(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 1 792 969 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
06.06.2007 Bulletin 2007/23

(21) Application number: **06255465.4**

(22) Date of filing: **24.10.2006**

(51) Int Cl.:
C10M 163/00 *(2006.01)* *C10N 10/02* *(2006.01)*
C10N 40/25 *(2006.01)*

(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

(30) Priority: **02.12.2005 US 293560**

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(54) **A lubricating oil composition comprising a lithium containing detergent for reducing catalyst poisoning**

(57) The present invention is directed to a lubricating oil composition comprising (a) an oil of lubricating viscosity (b) a lithium-containing detergent (c) a detergent other than a lithium-containing detergent (d) an amine-containing anti-oxidant (e) an ethylene carbonate treated dispersant and (f) a phosphorus-containing anti-wear agent, wherein the lubricating oil composition contains no more than 0.1 weight percent of lithium and no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a calcium-containing detergent. The present invention is also directed to method for reducing catalyst poisoning in exhaust after treatment systems in internal combustion engines, which comprises operating the engine with the lubricating oil compositions of the present invention.

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Description

FIELD OF THE INVENTION

[0001] The present invention is directed to a lubricating oil composition comprising (a) a major amount of an oil of lubricating viscosity (b) one or more lithium-containing detergents (c) one or more detergents other than a lithium-containing detergent (d) one or more anti-oxidants (e) one or more dispersants and (f) one or more anti-wear agents, wherein the lubricating oil composition contains no more than 0.1 weight percent of lithium-containing detergents and no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a calcium-containing detergent. The present invention is also directed to a lubricating oil composition comprising (a) an oil of lubricating viscosity (b) a lithium-containing detergent (c) a detergent other than a lithium-containing detergent (d) an amine-containing anti-oxidant (e) an ethylene carbonate treated dispersant and (f) a phosphorus-containing anti-wear agent, wherein the lubricating oil composition contains no more than 0.1 weight percent of lithium and no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a calcium-containing detergent. The present invention is also directed to a method for reducing catalyst poisoning in exhaust after treatment systems in internal combustion engines, which comprises operating the engine with the lubricating oil compositions of the present invention.

BACKGROUND OF THE INVENTION

[0002] Future internal combustion engines will be equipped with exhaust gas after-treatment systems to allow them to comply with future emission legislation. Some of these systems have proven to be sensitive to the combustion products of the fuel and the lubricant used in the engine. Certain types of systems are sensitive to phosphorus coming from the lubricant, others are sensitive to sulfur coming from both the fuel and the lubricant, yet others are sensitive to sulfated ash resulting from the combustion of the fuel and the lubricant. In order to ensure the durability of these different types of after-treatment systems, special lubricants are being developed that feature low levels of sulfated ash, sulfur and phosphorus. The most common of these lubricants provide low sulfated ash levels with reduced sulfur and phosphorus. Less common are low or no phosphorus lubricants that use specific, mostly sulfur or molybdenum based, zinc di-alkyl di-thiophosphate-replacement additives.

[0003] The guidelines for low emission internal combustion engine lubricants that will be commercialized in 2007 and 2008 are : (1) the sulfated ash must be equal to or lower than 1.0 weight percent for diesel engine lubricating oils and equal to or lower than 0.5 weight percent for passenger car diesel engine lubricating oils, (2) according to some engine builders, sulfur content of the lubricating oil must be less than 0.2 weight percent, while other engine builders allow up to a maximum of 0.4 weight percent, and (3) some engine builders require the maximum amount of phosphorus to be 0.08 weight percent, while other engine builders allow up to 0.12 weight percent of phosphorus. The reduction of sulfated ash closes the gap between diesel engine lubricating oils and gasoline and natural gas engine lubricating oils, so the use of low phosphorus, low sulfur and low sulfated ash engine lubricating oils will also be expanded to include gasoline and natural gas engine lubricating oils.

[0004] The first generations of low emission internal combustion engine lubricating oils were formulated to meet the above guidelines using low levels of detergent and zinc di-alkyl di-thiophosphate. However, the expectation is that at some point in the future, the maximum sulfur and phosphorus content may be further reduced beyond where we expect the industry to go between now and 2010. Lubricating oils with low phosphorus were expected to provide some wear protection, but they were also expected to poison the oxidation catalysts. In an attempt to explore the possibility of reducing catalyst poisoning while maintaining wear control, we developed experimental lubricating oils comprising detergents containing lithium salts of sulfurized phenates. Catalyst poisoning measurements were performed with these experimental lubricating oils employing lithium-containing phenates in an internal combustion engine and the results unexpectedly showed reduction in catalyst poisoning compared to lubricating oils employing detergents containing calcium salts of sulfurized phenates. Since the phosphorus content of both lubricating oils was the same, this result was surprising because it showed that catalyst poisoning could be reduced while maintaining wear control if a lithium-containing phenate was employed in the lubricating oil composition instead of a calcium-containing detergent.

