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(54) Titre : ADDITIF POUR LUBRIFIANT A FAIBLE TENEUR EN SOUFRE, EN CENDRES ET EN PHOSPHORE COMPORTANT DU PHENATE DE CALCIUM SURBASE

(54) Title: LOW SULFUR, LOW ASH AND LOW PHOSPHORUS LUBRICANT ADDITIVE PACKAGE USING OVERBASED CALCIUM PHENATE

(57) Abrégé/Abstract:
The present invention provides a low sulfur, low ash, and low phosphorus oil soluble lubricant additive package comprising an overbased metal phenate. Also included in the present invention are lubricating oils comprising the inventive oil soluble lubricant additive package, as well as machines lubricated by such oils. Several methods for lubricating machinery are also disclosed.

ABSTRACT OF THE DISCLOSURE

The present invention provides a low sulfur, low ash, and low phosphorus oil soluble lubricant additive package comprising an overbased metal phenate. Also included in the present invention are lubricating oils comprising the inventive oil soluble lubricant additive package, as well as machines lubricated by such oils. Several methods for lubricating machinery are also disclosed.

Low Sulfur, Low Ash, and Low Phosphorus Lubricant Additive Package Using Overbased Calcium Phenate

TECHNICAL FIELD OF THE INVENTION

[0001] The present invention relates to lubricating oil compositions, their method of preparation, and use. More specifically, this invention relates to oil soluble lubricating additive package to achieve low sulfur, low ash, and low phosphorus levels in fully formulated oil. The oil soluble lubricating package compositions herein are particularly useful in crankcase lubricants.

BACKGROUND OF THE INVENTION

[0002] Combustion engines generate emissions that can pollute our environment. In response to increasing regulation and environmental concerns, engine manufacturers have recognized the need to reduce engine emissions. In an effort to reduce emissions in exhaust gases, manufacturers have used particulate traps and catalytic converters. However, the lubricating oil used in the engine is often times detrimental to devices such as catalytic converters or particulate traps. For example, phosphorus present in the lubricating oil is believed to interfere with catalytic efficiency. Further, it is believed that sulfur present in the lubricating oil, after oxidation and neutralization, may form sulfates that plug exhaust gas traps thereby preventing them from oxidizing and burning off trapped organic particulate matter. Accordingly, engine manufacturers are requiring lubricating oils that have lower and lower sulfur, ash, and phosphorus levels.

[0003] An embodiment of the present invention provides an oil soluble lubricating additive package that can be used to formulate a low sulfur, low ash, and low phosphorus content oil for use in either gasoline or diesel engines. Further, a second embodiment provides lubricating oils that contain minimal sulfur, ash, and phosphorus levels.

[0004] Additionally, another embodiment provided herein is a method for lubricating the moving parts of a machine.

SUMMARY OF THE INVENTION

[0005] In one embodiment is provided an oil soluble lubricant additive package comprising at least one overbased metal phenate having a total base number of from about 120 to about 360 and at least one detergent, wherein the weight ratio of the overbased metal phenate to the detergent is from about 1:1 to about 3:1.

[0006] In another example, at least one of the detergent(s) is selected from the group consisting of calcium sulfonate, magnesium sulfonate, sodium sulfonate, non-sulfurized phenates, sulfurized phenates, salicylates, overbased saligenin, and combinations thereof.

[0007] In yet another embodiment is provided a method for lubricating an engine crankcase that comprises the step of: at least partially filling the crankcase with the oil soluble lubricant additive package disclosed herein.

[0008] Also provided is a method for lubricating the moving parts of a machine that comprises the step of contacting at least one moving part with the oil soluble lubricant additive package disclosed herein.

[0009] In another example is provided an oil soluble lubricant additive that comprises: an overbased metal phenate having a total base number of from about 120 to about 360; and at least one dispersant, wherein the weight ratio of the overbased metal phenate to the dispersant is from about 1:4 to about 1:12.

[0010] The oil soluble lubricant additive package herein can in one embodiment utilize dispersants having a molecular weight of at least 500. However, dispersants may also be used that have a molecular weight of from about 1000 to about 6000.

[0011] Additionally, in another example, at least one dispersant is a maleic anhydride functionalized polyisobutylene polymer that has been reacted with a polyamine. In one example, the at least one dispersant is the product of a Mannich reaction, and/or the at least one dispersant is an ethylene-propylene type dispersant.

[0012] Oil soluble lubricant additive package formulations herein may additionally comprise at least one component selected from the group consisting of: viscosity index improvers and pour point depressants.

[0013] Also provided is a method for lubricating an engine crankcase comprising the step of at least partially filling the crankcase with the oil soluble lubricant additive package disclosed herein.

[0014] Also provided is a method for lubricating moving parts of a machine comprising the step of contacting at least one moving part with the oil soluble lubricant additive package disclosed herein.

[0015] Also provided is an oil soluble lubricating additive package comprising: an overbased metal phenate having a total base number of from about 120 to about 360;

and at least one antioxidant, wherein the weight ratio of overbased metal phenate to antioxidant is from about 10:1 to about 1:3.

