30 carbon atoms in the alkyl group.

[0049] Usually the tertiary aliphatic primary amines are monoamines represented by the formula



wherein R is a hydrocarbyl group containing from one to about 30 carbon atoms. Such amines are illustrated by tertiary-butyl amine, tertiary-hexyl primary amine, 1-methyl-1-amino-cyclohexane, tertiary-octyl primary amine, tertiary-decyl primary amine, tertiary-dodecyl primary amine, tertiary-tetradecyl primary amine, tertiary-hexadecyl primary amine, ter-

tiary-octadecyl primary amine, tertiary-tetracosanyl primary amine, tertiary-octacosanyl primary amine. Mixtures of amines may also be used.

[0050] The oil-soluble amine salts may be prepared by mixing the above-described phosphoric acid esters with the above-described amines at room temperature or above. Generally, mixing at room temperature for a period of from up to about one hour is sufficient. The amount of amine reacted with the phosphoric acid ester to form the salts is at least about one equivalent weight of the amine (based on nitrogen) per equivalent of phosphoric acid, and the ratio of equivalents generally is about one.

[0051] Methods for the preparation of such amine salts are well known and reported in the literature. See for example, U.S. Pat. Nos. 2,063,629; 2,224,695; 2,447,288; 2,616,905; 3,984,448; 4,431,552; 5,354,484; and PCT International Application Publication No. WO 87/07638.

[0052] Alternatively, the amine salts may be formed in situ when the acidic phosphoric acid ester is blended with the above-described amines when forming a gear oil concentrate or the formulated gear oil itself. For example, primary hydrocarbyl amines that function as rust inhibitors may be added to a gear additive concentrate containing the acidic phosphoric acid ester leading to the formation of amine salts of phosphoric acid esters. As described in more detail below, enhanced solubility of the sulfurized extreme pressure agent is exhibited when the sulfurized extreme pressure agent is mixed with the additive concentrate or lubricant formulation subsequent to combining the amine and acid components for the concentrate or lubricant formulation.

Rust Inhibitors

[0053] Rust inhibitors may typically be included in lubricant formulations as described herein. Rust inhibitors may be a single compound or a mixture of compounds having the property of inhibiting corrosion of ferrous metal surfaces. Such materials include oil-soluble monocarboxylic acids such as 2-ethylhexanoic acid, lauric acid, myristic acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, behenic acid, cerotic acid, etc., and oil-soluble polycarboxylic acids including dimer and trimer acids, such as are produced from tall oil fatty acids, oleic acid, linoleic acid, or the like.

[0054] Other suitable corrosion inhibitors include alkenylsuccinic acids in which the alkenyl group contains 10 or more carbon atoms such as, for example, tetrapropenylsuccinic acid, tetradecenylsuccinic acid, hexadecenylsuccinic acid, and the like; long-chain α,Ω -dicarboxylic acids in the molecular weight range of 600 to 3000; and other similar materials.

[0055] Rust inhibitors as described above are commercially available from various commercial sources, such as, for example, dimer and trimer acids sold by Cromton Corporation of Middlebury, Connecticut.

[0056] Another useful type of acidic corrosion inhibitors are the half esters of alkenyl succinic acids having 8 to 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. Especially useful rust inhibitors include the primary and secondary amine compounds taught herein as the amine portion of the salt of a phosphoric acid ester as well as mixtures of said amines with other rust inhibitors described above. When an amine salt of a phosphoric acid ester is used as the phosphorus-containing anti-wear agent, it may not be necessary to add additional amine-containing rust inhibitors to the gear oil formulation. The primary and secondary amines may contribute from 40 to 125 ppm nitrogen (on a weight/weight basis) to the formulated gear oil, whether they are classified as a rust inhibitor, part of the anti-wear system or a combination of both.

Antioxidants

[0057] Antioxidants that may be employed in gear oil formulations include phenolic compounds and amines. Amounts of up to about 5 wt. % in the concentrate are generally sufficient. Gear oil lubricants may include one or more antioxidants, for example, one or more phenolic antioxidants, hindered phenolic antioxidants, additional sulfurized olefins, aromatic amine antioxidants, secondary aromatic amine antioxidants, sulfurized phenolic antioxidants, oil-soluble copper compounds and mixtures thereof.

[0058] Suitable exemplary compounds include 2,6-di-tert-butylphenol, liquid mixtures of tertiary butylated phenols, 2,6-di-tert-butyl-4-methylphenol, 4,4'-methylenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), mixed methylene-bridged polyalkyl phenols, 4,4'-thiobis(2-methyl-6-tert-butylphenol), N,N'-di-sec-butyl-p-phenylenediamine, 4-isopropylaminodiphenyl amine, alkylated diphenylamine and phenyl- α -naphthyl amine.