[0005] A number of patents and patent applications have discussed methods for reducing catalyst poisoning by reducing the phosphorus content of the lubricating oil, but none have disclosed a lubricating oil composition comprising (a) a major amount of an oil of lubricating viscosity and (b) one or more lithium-containing detergents (c) one or more detergents other than a lithium-containing detergent (d) one or more anti-oxidants (e) one or more dispersants and (f) one or more anti-wear agents, which lubricating oil despite containing phosphorus, provides significant reduction in catalyst poisoning while maintaining good wear control.

[0006] U. S. Patent No. 4,330,420 discloses low ash, low phosphorus motor oils having improved oxidation stability as a result of the addition thereto of synergistic amounts of a di-alkyl di-phenylamine antioxidant and a sulfurized polyolefin.

The synergy between the two additives compensates for the decreased amount of phosphorus in the form of zinc dithiophosphate such that the oils retain an SE quality rating.

[0007] U. S. Patent No. 4,797,217 discloses overbased additives containing lithium sulfonates suitable for use in lubricants and fuels and the process for their preparation. The TBN of the sulfonates is at least 250 milligrams KOH per gram.

[0008] U. S. Patent No. 5,0303,687 discloses alkylsalicylate-containing detergent-dispersant additives for lubricating oil obtained by (a) neutralizing an alkylphenol by means of an alkali metal hydroxide; (b) carboxylation of the product with carbon dioxide for maximum conversion of the initial alkali metal alkylphenate into alkali metal alkylsalicylate; (c) sulfurization-superalkalinization of the product in the presence of an alkaline earth base followed by carbonation of the product with carbon dioxide.

[0009] U. S. Patent No. 5,804,537 discloses a low phosphorus passenger car motor oil containing an oil of lubricating viscosity as the major component and an tri-metal detergent mixture as a minor component, wherein the tri-metal detergent mixture comprises at least one calcium overbased metal detergent, at least one magnesium overbased metal detergent and at least one sodium overbased metal detergent, wherein the tri-metal detergent mixture is present in the lubricating oil composition in an amount such that the total TBN contributed to the oil is from about 2 to about 12.

[0010] U. S. Patent No. 6,235,688 discloses non-thixotropic, sodium-free lubricant additive having from 10 percent to 50 percent of a liquid organic diluent and from 30 percent to 90 percent of a substituted hydrocarbyl metal salt. At least 30 mole percent of the metal in the metal salt is lithium, and the salt is essentially free of sodium. The BN of the non-thixotropic lubricant additive attributable to the lithium is less than 150. This additive is useful for decreasing black sludge deposits and piston deposits.

[0011] European Patent Application No. 96301587.0 (Publication No. EP 0 731 159 A2) discloses a lubricant additive concentrate which comprises a base oil of lubricating viscosity and: (a) at least one non-lithium oil-soluble overbased alkali or alkaline earth metal-containing overbased detergent; and (b) at least one oil-soluble overbased lithium salt detergent typically having a TBN in the range of 240 to 400.

[0012] U. S. Patent Application No. 10/744,871 (Publication No. US 2005/0137100 A1) discloses a lubricating oil composition comprises at least one alkali metal overbased detergents as lubricating additives effective for the lubrication of mechanical components in land and marine engines. The alkali metal overbased detergents may be sulfurized and may comprise at least 80 weight percent alkylhydroxybenzoate and the preferred alkali metal is potassium. The lubricating oil composition provides improved thermal stability and black sludge deposit control.

[0013] U. S. Patent Application No. 10/745,125 (Publication No. US 2005/0137098 A1) discloses overbased detergents as lubricating oil additives effective for the lubrication of mechanical components in land and marine engines, such as for example, hydraulic systems, transmissions, two-stroke and four-stroke vehicular engines, trunk piston and two-stroke crosshead marine engines. The overbased detergents lead to improved detergency and thermal stability performance versus high overbased sulfonates. Moreover, they are more compatible with commercial phenates than conventional sulfonates.