[0016] It is desired but not required that at least one of the antioxidants is selected from the group consisting of: zinc dithiophosphates, alkylated diphenylamines, sulfurized olefins, phenols, hindered phenols, and sulfurized phenols.

[0017] Also included herein are machines lubricated by the inventive lubricating oils disclosed herein. While the machine may be any machine that uses a lubricating oil to maintain the operability of its moving parts, it is preferred that the machine is selected from the group consisting of: gas engines, diesel engines, turbine engines, automatic transmissions, manual transmissions, hypoid axles, and gear boxes.

[0018] Also provided is a method for lubricating an engine crankcase comprising the step of at least partially filling the crankcase with the oil soluble lubricant additive package disclosed herein.

[0019] Also provided is a method for lubricating moving parts of a machine comprising the step of contacting at least one moving part with the oil soluble lubricant additive package disclosed herein.

[0020] Also provided is an oil soluble lubricant additive package comprising: an overbased calcium phenate having a total base number of at least 120; and at least one component selected from the group consisting of: detergents, dispersants, antioxidants, friction modifiers, viscosity index improvers, and pour point depressants.

[0021] It may be desired that the oil soluble lubricant additive package herein has at least one property selected from the group consisting of: a sulfur content less than about 3 wt% and a phosphorus content less than about 1.2 wt%.

[0022] In another embodiment, the oil soluble lubricant additive package herein is essentially free of non-sulfurized Mannich phenates.

[0023] Also provided is a method for lubricating an engine crankcase comprising the step of at least partially filling the crankcase with the oil soluble lubricant additive package disclosed herein.

[0024] Also provided is a method for lubricating moving parts of a machine comprising the step of contacting at least one moving part with the oil soluble lubricant additive package disclosed herein.

[0025] One method of achieving a low sulfur, low ash, and low phosphate oil formulation of the present invention can comprise the steps of: providing an oil soluble lubricant additive package comprising an overbased metal phenate having a total base number of from about 120 to about 360; and admixing the oil soluble lubricant additive package with at least a base oil so as to form a lubricating oil having a total base number of less than about 10, and at least one property selected from the group consisting of: a sulfur content less than about 0.3 wt%, a phosphorus content of less than about 0.11 wt%, and an ash content less than about 1.2 wt%.

[0026] The overbased metal phenate can in an embodiment be selected from the group consisting of: overbased calcium phenate and overbased magnesium phenate.

[0027] Additionally, the oil soluble lubricant additive package herein can comprise at least one additive selected from the group consisting of: detergents, dispersants, antioxidants, friction modifiers, viscosity index improvers, and pour point depressants.

[0028] It is also effective herein for each oil soluble lubricant additive package to have a sulfur content and a phosphorus content sufficient to yield a lubricating oil having a sulfur content less than about 0.3 wt% and a phosphorus content of less than about 0.11 wt% when the lubricating oil comprises less than 20 wt% of the oil soluble lubricant additive package.

[0029] It is also possible herein for each of the above disclosed formulations to include at least one of the metal phenates as an overbased metal phenate. In one example, the overbased metal phenate is selected from the group consisting of: overbased calcium phenate and overbased magnesium phenate.

[0030] The invention described herein also includes lubricating oils comprising the oil soluble lubricant additive packages disclosed herein. It is preferred that the lubricating oil has a total base number of less than about 10, and at least one property selected from the group consisting of: a sulfur content less than about 0.3 wt%, a phosphorus content of less than about 0.11 wt%, and an ash content less than about 1.2 wt%.

[0031] Also included herein are machines lubricated by the inventive lubricating oils disclosed herein. While the machine may be any machine that uses a lubricating oil to maintain the operability of its moving parts, in one embodiment the machine is selected from the group consisting of: gas engines, diesel engines, turbine engines, automatic transmissions, manual transmissions, hypoid axles, and gear boxes.

[0032] Further, the present invention also includes vehicles comprising at least one of the oil soluble lubricant additive packages disclosed herein.

[0033] Although any of the inventive methods and articles disclosed herein may be practiced on or with a wide variety of machines, it is preferred that the machine is selected from the group consisting of: gas engines, diesel engines, turbine engines, automatic transmissions, manual transmissions, hypoid axles, and gear boxes.

[0034] In addition to the novel features and advantages mentioned above, other objects and advantages of the present invention will be readily apparent from the following descriptions of the drawing(s) and preferred embodiment(s).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

[0035] In accordance with the foregoing summary, the following presents a detailed description of the preferred embodiment of the invention that is currently considered to be the best mode.

[0036] We begin with a discussion of the various components employed in the present invention. Then we shall present an example of an oil formulation based upon the oil soluble additive package of the present invention. Finally, we conclude with a comparison of an inventive oil formulation against a control formulation in the CAT 1N engine test.

BASE OIL

[0037] The base oils useful herein include natural lubricating oils, synthetic lubricating oils and mixtures thereof. Suitable lubricating oils also include basestocks obtained by isomerization of synthetic wax and slack wax, as well as basestocks produced by hydrocracking the aromatic and polar components of the crude. In general, both the natural and synthetic lubricating oils will each have a kinematic viscosity ranging from about 1 to about 40 mm^2/s (cSt) at 100° C, although typical applications will require each of the base oils to have a viscosity ranging from about 1 to about 12, preferably 2 to 8, mm^2/s (cSt) at 100° C.