[0059] In the class of amine antioxidants, oil-soluble aromatic secondary amines; aromatic secondary monoamines; and others are suitable. Aromatic secondary monoamines include diphenylamine, alkyl diphenylamines containing 1 to 2 alkyl substituents each having up to about 16 carbon atoms, phenyl- α -naphthylamine, alkyl- or aralkylsubstituted phenyl- α -naphthylamine containing one or two alkyl or aralkyl groups each having up to about 16 carbon atoms, alkyl- or aralkyl-substituted phenyl- α -naphthylamine containing one or two alkyl or aralkyl groups each having up to about 16 carbon atoms.

[0060] In the class of phenolic antioxidants, suitable compounds include ortho-alkylated phenolic compounds, e.g. 2-tert-butylphenol, 2,6-di-tertbutylphenol, 4-methyl-2,6-di-tertbutylphenol, 2,4,6-tri-tertbutylphenol, and various analogs

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and homologs or mixtures thereof; one or more partially sulfurized phenolic compounds as described in U.S. Pat. No. 6,096,695, and methylene-bridged alkylphenols as described in U.S. Pat. No. 3,211,652.

[0061] Antioxidants may be optionally included in the fully formulated final lubricating composition at from about 0.00 to about 5.00 weight percent, typically from about 0.01 weight % to about 1.00 weight %.

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Defoaming Agents

[0062] Defoaming agents which may be used include silicone oils of suitable viscosity, glycerol monostearate, polyglycol palmitate, trialkyl monothiophosphates, esters of sulfonated ricinoleic acid, benzoylacetone, methyl salicylate, glycerol monooleate, glycerol dioleate and polyacrylates. Defoamers are generally employed at concentrations of up to about 1 wt. % in the additive concentrate.

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Demulsifiers

[0063] Typical additives which may be employed as demulsifiers in gear oils include alkyl benzene sulfonates, polyethylene oxides, polypropylene oxides, esters of oil soluble acids and the like. Such additives are generally employed at concentrations of up to about 3 wt. % in the additive concentrate.

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Friction Modifiers

[0064] One or more friction modifiers may also be included to provide, for example, limited slip performance and enhanced positraction performance. Friction modifiers typically include such compounds as fatty amines or ethoxylated fatty amines, aliphatic fatty acid amides, ethoxylated aliphatic ether amines, aliphatic carboxylic acids, glycerol esters, aliphatic carboxylic ester-amides and fatty imidazolines, fatty tertiary amines, wherein the aliphatic group usually contains above about eight carbon atoms so as to render the compound suitably oil soluble. Also suitable are aliphatic substituted succinimides formed by reacting one or more aliphatic succinic acids or anhydrides with ammonia or other primary amines.

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Seal Swell Agents

[0065] The lubricating oil compositions may further contain from 0 to 20 weight percent of a seal swell agent. Suitable seal swell agents include hindered polyol esters and oil-soluble diesters. The diesters include the adipates, azelates, and sebacates of C₈-C₁₃ alkanols (or mixtures thereof), and the phthalates of C₄-C₁₃ alkanols (or mixtures thereof). Mixtures of two or more different types of esters (e.g., dialkyl adipates and dialkyl azelates, etc.) can also be used. Examples of such materials include the n-octyl, 2-ethylhexyl, isodecyl, and tridecyl diesters of adipic acid, azelaic acid, and sebacic acid, and the n-butyl, isobutyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and tridecyl diesters of phthalic acid. Specific examples include di-2-ethylhexyl adipate, di-isooctyl adipate, (2-ethylhexyl)(isodecyl) adipate, di-2-ethylhexyl sebacate and di-isodecyl adipate.

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[0066] Although the additive components are described occasionally with reference to a function, that function may be one of other functions served by the same component and should not be construed as a mandatory limiting function.

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Diluent Oil

[0067] The additive concentrates described herein may contain a suitable diluent, typically an oleaginous diluent of suitable viscosity. Such diluent may be derived from natural or synthetic sources. Among the mineral (hydrocarbonaceous) oils are paraffin base, naphthenic base, asphaltic base and mixed base oils. Typical synthetic base oils include polyolefin oils (especially hydrogenated α -olefin oligomers), alkylated aromatic, polyalkylene oxides, aromatic ethers, and carboxylate esters (especially diester oils), among others. Blends of natural and synthetic oils can also be used. The diluents may be light hydrocarbon base oils, selected from both natural and synthetic base oils. Generally the diluent oil will have a viscosity in the range of 13 to 35 centistokes at 40° C.