[0014] International Application No. PCT/US92/01476 (Publication No. WO 92/18587) discloses a composition comprising at least one basic alkali metal salt of at least one hydrocarbyl-substituted acidic organic compound, wherein the hydrocarbyl group is derived from a polyalkylene having an Mn of at least 600, provided that when the organic compound is a sulfonic acid, the polyalkylene has a Mn of at least 900; and provided that when the acidic organic compound is a mixture of acidic organic compounds containing a carboxylic acid and a sulfonic acid which has a hydrocarbyl group derived from a polyalkylene having an Mn of less than 900, then the carboxylic acid comprises at least 10 % of the equivalents of the mixture.

[0015] International Application No. PCT/EP95/02271 (Publication No. WO 95/34619) discloses lubricating oils containing certain ashless dispersants comprising an oil soluble polymeric hydrocarbon backbone having functional groups in which the hydrocarbon backbone is derived from an ethylene alpha-olefin (EAO) copolymer or alpha-olefin homo or copolymer having > 30 % of terminal vinylidene unsaturation and an Mn of 500 to 7,000, in combination with overbased alkali metal additives. It particularly concerns crankcase lubricants having excellent properties of sludge and varnish control, giving good engine cleanliness and yet resistant to oxidation and/or with reduced tendency to thickening due to interactions in the package.

SUMMARY OF THE INVENTION

[0016] The present invention is directed to a lubricating oil composition comprising (a) a major amount of an oil of lubricating viscosity (b) one or more lithium-containing detergents (c) one or more detergents other than a lithium-containing detergent (d) one or more anti-oxidants (e) one or more dispersants and (f) one or more anti-wear agents, wherein the lubricating oil composition contains no more than 0.1 weight percent of lithium-containing detergents and no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a calcium-containing detergent. The present invention is also directed to a lubricating oil composition comprising (a) an oil of

lubricating viscosity (b) a lithium-containing detergent (c) a detergent other than a lithium-containing detergent (d) an amine-containing anti-oxidant (e) an ethylene carbonate treated dispersant and (f) a phosphorus-containing anti-wear agent, wherein the lubricating oil composition contains no more than 0.1 weight percent of lithium and no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a calcium-containing detergent. The present invention is also directed to a method for reducing catalyst poisoning in exhaust after treatment systems in internal combustion engines, which comprises operating the engine with the lubricating oil compositions of the present invention.

[0017] Specifically, the present invention is directed to a lubricating oil composition comprising:

(a) a major amount of an oil of lubricating viscosity;

(b) a lithium-containing detergent;

(c) one or more detergents other than a lithium-containing detergent;

(d) one or more anti-oxidants;

(e) one or more dispersants; and

(f) one or more anti-wear agents;

wherein the lubricating oil composition contains no more than 0.1 weight percent of lithium and no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a calcium-containing detergent.

[0018] In the above lubricating oil composition of the present invention, preferably the concentration of the lithium is less than 0.08 weight percent based on the total weight of the lubricating oil composition. More preferably the concentration of the lithium is less than 0.07 weight percent based on the total weight of the lubricating oil composition, and most preferably the concentration of the lithium is less than 0.05 based on the total weight of the lubricating oil composition.

[0019] Preferably the lubricating oil composition of the present invention has a low sulfur and sulfated ash content.

[0020] Preferably the phosphorus content of the lubricating oil composition of the present invention is in the range of 0.03 weight percent to about 0.12 weight percent based on the total weight of the lubricating oil composition. More preferably the phosphorus content of the lubricating oil composition of the present invention is in the range of 0.05 weight percent to about 0.1 weight percent based on the total weight of the lubricating oil composition. Most preferably the phosphorus content of the lubricating oil composition of the present invention is in the range of 0.07 weight percent to about 0.09 weight percent based on the total weight of the lubricating oil composition.

[0021] Examples of the preferred low and medium overbased metal detergents that may be employed in the lubricating oil composition of the present invention are low and medium overbased phenates, sulfurized phenates, aromatic sulfonates, salicylates, sulfurized salicylates or Mannich condensation products of alkylphenols, aldehydes and amines. More preferred are low and medium overbased phenates and sulfurized phenates. These detergents may be alkali metal detergents or alkaline earth metal detergents, provided the alkaline earth metal is not calcium. Preferably they are alkali metal detergents and more preferably they are medium overbased lithium detergents. The TBN of these detergents is greater than 1 and less than 200. The lithium-containing detergents may be prepared using the procedures described in U.S. patent No. 6,235,688 or by any procedure known to a person skilled in the art.