[0038] Natural lubricating oils include animal oils, vegetable oils (e.g., castor oil and lard oil), petroleum oils, mineral oils, and oils derived from coal or shale. The preferred natural lubricating oil is mineral oil.

[0039] The mineral oils useful in this invention can include but are not limited to all common mineral oil base stocks. This would include oils that are naphthenic or paraffinic in chemical structure. Oils that are refined by conventional methodology using acid, alkali, and clay or other agents such as aluminum chloride, or be extracted oils produced, for example, by solvent extraction with solvents such as phenol, sulfur dioxide, furfural, dichlorodiethyl ether, etc. They may be hydrotreated or hydrorefined, dewaxed by chilling or catalytic dewaxing processes, or hydrocracked. The mineral oil may be produced from natural crude sources or be composed of isomerized wax materials or residues of other refining processes. In one embodiment, the oil of lubricating viscosity is a hydrotreated, hydrocracked and/or iso-dewaxed mineral oil having a Viscosity Index (VI) of greater than 80, preferably greater than 90; greater than 90 volume % saturates and less than 0.03 wt. % sulfur.

[0040] Group II and Group III basestocks are also particularly suitable for use in the present invention, and are typically prepared from conventional feedstocks using a severe hydrogenation step to reduce the aromatic, sulfur and nitrogen content, followed by dewaxing, hydrofinishing, extraction and/or distillation steps to produce the finished base oil. Group II and III basestocks differ from conventional solvent refined Group I basestocks in that their sulfur, nitrogen and aromatic contents are very low. As a result, these base oils are compositionally very different from conventional solvent refined basestocks. The American Petroleum Institute has categorized these different basestock types as follows: Group I, >0.03 wt. % sulfur, and/or <90 vol% saturates, viscosity index between 80 and 120; Group II, $\leq$ 0.03 wt. % sulfur, and $\geq$ 90 vol% saturates, viscosity index between 80 and 120; Group III, $\leq$ 0.03 wt. % sulfur, and $\geq$ 90 vol% saturates, viscosity index > 120; Group IV, poly-alpha-olefins. Hydrotreated basestocks and catalytically dewaxed basestocks, because of their low sulfur and aromatics content, generally fall into the Group II and Group III categories.

[0041] There is no limitation as to the chemical composition of the various basestocks used in the present invention. For example, the proportions of aromatics, paraffinics, and naphthenics in the various Group I, Group II and Group III oils can vary substantially. The degree of refining and the source of the crude used to produce the oil generally determine this composition.

[0042] In one embodiment, the base oil comprises a mineral oil having a VI of at least 110.

[0043] The lubricating oils may be derived from refined, re-refined oils, or mixtures thereof. Unrefined oils are obtained directly from a natural source or synthetic source (e.g., coal, shale, or tar sands bitumen) without further purification or treatment. Examples of unrefined oils include shale oil obtained directly from a retorting operation, petroleum oil obtained directly from distillation, or an ester oil obtained directly from an esterification process, each of which is then used without further treatment. Refined oils are similar to the unrefined oils except that refined oils have been treated in one or more purification steps to improve one or more properties. Suitable purification techniques include distillation, hydrotreating, dewaxing, solvent extraction, acid or base extraction, filtration, and percolation, all of which are known to those skilled in the art. Re-refined oils are obtained by treating used oils in processes similar to those used to obtain the refined oils. These re-refined oils are also known as reclaimed or reprocessed oils and are often additionally processed by techniques for removal of spent additives and oil breakdown products.

[0044] Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as oligomerized, polymerized, and interpolymerized olefins; alkylbenzenes; polyphenyls; and alkylated diphenyl ethers, alkylated diphenyl sulfides, as well as their derivatives, analogs, and homologs thereof, and the like. Preferred synthetic oils are oligomers of α-olefins, particularly oligomers of 1-decene, having a viscosity ranging from about 1 to about 12, preferably 2 to 8, mm^2/s (cSt) at 100° C. These oligomers are known as poly-α-olefins or PAOs.

[0045] Synthetic lubricating oils also include alkylene oxide polymers, interpolymers, copolymers, and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc. This class of synthetic oils is exemplified by polyoxyalkylene polymers prepared by 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 1000, diphenyl ether of polypropylene glycol having a molecular weight of 100-1500); and mono- and poly-carboxylic esters thereof (e.g., the acetic acid esters, mixed C_3-C_8 fatty acid esters, and C_{12} oxo acid diester of tetraethylene glycol).

[0046] Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, subric acid, sebasic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic 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 monoethers, 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 isothalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebasic acid with two moles of tetraethylene glycol and two moles of 2-ethyl-hexanoic acid, and the like. A preferred type of oil from this class of synthetic oils is adipates of C_4 to C_{12} alcohols.

[0047] Esters useful as synthetic lubricating oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane pentaeythritol, dipentaerythritol, tripentaerythritol, and the like.