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[0068] For certain applications, pour point depressants may be added to the gear oil formulation. If present, the gear oil compositions typically can contain up to 5 wt. % of the pour point depressant.

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[0069] The compositions of the disclosure may be top treated to achieve multifunctional performance (i.e., both automotive and industrial applications).

[0070] The multi-grade gear oils described above may be suitable for use in automotive gear applications such as final drives, power-dividers or axles in light and heavy-duty vehicles or manual transmissions in a truck or heavy equipment and industrial gear applications.

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[0071] In the following illustrative examples gear oil additive packages were made by a conventional process and by a process as described in the disclosure. The gear oil additive packages contained the following components in the

amounts indicated.

Table 2

Gear Oil Additive Components	
Component	Wt. %
Tolytrizole	0.0 - 0.3
Primary amine	2.0 - 7.0
Acid phosphate	5.0 - 15.0
Polyacrylate antifoam agent	1.0 - 5.0
Mineral oil diluent	5.0 - 10.0
Carboxylic acid rust inhibitor	0.0 - 2.0
Thiadiazole corrosion inhibitor	2.0 - 5.0
Sulfurized isobutylene	50.0 - 95.0

Example 2

[0072] In this example, the order of mixing the foregoing components and amounts of each component are given in Table 3. This example represents a conventional method for making additive concentrates for use in lubricant formulations.

Table 3

Order of Addition	Component	Wt. %
1	Sulfurized isobutylene	0.0-20.0
2	Primary amine	2.0-7.0
3	Tolytrizole	0.0-0.3
4	Mineral oil diluent	5.0 - 10.0
5	Thiadiazole corrosion inhibitor	2.0-5.0
6	Sulfurized isobutylene	0.0-95.0
7	Acid phosphate	5.0-15.0
8	Polyacrylate antifoam agent	1.0 - 5.0
9	Carboxylic acid rust inhibitor	0.0-2.0

Example 3

[0073] In following example, the order of addition of the foregoing components and amounts of each component are given in Table 4. This example represents an exemplary embodiment of the disclosure, but is not intended to limit the disclosure.

Table 4

Order of Addition	Component	Wt. %
1	Tolytrizole	0.0 - 0.3
2	Primary amine	2.0 - 7.0
3	Thiadiazole corrosion inhibitor	2.0 - 5.0
4	Acid phosphate	5.0 - 15.0
5	Polyacrylate antifoam agent	1.0 - 5.0

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(continued)

Order of Addition	Component	Wt. %
6	Mineral oil diluent	5.0 - 10.0
7	Carboxylic acid rust inhibitor	0.0 - 2.0
8	Sulfurized isobutylene	50.0 - 95.0

[0074] In Table 3, the sulfurized isobutylene was added in the first and sixth steps for preparing the additive package. In Table 4, the sulfurized isobutylene (SIB) was added in the last step of the mixture process for the additive package. Each of the additive packages prepared in Tables 3 and 4 were combined with a polyalphaolefin-based gear oil and with a Group II base oil to provide a lubricating oil composition containing about 4 percent by weight of the additive package. The polyalphaolefin-based gear oil had a base NTU of 0.3 and the Group II base oil had a base NTU of 2. The turbidity of each of the lubricating oil compositions made from the additive packages are provided in the following table.

Table 5

Sample No.	Base Oil	Table 2 Procedure (NTU)		Table 3 Procedure (NTU)	
		Std. SIB	Low Vis. SIB	Std. SIB	Low Vis. SIB
1	PAO	>2000	---	----	----
2	PAO	----	>700	----	----
3	PAO	----	----	----	<5
4	PAO	----	----	123	----
5	Group II	205	----	----	----
6	Group II	----	2	----	----
7	Group II	----	----	2	----
8	Group II	----	----	----	2

[0075] As shown by the foregoing table, there is an unexpected and dramatic decrease in the turbidity or haziness of lubricant formulations made containing the additive package formulated by the procedure of Table 4 (Sample Nos. 3 and 4 compared to Sample No. 1) wherein the sulfurized isobutylene is added in the last stage of the process for making the additive package. Similar result may be obtained by combining the acidic and basic or amine components for a lubricant or additive package in any step prior to adding sulfurized extreme pressure agents to the package or lubricant when the lubricant is formulated with at least one substantially non-polar base oil. Thus it is not critical that the sulfurized extreme pressure agent be added in the last step for making the additive or lubricant.