[0022] Preferably the concentration of the lithium in the lithium-containing detergent employed in the lubricating oil of the present invention is in the range of from about 0.5 weight percent to about 2.5 weight percent based on the total weight of the lithium-containing detergent. More preferably the concentration of the lithium in the lithium-containing detergent is in the range of from about 1.0 weight percent to about 2.0 weight percent based on the total weight of the lithium-containing detergent. Most preferably the concentration of the lithium in the lithium-containing detergent is in the range of from about 1.3 weight percent to about 1.75 weight percent based on the total weight of the lithium-containing detergent.

[0023] Preferred examples of anti-oxidants employable in the lubricating oil of the present invention are diphenylamine-type compounds, which include but are not limited to, alkylated diphenylamine, phenyl-alpha-naphthylamine, and alkylated-alpha-naphthylamine. Also useful anti-oxidants are esters of thiodicarboxylic acids, di-thiocarbamates, such as 15-methylenebis(di-butyl dithiocarbamate), salts of di-thiophosphoric acids, alkyl or aryl phosphates. Molybdenum compounds, such as amine-molybdenum complex compound and molybdenum di-thiocarbamates may also be used as anti-oxidants and hindered phenols, such as 4,4'-methylene-bis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-tert-butylphenol), 4,4'-butylidene-bis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidene-bis(2,6-di-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-nonylphenol), 2,2'-isobutylidene-bis(4,6-dimethylphenol), 2,2'-5-methylene-bis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methylphe-

nol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butyl-phenol, 2,6-di-tert-I-dimethylamino-p-cresol, 2,6-di-tert-4-(N,N'-dimethylaminomethylphenol), 4,4'-thiobis(2-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), bis(3-methyl-4-hydroxy-5-tert-10-butylbenzyl)-sulfide, and bis(3,5-di-tert-butyl-4-hydroxybenzyl). More preferred are diphenylamine-type compounds, and most preferred are alkylated di-phenylamines.

[0024] Preferred dispersants that may be employed in the lubricating oil composition of the present invention are ashless dispersants. Examples of ashless dispersants are alkenyl succinimides and succinamides. These dispersants can be further modified by reaction with, for example, with boron or ethylene carbonate. Ester-based ashless dispersants derived from long chain hydrocarbon-substituted carboxylic acids and hydroxy compounds may also be employed. More preferred ashless dispersants are those derived from polyisobutenyl succinic anhydride, and the most preferred are ethylene carbonate treated polyisobutenyl succinic anhydride derived dispersants.

[0025] Examples of anti-wear agents include, but are not limited to, phosphates and thiophosphates and salts thereof, carbamates, esters, and molybdenum complexes. Preferred anti-wear agents included in the lubricating oil composition of the present invention are metal di-alkyl di-thiophosphates. However, it may be advantageous to control the amount of this additive because of its metal and phosphorus contribution to the lubricating oil. Examples of metal di-alkyl di-thiophosphates are zinc and molybdenum salts of di-alkyl di-thiophosphates. Most preferred anti-wear agents employed in the lubricating oil composition of the present invention are zinc di-alkyl di-thiophosphates.

[0026] Another embodiment of the present invention is directed to a lubricating oil composition comprising:

(a) a major amount of an oil of lubricating viscosity;

(b) a lithium-containing detergent;

(c) one or more detergents other than a lithium-containing detergent;

(d) a amine-containing anti-oxidant;

(e) an ethylene carbonate treated dispersant; and

(f) a phosphorus-containing anti-wear agent;

wherein the lubricating oil composition contains no more than 0.1 weight percent of lithium and no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a calcium-containing detergent.

[0027] The above lubricating oil compositions may also employ one or more additives selected from one or more detergents different from those recited in (b), provided the alkaline earth metal is not calcium, anti-oxidants different from those recited in (c), dispersants different from those recited in (d), anti-wear agent different from those recited in (e), viscosity index improvers, ashless sulfur extreme pressure agents, alkaline earth metal and alkali metal borated extreme pressure agents, molybdenum-containing extreme pressure agents, pour point depressants, rust inhibitors, corrosion inhibitors, ash-containing friction modifiers, ashless friction modifiers, molybdenum-containing friction modifiers, metal deactivators, seal swell agents, demulsifiers and anti-foaming agents.

[0028] Preferably the lubricating oil composition of the above embodiment has low sulfur and sulfated ash.

[0029] Another embodiment of the present invention is directed to a lubricating oil concentrate comprising:

(a) about 10 weight percent to about 90 weight percent of an oil of lubricating viscosity;

(b) a lithium-containing detergent;

(c) one or more detergents other than a lithium-containing detergent;

(d) one or more anti-oxidants;

(e) one or more ash-containing dispersants; and

(f) one or more anti-wear agents;

wherein the lubricating oil concentrate contains no more than 0.1 weight percent of lithium and no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a calcium-containing detergent.