[0048] Silicon-based oils (such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils) comprise another useful class of synthetic lubricating oils. These oils include tetra-ethyl silicate, tetra-isopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra-(p-*tert*-butylphenyl) silicate, hexa-(4-methyl-2-pentoxy)-disiloxane, poly(methyl)-siloxanes and poly (methylphenyl) siloxanes, and the like. Other synthetic lubricating oils include liquid esters of phosphorus containing acids (e.g., tricresyl phosphate, trioctylphosphate, and diethyl ester of decylphosphonic acid), polymeric tetra-hydrofurans, poly-alpha-olefins, and the like.

OVERBASED METAL PHENATE

[0049] The oil soluble lubricating additive package of one example of the present invention contains at least one metal salt of an acidic organic compound. These salts are generally referred to as overbased materials or overbased metal salts. Overbased materials are single phase, homogeneous Newtonian systems characterized by a metal content in excess of that which would be present according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal.

[0050] The amount of excess metal is commonly expressed in terms of metal ratio. The term "metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. A neutral metal salt has a metal ratio of one. A salt having 4.5 times as much metal as present in a normal salt will have metal excess of 3.5 equivalents, or a ratio of 4.5.

[0051] The overbased metal salts used herein are prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid, preferably carbon dioxide) with a mixture comprising an acidic organic compound, a reaction medium comprising at least one inert, organic solvent (mineral oil, naphtha, toluene, xylene, etc.) for the acidic organic compound, a stoichiometric excess of a metal base, and a promoter.

[0052] The metals useful in making the overbased compositions of the present invention can include magnesium and calcium, as well as any other suitable or desirable metal.

[0053] We found that the following synthesis methods produce overbased calcium phenates that are useful in the formulations of the present invention:

SYNTHESIS METHOD #1

[0054] Into a round bottom flask equipped with a mechanical stirrer, thermometer, gas inlet tube, condenser and trap is charged 300 gms (1.17 moles) dodecylphenol, 21.1 gms (0.66 moles) elemental sulfur, 75.8 gms (1.22 moles) ethylene glycol, 91.1 gms (1.23 moles) calcium hydroxide, 391.3 gms diluent oil and 23.5 gms of neutral calcium sulfonate. After charging the flask, begin to bubble nitrogen gas into the reagents. While vigorously stirring, heat the contents of the flask to 170 °C and maintain for four hours. Next stop the flow of nitrogen gas, and blow carbon dioxide gas into the reaction mixture for 82 minutes at 80 ml/min. Vacuum strip the product at 170 °C as needed and filter. Found analyticals: %Ca = 5.65, %S = 1.60, TBN = 156.6, 100 °C Viscosity = 24.50.

[0055] SYNTHESIS METHOD #2

[0056] Into a round bottom flask equipped with a mechanical stirrer, thermometer, gas inlet tube, condenser and trap is charged 300 gms (1.17 moles) dodecylphenol, 21.1 gms (0.66 moles) elemental sulfur, 75.8 gms (1.22 moles) ethylene glycol, 134.1 gms (1.181 moles) calcium hydroxide, 449.8 gms diluent oil and 81.0 gms neutral calcium sulfonate. After charging the flask, begin bubbling nitrogen gas into the reagents. While vigorously stirring, heat the reactants to 170 °C and maintain for four hours. Next stop the flow of nitrogen gas and blow carbon dioxide gas into the reaction mixture for 163 minutes at 80 ml/min. Vacuum strip the product at 170 °C as needed and filter. Found analyticals: %Ca = 7.03, %S 1.45, TBN = 182, 100 °C Viscosity = 18.4.

[0057] SYNTHESIS METHOD #3

[0058] Into a round bottom flask equipped with a mechanical stirrer, thermometer, gas inlet tube, condenser and trap is charged 300 gms (1.17 moles) dodecylphenol, 10.6 gms (0.33 moles) elemental sulfur, 75.8 gms (1.22 moles) ethylene glycol, 91.1 gms (1.23 moles) calcium hydroxide, 387.2 gms diluent oil and 23.2 gms neutral calcium sulfonate. After charging the flask, begin bubbling nitrogen gas into the reagents. While vigorously stirring, heat the reactants to 170 °C and maintain for four hours. Next stop the flow of nitrogen gas and blow carbon dioxide gas into the reaction mixture for 82 minutes at 80 ml/min. Vacuum strip the product at 170 °C as needed and filter. Found analyticals: %Ca = 5.41, %S = 0.92, TBN = 164, 100 °C Viscosity = 56.3.

[0059] An example of a comparative conventional commercially available sulfurized overbased calcium phenate is Oloa 218E having a sulfur content of 3% and commercially available from Oronite, a division of Chevron-Texaco.

DETERGENTS

[0060] A detergent is an additive that reduces the formation of piston deposits, for example high-temperature varnish and lacquer deposits, in engines. Detergents typically possess acid-neutralizing properties and are capable of keeping finely divided solids in suspension. Metal detergents are used preferably for improving the acid-neutralizing properties, high-temperature detergency, and anti-wear properties of the resulting lubricating oil composition.