[0076] Furthermore, a significant decrease in turbidity may be obtained in PAO or in a Group II base oil by using a low viscosity (soluble) SIB as shown by Sample Nos. 2 and 3 compared to Sample No. 1, and Sample Nos. 6 and 8 compared to Sample No. 5. The results indicated that the particular SIB used in the formulation is less important in a Group II base oil than in a more non-polar base oil such as PAO when the Table 4 procedure is used as shown by comparing Sample Nos. 7 and 8. Accordingly, a combination of low viscosity SIB and/or the addition of SIB to previously combined acid and basic or amine components are particularly useful for reducing the turbidity of formulations including substantially non-polar base oils such as, but not limited to, Group II, Group III, and Group IV base oils.

[0077] At numerous places throughout this specification, reference has been made to a number of U.S. Patents. All such cited documents are expressly incorporated in full into this disclosure as if fully set forth herein.

[0078] The foregoing embodiments are susceptible to considerable variation in its practice. Accordingly, the embodiments are not intended to be limited to the specific exemplifications set forth hereinabove. Rather, the foregoing embodiments are within the spirit and scope of the appended claims, including the equivalents thereof available as a matter of law.

[0079] The patentees do not intend to dedicate any disclosed embodiments to the public, and to the extent any disclosed modifications or alterations may not literally fall within the scope of the claims, they are considered to be part hereof under the doctrine of equivalents.

Claims

- 5 1. A method for improving the solubility of a sulfurized extreme pressure agent in a lubricant composition including a substantially non-polar base oil component, the method including the steps of pre-blending organic acid and amine components of a lubricant additive package for the lubricant composition to provide a premixture of organic acid and amine components and combining the premixture with a sulfurized extreme pressure agent having a viscosity of less than 5.5 centistokes at 100° C to provide a lubricant additive package, whereby a turbidity characteristic of the lubricant composition containing the additive package is lower than a turbidity characteristic of a lubricant composition that is made by combining the organic acid and amine components with the sulfurized extreme pressure agent in the absence of use of the premixture.
- 10 2. The method of claim 1, wherein the sulfurized extreme pressure agent includes a sulfurized olefin.
- 15 3. The method of claim 2, wherein the sulfurized olefin includes sulfurized isobutylene.
4. The method of any one of claims 1-3, further including the step of combining the lubricant additive package with the substantially non-polar base oil component.
- 20 5. The method of any one of claims 1-4, wherein the substantially non-polar base oil component includes a polyolefin base oil.
6. The method of any one of claims 1-4, wherein the substantially non-polar base oil component includes a base oil selected from a Group II base oil, a Group III base oil, and a Group IV base oil.
- 25 7. A method as claimed in any one of claims 1-6, further including the step of:
- reacting a sulfur monochloride/isobutylene adduct with aqueous sodium hydrosulfide under conditions sufficient to provide a sulfurized isobutylene having a viscosity at 100° C no higher than 5.5 centistokes, prior to said combining step;
- 30 and wherein the pre-mixture is combined with from 50 to 95 percent by weight of the sulfurized isobutylene as the sulfurized extreme pressure agent; and
- treating a base oil with the additive composition to provide a non-hazy lubricant composition.
- 35 8. A method for making a sulfurized extreme pressure agent for use in the method of any one of claims 1-7, having characteristics that assist in the formation of a low turbidity substantially non-polar base oil containing lubricant, the method including the steps of:
- reacting sulfur monochloride and an olefin under conditions sufficient to provide a sulfur/olefin adduct;
- 40 mixing and reacting the sulfur/olefin adduct with an aqueous sulfur source over a period of time sufficient to provide a sulfurized extreme pressure agent in an organic phase having a viscosity of no higher than 5.5 centistokes at 100° C; and
- separating an aqueous phase and the organic phase containing the sulfurized extreme pressure agent from one another.
- 45 9. The method of claim 8, wherein the sulfurized extreme pressure agent includes sulfurized isobutylene.
10. The method of claim 9, wherein the sulfurized isobutylene has a viscosity ranging from 4.0 to 5.5 centistokes at 100° C.
- 50 11. The method of any one of claims 9-10, wherein the sulfurized isobutylene has a sulfur content ranging from 40 to 50 percent by weight.
12. The method of any one of claims 8-11, wherein the step of mixing and reacting the sulfur/olefin adduct with an aqueous sulfur source is conducted over a period of time ranging from 10 to less than 60 minutes.
- 55 13. A method as claimed in any one of claims 1-6, wherein the sulfurized extreme pressure agent is made by a method as claimed in any one of claims 8-12.
14. A gear lubricant made by the method of any one of claims 1-7 and 13.

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15. A gear lubricant including a mineral oil component and an additive composition made by the method of any one of claims 1-7 and 13.
16. A vehicle having moving parts containing the gear lubricant of any one of claims 14-15 for lubricating the moving parts.

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