[0030] The above lubricating oil concentrate may also employ one or more additives selected from one or more detergents, different from those recited in (b), provided the alkaline earth metal is not calcium, anti-oxidants different

from those recited in (c), dispersants s different from those recited in (d), anti-wear agent different from those recited in (e), viscosity index improvers, ashless sulfur extreme pressure agents, alkaline earth metal and alkali metal borated extreme pressure agents, molybdenum-containing extreme pressure agents, pour point depressants, rust inhibitors, corrosion inhibitors, ash-containing friction modifiers, ashless friction modifiers, molybdenum-containing friction modifiers, metal deactivators, seal swell agents, demulsifiers and anti-foaming agents.

[0031] Another embodiment of the present invention is directed to a lubricating oil concentrate comprising:

(a) a major amount of an oil of lubricating viscosity;

(b) a lithium-containing detergent;

(c) one or more detergents other than a lithium-containing detergent;

(d) an amine- containing anti-oxidant;

(e) an ethylene carbonate treated dispersant;

(f) a phosphorus-containing anti-wear agent; and

(g) one or more additives selected from one or more detergents, different from those recited in (b), provided the alkaline earth metal is not calcium, anti-oxidants different from those recited in (c), dispersants s different from those recited in (d), anti-wear agent different from those recited in (e), viscosity index improvers, ashless sulfur extreme pressure agents, alkaline earth metal and alkali metal borated extreme pressure agents, molybdenum-containing extreme pressure agents, pour point depressants, rust inhibitors, corrosion inhibitors, ash-containing friction modifiers, ashless friction modifiers, molybdenum-containing friction modifiers, metal deactivators, seal swell agents, demulsifiers and anti-foaming agents;

wherein the lubricating oil composition contains no more than 0.1 weight percent of lithium and no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a calcium-containing detergent.

[0032] A further embodiment of the present invention is directed to a method for reducing catalyst poisoning in exhaust after treatment systems in internal combustion engines, which comprises operating the engine with a lubricating oil composition comprising:

(a) a major amount of an oil of lubricating viscosity;

(b) a lithium-containing detergent;

(c) one or more detergents other than a lithium-containing detergent;

(d) an-amine-containing anti-oxidants;

(e) an ethylene carbonate treated dispersant; and

(f) a phosphorus-containing anti-wear agent;

wherein the lubricating oil composition contains no more than 0.1 weight percent of lithium and no more than 0.12 weight percent phosphorus, provided the lubricating oil composition does not contain a calcium-containing detergent.

[0033] In the above a method for reducing catalyst poisoning in internal combustion engines the engines are diesel engines, gasoline engines and natural gas engines.

[0034] The lubricating oil composition in the above embodiment may also employ one or more additives selected from one or more detergents, different from those recited in (b), provided the alkaline earth metal is not calcium, anti-oxidants different from those recited in (c), dispersants s different from those recited in (d), anti-wear agent different from those recited in (e), viscosity index improvers, ashless sulfur extreme pressure agents, alkaline earth metal and alkali metal borated extreme pressure agents, molybdenum-containing extreme pressure agents, pour point depressants, rust inhibitors, corrosion inhibitors, ash-containing friction modifiers, ashless friction modifiers, molybdenum-containing friction modifiers, metal deactivators, seal swell agents, demulsifiers and anti-foaming agents.

DETAILED DISCRIPTION OF THE INVENTION

DEFINITIONS

[0035] As used herein, the following terms have the following meanings unless expressly stated to the contrary:

[0036] The term "alkali metal" as used herein refers to Group IA metals of the Periodic Table.

[0037] The term "alkaline earth metal" as used herein refers to Group II metals of the Periodic Table, such as magnesium, and provided the alkaline earth metal is not calcium.

[0038] The term "overbased" as used herein refers to alkali metal and alkaline earth metal alkyl sulfonates in which the ratio of the number of equivalents of an alkali metal or alkaline earth metal to the number of equivalents of the organic moiety is greater than 1. Low overbased refers to alkali metal or alkaline earth metal alkyl sulfonates having a Total Base Number (TBN) greater than 1 and less than 20, medium overbased refers to alkali metal or alkaline earth metal alkyl sulfonates having a TBN greater than 20 and less than 200. High overbased refers to alkali metal or alkaline earth metal alkyl sulfonates having a TBN greater than 200.

[0039] The term "sulfated ash" as used herein refers to the non-combustible residue resulting from detergents and metallic additives in lubricating oil. Sulfated ash may be determined using ASTM Test D874.