[0061] Detergents used herein may be any detergent used in lubricating oil formulations, and may be of the ash-producing or ashless variety. Detergents suitable for use in the present invention include all of the detergents customarily used in lubricating oils, including metal detergents. Specific examples of metal detergents are those selected from alkali metal or alkaline earth metal sulfonates, alkali metal or alkaline earth metal phenates, and alkali metal or alkaline earth metal salicylates.

[0062] Representative examples of suitable detergents useful in the present invention are found in U.S. Pat. Nos. 6,008,166. Additional representative examples of suitable detergents are found in U.S. Patent Application Nos. 2002/0142922A1, 2002/0004069A1, and 2002/0147115A1. The disclosures of the afore-mentioned references are incorporated by reference herein.

DISPERSANTS

[0063] Dispersants used in the present invention may be ash-producing or ashless. Suitable dispersants for use herein can typically comprise amine, alcohol, amide, or ester polar moieties attached to the polymer backbone via a bridging group. The dispersant may be, for example, selected from oil-soluble salts, esters, amino-esters, amides, imides, and oxazolines of long chain hydrocarbon substituted mono- and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of chain hydrocarbons; long chain aliphatic hydrocarbons having a polyamine attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine, and Koch reaction products. The long chain aliphatic hydrocarbons can be polymers such as polyalkylenes, including, for example, polyisobutylene, polyethylene, polypropylene, and copolymers thereof and/or copolymers with other alpha-olefins. Typical PIB molecular weights useful herein can range from about 950 to 6000.

[0064] Representative examples of dispersants suitable for use in the present invention are found in U.S. Patent Nos. 5,075,383; 5,139,688; 5,238,588; and 6,107,257. Additional representative examples are found in U.S. Patent Application Publication No. 2001/0036906A1. The disclosures of the afore-mentioned references are incorporated herein by reference.

ANTIOXIDANTS

[0065] Useful antioxidant materials include oil soluble phenolic compounds, oil soluble sulfurized organic compounds, oil soluble amine antioxidants, oil soluble organo borates, oil soluble organo phosphites, oil soluble organo phosphates, oil soluble organo dithiophosphates and mixtures thereof. Such antioxidants can be metal free (that is, free of metals which are capable of generating sulfated ash), and therefore are most preferably ashless (having a sulfated ash value not greater than 1 wt. % SASH, as determined by ASTM D874). The oil soluble organo dithiophosphates can include zinc dialkyldithiophosphates.

[0066] Further, zinc dithiophosphates are well known antioxidants. Specific examples of preferred zinc dithiophosphates are zinc dipropyldithiophosphate, zinc dibutyldithiophosphate, zinc dipentyldithiophosphate, zinc dihexyldithiophosphate, zinc diheptyldithiophosphate, and zinc dioctyldithiophosphate, of which alkyl groups may be straight-chain or branched, and mixtures thereof. Furthermore, zinc dialkyldithiophosphates having alkyl groups having different carbon number (3 to 8 carbon atoms) or structure in one molecule are also eligible.

[0067] Representative examples of suitable antioxidants useful in the present invention are found in U.S. Patent No. 5,102,566. Additional representative examples of suitable antioxidants useful in the present invention are found in U.S. Patent Application Publication No. 2001/0012821A1. The disclosures of the afore-mentioned references are incorporated by reference herein.

FRICTION MODIFIERS

[0068] Friction modifiers serve to impart the proper friction characteristics to lubricating oil compositions.

[0069] Friction modifiers include such compounds as aliphatic amines or ethoxylated aliphatic amines, aliphatic fatty acid amines, aliphatic carboxylic acids, aliphatic carboxylic esters of polyols such as glycerol esters of fatty acid as exemplified by glycerol phenate, aliphatic carboxylic ester-amides, aliphatic phosphonates, aliphatic phosphates, aliphatic thiophosphonates, aliphatic thiophosphates, etc., 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. Additionally suited for use in the present invention are friction modifiers containing molybdenum.

[0070] Representative examples of molybdenum-containing friction modifiers include those found in U.S. Patent Nos. 5,650,381; RE37,363E; 5,628,802; 4,889,647;

5,412,130; 4,786,423; 4,812,246; 5,137,647; 5,364,545; 5,840,672; 5,925,600; 5,962,377; 5,994,277; 6,017,858; 6,150,309; 6,174,842; 6,187,723; 6,268,316; European Patent Nos. EP 222 143 B1; EP 281 992 B1; EP 719 314 B1; EP 719 315 B1; EP 874 040 A1; EP 892 037 A1; EP 931 827 A1; EP 1 041 134 A1; EP 1 041 135 A1; EP 1 087 008 A1; EP 1 088 882 A1; EP; Japanese Patent No. JP 11035961; and International Publication Nos. WO 95/07965; WO 00/08120; WO 00/71649.

[0071] Representative examples of suitable friction modifiers are found in U.S. Pat. Nos. 3,933,659; 4,105,571; 3,779,928; 3,778,375; 3,852,205; 3,879,306; 3,932,290; 3,932,290; 4,028,258; 4,344,853; 5,102,566; 6,103,674; 6,174,842; 6,500,786; 6,500,786; and 6,509,303. Additional representative examples of suitable friction modifiers are found in U.S. Patent Application Publication No. 2002/0137636 A1. The disclosures of the above references are incorporated herein by reference.

VISCOSITY INDEX IMPROVERS

[0072] Viscosity index improvers impart high and low temperature operability to the lubricating oil and permit it to remain relatively viscous at elevated temperatures and also exhibit acceptable viscosity or fluidity at low temperatures. Viscosity index improvers are generally high molecular weight hydrocarbon polymers including polyesters. The viscosity index improvers may also be derivatized to include other properties or functions, such as the addition of dispersancy properties. These oil soluble viscosity modifying polymers will generally have number average molecular weights of from 10^3 to 10^6, preferably 10^4 to 10^6, as determined by gel permeation chromatography or osmometry.

[0073] The viscosity index improvers useful herein can include polymethacrylate-based ones, olefin copolymer-based ones, (e.g., isobutylene-based and ethylene-propylene copolymer based ones), polyalkyl styrene-based ones, hydrogenated styrene-butadiene copolymer-based ones, and styrene-maleic anhydride ester copolymer-based ones.

[0074] Representative examples of suitable viscosity index improvers are found in U.S. Pat. Nos. 5,075,383; 5,102,566; 5,139,688; 5,238,588; and 6,107,257. The above references are incorporated herein by reference.

POUR POINT DEPRESSANTS

[0075] Pour point depressants are used to improve low temperature properties of oil-based compositions. See, for example, page 8 of "Lubricant Additives" by C.V. Smalheer and R. Kennedy Smith (Lezius Hiles Co. publishers, Cleveland, Ohio, 1967). Examples of useful pour point depressants are polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and ter-polymers of dialkylfumarates, vinyl esters of fatty acids and alkyl vinyl ethers. Pour point depressants are described in U.S. Patent Nos. 2,387,501; 2,015,748; 2,655,479; 1,815,022; 2,191,498; 2,666,746; 2,721,877; 2,721,878; and 3,250,715, which are herein incorporated by reference for their relevant disclosures.

CAT 1N ENGINE TEST RESULTS

[0076] The CAT 1N engine test is a commonly used test for evaluating the acceptability of heavy-duty diesel engine oils for Caterpillar engines. The test employs a single cylinder aluminum piston diesel engine. The acceptability of an oil formulation is based upon the following parameters: average oil consumption, piston deposits, % top groove fill, % top land heavy carbon. Further, in order to pass the CAT 1N diesel test, no stuck pistons, piston rings or liner distress is permitted.

[0077] To determine the efficacy of the inventive additive, a control formulation comprising a non-sulfurized phenate prepared by a Mannich reaction between an alkylphenol and a polyamine was compared to a formulation wherein the sulfur-free Mannich phenate was replaced with a low sulfur overbased calcium phenate of the present invention.

Composition, wt% basis	Control Formulation	Inventive Formulation
Base Oil #1	52.00	52.00
Base Oil #2	27.00	27.00
Viscosity Index Improver	8.50	8.50
Pour Point Depressant	0.20	0.20
Dispersant #1	3.00	3.00
Dispersant #2	5.03	5.03
Non-Sulfurized Phenate	0.95	0.00
Detergent	0.50	0.50
Overbased Calcium Phenate	0.00	0.95
Zinc Dialkyldithiophosphate	0.25	0.25
Antioxidant #1	0.50	0.50
Antioxidant #2	0.50	0.50
Anti-foaming Agent	0.01	0.01
Friction Modifier	0.50	0.50
Process Oil	1.06	1.06
Kinematic Viscosity @ 100°C	14.31 centistoke	13.66 centistoke

[0078] The following table compares the control formulation's performance against the inventive formulation. The column marked "Test #1" provides the pass/fail limits for the CAT 1N test for a single trial. If a given oil formulation does not provide satisfactory results with a single trial, multiple trials may be averaged together and this average compared against the corresponding pass/fail limits for the number of tests being averaged. That is to say, if two trials of the inventive formulation were averaged together, the averaged results would be compared against the pass/fail limits provided in the "Test #2" column.

	Control Formulation	Inventive Formulation	Test #1	Test #2	Test #3
TLHC, %	0	0	3	4	5
TGF, %	25	9	20	23	25
WD	698.6	280.7	286.2	311.7	323
O.C., avg	0.22	0.145	0.5 max (0-252 hr)		
O.C. E.O.T.	0.23	0.189	No scuffing		

TLHC, % - Top Land Heavy Carbon
TGF, % - Top Groove Fill
WD - Weight of Deposit
O.C. - Oil Consumption
O.C.E.O.T. - Oil Consumption at End of Test

[0079] As can be seen from the table above, the inventive formulation performed well in the CAT 1N test. The inventive formulation did not require additional trials, as single trial performance was satisfactory. The inventive formulation exhibited a marked reduction in top groove fill percentage. Further, the inventive formulation exhibited a significant reduction in deposit weight. The inventive formulation also outperformed the control formulation in both oil consumption and oil consumption at the end of the test. These results demonstrate the improved performance imparted to the formulated oil by the inclusion of the overbased calcium phenate.