[0040] The term "Total Base Number" or "TBN" as used herein refers to the amount of base equivalent to milligrams of KOH in one gram of sample. Thus, higher TBN numbers reflect more alkaline products, and therefore a greater alkalinity. TBN was determined using ASTM D 2896 test.

[0041] Unless otherwise specified, all percentages are in weight percent.

LUBRICATING OIL COMPOSITION

[0042] It has been discovered that the lubricating oil composition of the present invention provides a reduction in catalyst poisoning while maintaining wear control. Wear control in conventional lubricating oil compositions is achieved by the addition of metal salts of di-alkyl di-thiophosphates, for example zinc di-alkyl di-thiophosphates. However, the phosphorus in the di-alkyl di-thiophosphates causes inactivation of oxidation catalysts used in exhaust after-treatment devices. The lubricating oil composition of the present invention provides reduction in catalyst poisoning even though it contains the same amount of phosphorus as the comparative example. It is conventional wisdom that phosphorus-containing additives in lubricating oil poison catalysts, what is not known is that the lithium-containing phenate is capable of reducing catalyst poisoning even in the presence of phosphorus.

[0043] The lubricating oil composition of the present invention may be prepared by simple blending or mixing of the compounds described in more detail below. These compounds may also be preblended as a concentrate or package with various other additives in appropriate ratios to facilitate blending of a lubricating oil composition containing the desired concentration of additives.

Oil of Lubricating Viscosity

[0044] Oil of lubricating viscosity, or base oil as used herein refer to lubricating oils which may be mineral oil or synthetic oils of lubricating viscosity and preferably useful in the crankcase of an internal combustion engine. Crankcase lubricating oils ordinarily have a viscosity of about 1300 centistokes at -17.8°C to 22.7 centistokes at 98.9°C.

[0045] The lubricating oils may be derived from synthetic or natural sources. Mineral oil for use as the base oil in this invention includes paraffinic, naphthenic and other oils that are ordinarily used in lubricating oil compositions. Synthetic oils include hydrocarbon synthetic oils and synthetic esters. Useful synthetic hydrocarbon oils include liquid polymers of alpha-olefins having the proper viscosity. Especially useful are the hydrogenated liquid oligomers of C_6 to C_{12} alpha-olefins such as 1-decene trimer. Similarly, alkyl benzenes of proper viscosity, such as didodecyl benzene, may be used. Useful synthetic esters include the esters of both mono-carboxylic acids and polycarboxylic acids as well as mono-hydroxy alkanols and polyols. Typical examples are didodecyl adipate, pentaerthritol tetracapoate, di-2-ethylhexyl adipate, di-laurylsebacate and the like. Complex esters prepared from mixtures of mono- and dicarboxylic acid and mono- and di-hydroxy alkanols can also be used.

[0046] Blends of hydrocarbon oils and synthetic oils may also be used. For example, blends of 10 weight percent to 25 weight percent hydrogenated 1-decene trimer with 75 weight percent to 90 weight percent 683 centistokes at 37.8°C mineral oil gives an excellent oil base. Fischer-Tropsch derived base oils may also be employed in the lubricating oil composition of the present invention.

[0047] It is further contemplated that the oil of lubricating viscosity employed for preparing the lubricating oil composition of the present invention is a low sulfur base oil. Use of a low sulfur base oil assists in obtaining a lubricating oil composition which is ultra low in sulfur content. Sulfur content of base oils is well known by persons skilled in the art, thus, selection of a low sulfur base oil may be conveniently made for the purpose of the present invention.

Low and Medium Overbased Metal Detergents

[0048] Examples of the preferred low and medium overbased metal detergents that may be employed in the lubricating oil composition of the present invention are low and medium overbased phenates, sulfurized phenates, aromatic sulfonates, salicylates, sulfurized salicylates or Mannich condensation products of alkylphenols, aldehydes and amines. More preferred are low and medium overbased phenates and sulfurized phenates. These detergents may be alkali metal detergents or alkaline earth metal detergents, provided the alkaline earth metal is not calcium. Preferably they are alkali metal detergents and more preferably they are medium overbased lithium detergents. The TBN of these detergents is greater than 1 and less than 200.

[0049] Preferably the concentration of the lithium in the lithium-containing detergent employed in the lubricating oil of the present invention is in the range of from about 0.5 weight percent to about 2.5 weight percent based on the total weight of the lithium-containing detergent. More preferably the concentration of the lithium in the lithium-containing detergent is in the range of from about 1.0 weight percent to about 2.0 weight percent based on the total weight of the lithium-containing detergent. Most preferably the concentration of the lithium in the lithium-containing detergent is in the range of from about 1.3 weight percent to about 1.75 weight percent based on the total weight of the lithium-containing detergent.