[0080] While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiments, it is to be understood that the invention is not to be limited to the disclosed embodiment(s), but on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims, which are incorporated herein by reference.

What is claimed is:

1. An oil soluble lubricant additive package comprising:

   at least one overbased metal phenate having a total base number of from about 120 to about 360; and

   at least one detergent, wherein the weight ratio of said overbased metal phenate to said detergent is from about 1:1 to about 3:1.

2. The oil soluble lubricant additive package as in claim 1, wherein said oil soluble lubricant additive package has a sulfur content and a phosphorus content sufficient to yield a lubricating oil having a sulfur content less than about 0.3 wt% and a phosphorus content of less than about 0.11 wt.

3. The oil soluble lubricant additive package as in claim 1, wherein at least one of said at least one overbased metal phenate is an overbased calcium phenate.

4. The oil soluble lubricant additive package as in claim 3, wherein said overbased metal phenate is selected from the group consisting of: overbased calcium phenate and overbased magnesium phenate.

5. The oil soluble lubricating additive package as in claim 1, wherein at least one of said at least one detergent is selected from the group consisting of calcium sulfonate, magnesium sulfonate, sodium sulfonate, non-sulfurized Mannich phenates, sulfurized phenates, salicylates, overbased saligenin, and combinations thereof.

6. A lubricating oil comprising the oil soluble lubricant additive package of claim 1, wherein said lubricating oil has a total base number of less than about 10, and at least one property selected from the group consisting of: a sulfur content less than about 0.3 wt%, a phosphorus content of less than about 0.11 wt%, and an ash content less than about 1.2 wt%.

7. A machine lubricated by the lubricating oil of claim 6.

8. The machine lubricated by the lubricating oil of claim 7, wherein said machine is selected from the group consisting of: gas engines, diesel engines, turbine engines, automatic transmissions, manual transmissions, hypoid axles, and gear boxes.

9. A vehicle comprising the oil soluble lubricant additive package of claim 1.

10. A method for lubricating an engine crankcase, said method comprising the step of:

at least partially filling said crankcase with a lubricant comprising the oil soluble lubricant additive package of claim 1.

11. A method for lubricating moving parts of a machine, said method comprising the step of:

contacting at least one said moving part with a lubricant comprising the oil soluble lubricant additive package as in claim 1.

12. The method for lubricating moving parts of a machine as in claim 11, wherein said machine is selected from the group consisting of: gas engines, diesel engines, turbine engines, automatic transmissions, manual transmissions, hypoid axles, and gear boxes.

13. An oil soluble lubricant additive package comprising:

an overbased metal phenate having a total base number of from about 120 to about 360; and

at least one dispersant, wherein the weight ratio of said overbased metal phenate to said dispersant is from about 1:4 to about 1:12.

14. The oil soluble lubricant additive package as in claim 13, wherein said oil soluble lubricant additive package has a sulfur content and a phosphorus content sufficient to yield a lubricating oil having a sulfur content less than about 0.3 wt% and a phosphorus content of less than about 0.11 wt%.

15. The oil soluble lubricant additive package as in claim 13, wherein said at least one overbased metal phenate is an overbased calcium phenate.

16. The oil soluble lubricant additive package as in claim 15, wherein said overbased metal phenate is selected from the group consisting of: overbased calcium phenate and overbased magnesium phenate.

17. The oil soluble lubricant additive package as in claim 13, wherein said at least one dispersant has a molecular weight of from about 1000 to about 6000.

18. The oil soluble lubricant additive package as in claim 13, wherein said at least one dispersant is a maleic anhydride functionalized polyisobutylene polymer that has been reacted with a polyamine.

19. The oil soluble lubricant additive package as in claim 13, wherein said at least one dispersant is a product of a Mannich reaction.

20. The oil soluble lubricant additive package as in claim 13, where in said at least one dispersant is an ethylene-propylene type dispersant.

21. The oil soluble lubricant additive package as in claim 13, additionally comprising at least one component selected from the group consisting of: viscosity index improvers and pour point depressants.

22. A lubricating oil comprising the oil soluble lubricant additive package of claim 13, wherein said lubricating oil has a total base number of less than about 10, and at least one property selected from the group consisting of: a sulfur content less than about 0.3 wt%, a phosphorus content of less than about 0.11 wt%, and an ash content less than about 1.2 wt%.

23. A machine lubricated by the lubricating oil of claim 13.

24. The machine lubricated by the lubricating oil of claim 23, wherein said machine is selected from the group consisting of: gas engines, diesel engines, turbine engines, automatic transmissions, manual transmissions, hypoid axles, and gear boxes.

25. A vehicle comprising the oil soluble lubricant additive package of claim 13.

26. A method for lubricating an engine crankcase, said method comprising the step of:

at least partially filling said crankcase with a lubricant comprising the oil soluble lubricant additive package of claim 13.

27. A method for lubricating moving parts of a machine, said method comprising the step of:

contacting at least one said moving part with a lubricant comprising the oil soluble lubricant additive package of claim 13.

28. The method for lubricating moving parts of a machine as in claim 27, wherein said machine is selected from the group consisting of: gas engines, diesel engines, turbine engines, automatic transmissions, manual transmissions, hypoid axles, and gear boxes.

29. An oil soluble lubricating additive package comprising:

an overbased metal phenate having a total base number of from about 120 to about 360; and

at least one antioxidant, wherein the weight ratio of overbased metal phenate to antioxidant is from about 10:1 to about 1:3.

30. The oil soluble lubricant additive package as in claim 29, wherein said oil soluble lubricant additive package has a sulfur content and a phosphorus content sufficient to yield a lubricating oil having a sulfur content less than about 0.3 wt% and a phosphorus content of less than about 0.11 wt%.

31. The oil soluble lubricant additive package as in claim 29, wherein said overbased metal phenate is an overbased calcium phenate.

32. The oil soluble lubricant additive package as in claim 31 wherein said overbased metal phenate is selected from the group consisting of: overbased calcium phenate and overbased magnesium phenate.

33. The oil soluble lubricant additive package as in claim 29 wherein at least one of said at least one antioxidant is selected from the group consisting of: zinc dialkyldithiophosphates, alkylated diphenylamines, sulfurized olefins, phenols, hindered phenols, and sulfurized phenols.

34. A lubricating oil comprising the oil soluble lubricant additive package of claim 29, wherein said lubricating oil has a total base number of less than about 10, and at least one property selected from the group consisting of: a sulfur content less than about 0.3 wt%, a phosphorus content of less than about 0.11 wt%, and an ash content less than about 1.2 wt%.

35. A machine lubricated by the lubricating oil of claim 34.

36. The machine of claim 35, wherein said machine is selected from the group consisting of: gas engines, diesel engines, turbine engines, automatic transmissions, manual transmissions, hypoid axles, and gear boxes.

37. A vehicle comprising the oil soluble lubricant additive package of claim 29.

38. A method for lubricating an engine crankcase, said method comprising the step of:

at least partially filling said crankcase with a lubricant comprising the oil soluble lubricant additive package of claim 29.

39. A method for lubricating moving parts of a machine, said method comprising the step of:

contacting at least one said moving part with a lubricant comprising the oil soluble lubricant additive package as in claim 29.

40. The method of claim 39, wherein said machine is selected from the group consisting of: gas engines, diesel engines, turbine engines, automatic transmissions, manual transmissions, hypoid axles, and gear boxes.

41. An oil soluble lubricant additive package comprising:

an overbased calcium phenate having a total base number of at least 120; and at least one component selected from the group consisting of: detergents, dispersants, antioxidants, friction modifiers, viscosity index improvers, and pour point depressants.

42. The oil soluble lubricant additive package as in claim 41, wherein said oil soluble lubricant additive package has at least one property selected from the group consisting of: a sulfur content less than about 3 wt% and a phosphorus content less than about 1.2 wt%.

43. The oil soluble lubricant additive package as in claim 41 wherein said oil soluble lubricant additive package is essentially free of non-sulfurized Mannich phenate.

44. A lubricating oil comprising the oil soluble lubricant additive package of claim 41, wherein said lubricating oil has a total base number of less than about 10, and at least one property selected from the group consisting of: a sulfur content less than about 0.3 wt%, a phosphorus content of less than about 0.11 wt%, and an ash content less than about 1.2 wt%.

45. A machine lubricated by the lubricating oil of claim 44.

46. The machine lubricated by the lubricating oil of claim 44, wherein said machine is selected from the group consisting of: gas engines, diesel engines, turbine engines, automatic transmissions, manual transmissions, hypoid axles, and gear boxes.

47. A vehicle comprising the oil soluble lubricating additive package of claim 41.

48. A method for lubricating an engine crankcase, said method comprising the step of:

at least partially filling said crankcase with a lubricant comprising the oil soluble lubricant additive package of claim 41.

49. A method for lubricating moving parts of a machine, said method comprising the step of:

contacting at least one said moving part with a lubricant comprising the oil soluble lubricant additive package as in claim 41.

50. The method for lubricating moving parts of a machine as in claim 49, wherein said machine is selected from the group consisting of: gas engines, diesel engines, turbine engines, automatic transmissions, manual transmissions, hypoid axles, and gear boxes.

51. A method of achieving a low sulfur, low ash, and low phosphate oil formulation, said method comprising:

providing an oil soluble lubricant additive package, said oil soluble lubricant additive package comprising an overbased metal phenate having a total base number of from about 120 to about 360; and

admixing said oil soluble lubricant additive package with at least a base oil so as to form a lubricating oil having a total base number of less than about 10, and at least one property selected from the group consisting of: a sulfur content less than about 0.3 wt%, a phosphorus content of less than about 0.11 wt%, and an ash content less than about 1.2 wt%.

52. The method of claim 51, wherein said overbased metal phenate is selected from the group consisting of: overbased calcium phenate and overbased magnesium phenate.

53. The method of claim 51, wherein said lubricating oil additionally comprises at least one additive selected from the group consisting of: detergents, dispersants, antioxidants, friction modifiers, viscosity index improvers, and pour point depressants.