[0050] A large number of these detergents are well known in the art and are commercially available. The lithium-containing detergents may be prepared using the procedures described in U.S. patent No. 6,235,688 or by any procedure known to a person skilled in the art.

Anti-oxidants

[0051] Preferred examples of anti-oxidants employable in the lubricating oil of the present invention are diphenylamine-type compounds, which include but are not limited to, alkylated diphenylamine, phenyl-alpha-naphthylamine, and alkylated-alpha-naphthylamine. Also useful anti-oxidants are esters of thiodicarboxylic acids, di-thiocarbamates, such as 15-methylenebis(di-butyl dithiocarbamate), salts of di-thiophosphoric acids, alkyl or aryl phosphates. Molybdenum compounds, such as amine-molybdenum complex compound and molybdenum di-thiocarbamates may also be used as anti-oxidants and hindered phenols, such as 4,4'-methylene-bis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-tert-butylphenol), 4,4'-butylidene-bis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidene-bis(2,6-di-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-nonylphenol), 2,2'-isobutylidene-bis(4,6-dimethylphenol), 2,2'-5-methylene-bis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butyl-phenol, 2,6-di-tert-I-dimethylamino-p-cresol, 2,6-di-tert-4-(N,N'-dimethylaminomethylphenol), 4,4'-thiobis(2-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), bis(3-methyl-4-hydroxy-5-tert-10-butylbenzyl)-sulfide, and bis(3,5-di-tert-butyl-4-hydroxybenzyl). More preferred are diphenylamine-type compounds, and most preferred are alkylated di-phenylamines.

Dispersants

[0052] Preferred dispersants that may be employed in the lubricating oil composition of the present invention are ashless dispersants. Examples of ashless dispersants are alkenyl succinimides and succinamides. These dispersants can be further modified by reaction with, for example, with boron or ethylene carbonate. Ester-based ashless dispersants derived from long chain hydrocarbon-substituted carboxylic acids and hydroxy compounds may also be employed. More preferred ashless dispersants are those derived from polyisobutenyl succinic anhydride, and the most preferred are ethylene carbonate treated polyisobutenyl succinic anhydride derived dispersants. A large number of dispersants are commercially available.

Anti-wear Agents

[0053] Examples of anti-wear agents include, but are not limited to, phosphates and thiophosphates and salts thereof, carbamates, esters, and molybdenum complexes. Preferred anti-wear agents included in the lubricating oil composition of the present invention are metal di-alkyl di-thiophosphates. However, it may be advantageous to control the amount of this additive because of its metal and phosphorus contribution to the lubricating oil. Examples of metal di-alkyl di-thiophosphates are zinc and molybdenum salts of di-alkyl di-thiophosphates. Most preferred anti-wear agents employed in the lubricating oil composition of the present invention are zinc di-alkyl di-thiophosphates.

Other Additives

[0054] The lubricating oil composition of the present invention may also contain, in addition to the additives discussed

above, other additives used to impart desirable properties to the lubricating oil composition of the present invention. Thus, the lubricating oil may contain one or more of additives, such as viscosity index improvers, pour point depressants, demulsifiers, extreme pressure agents and foam inhibitors. These additional additives are described in more detail below.

Viscosity Index Improvers

[0055] Viscosity index improvers are added to lubricating oil to regulate viscosity changes due to the change in temperature. Some commercially available examples of viscosity index improvers are olefin copolymers, such as ethylene-propylene copolymers, styrene-isoprene copolymers, hydrated styrene-isoprene copolymers, polybutene, polyisobutylene, polymethacrylates, vinylpyrrolidone and methacrylate copolymers and dispersant type viscosity index improvers.

Extreme Pressure Agents

[0056] Extreme pressure agents that may be used in the lubricating oil composition of the present invention include alkaline earth metal borated extreme pressure agents and alkali metal borated extreme pressure agents. Extreme pressure agents containing molybdenum may also be employed in the lubricating oil composition of the present invention, provided the molybdenum compounds do not include tri-nuclear molybdenum. Sulfurized olefins, zinc dialky-1-dithiophosphate (primary alkyl, secondary alkyl, and aryl type), diphenyl sulfide, methyl tri-chlorostearate, chlorinated naphthalene, fluoroalkylpolysiloxane, lead naphthenate, neutralized or partially neutralized phosphates, di-thiophosphates, and sulfur-free phosphates. The preferred extreme pressure agents are those that will not contribute to the phosphorus content of the lubricating oil.

Pour Point Depressants

[0057] Polymethyl methacrylate is an example of a pour point depressant useful for addition to the lubricating oil of the present invention.

Rust Inhibitors

[0058] Rust inhibitors include nonionic polyoxyethylene surface active agents, such as polyoxyethylene lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonyl phenyl ether, polyoxyethylene octyl phenyl ether, polyoxyethylene octyl stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol mono-oleate, and polyethylene glycol mono-oleate. Other compounds that may also be employed as rust inhibitors include stearic acid and other fatty acids, dicarboxylic acids, metal soaps, fatty acid amine salts, metal salts of heavy sulfonic acid, partial carboxylic acid ester of polyhydric alcohol, and phosphoric ester. However, preferred rust inhibitors are those that do not contribute to the phosphorus or sulfur content of the lubricating oil.

Corrosion inhibitors

[0059] Corrosion inhibitors are included in lubricating oils to protect vulnerable metal surfaces. Such corrosion inhibitors are generally used in very small amounts in the range of from about 0.02 weight percent to about 1.0 weight percent. Examples of corrosion inhibitors that may be used are sulfurized olefin corrosion inhibitor and the co-sulfurized alkenyl ester/alpha olefin corrosion inhibitor. The corrosion inhibitors should not be a metal di-thiophosphates, especially zinc di-alkyl di-thiophosphate because addition of this corrosion inhibitor will contribute to the zinc, phosphorus and sulfur content of the lubricating oil.

Friction modifiers

[0060] Friction modifiers that are employable in the lubricating oil composition of the present invention, include both ash-containing as well as ashless friction modifiers. Friction modifiers include, but are not limited to, fatty alcohols, fatty acids, such as stearic acid, isostearic acid, oleic acid and other fatty acids or salts and esters thereof, borated esters, amines, phosphates, and di-, and trihydrocarbyl phosphates, hydrocarbyl phosphites and phosphonates, hydrocarbyl phosphites. Friction modifiers may also contain molybdenum, provided the molybdenum compounds do not include tri-nuclear molybdenum. Preferably the friction modifiers used in the lubricating oil composition of the present invention are ashless friction modifiers.

Metal Deactivators

[0061] Metal deactivators that may be employed in the lubricating oil composition of the present invention include but are not limited to di-salicylidene propylenediamine, triazole derivatives, mercaptobenzothiazoles, thiodiazole derivatives, and mercaptobenzimidazoles.

Seal Swell Agents

[0062] The lubricating oil composition of the present invention may employ seal swell agents, including but are not limited to, di-esters such as di-2-ehtylhexylsebacate, di-octyladipate and di-2-ethylhexylphthalate, mineral oils with aliphatic alcohols, such as tri-decyl alcohol and Trisphosphite ester in combination with a hydrocarbonyl-substituted phenol.

Demulsifiers

[0063] Addition product of alkylphenol and ethylene oxide, polyoxyethylene alkyl ether, and polyoxyethylene sorbitan ester may be employed in the lubricating oil composition of the present invention.

Foam Inhibitors

[0064] Useful foam inhibitors for the present invention are alkyl methacrylate polymers, dimethyl silicone polymers and polysiloxane type foam inhibitors.

[0065] For best overall results in terms of affording the properties desired in a conventional lubricating oil composition for lubricating diesel engines, gasoline engines and natural gas engines, the lubricating oil may contain a compatible combination of additives of each of the above classes of additives in effective amounts.

[0066] The various additive materials or classes of materials herein described are well known materials and can be readily purchased commercially or prepared by known procedures or obvious modification thereof.

[0067] In Table I below are given treatment rates for additives contemplated for use in the lubricating oil of the present invention. All component amounts are given as a weight percent of the active additive.

Table I

Component	Range (wt %)	Preferred Range (wt %)	Most Preferred Range (wt %)
Detergents	0 to 10	0.5 to 8	1 to 6
Anti-oxidants	0 to 3.0	0.2 to 2.0	0.2 to 1.5
Dispersants	0 to 12	1 to 10	2 to 8
Anti-wear Agents	0 to 5	0.1 to 3	0.2 to 2
Viscosity Index Improvers	0 to 3	0.2 to 2	0.3 to 1
Extreme Pressure Agents	0 to 2.0	0 to 1.0	0.1 to 0.5
Pour Point Depressants	0 to 1.0	0.05 to 0.5	0.05 to 0.3
Rust Inhibitors	0 to 1.0	0 to 0.75	0.05 to 0.5
Corrosion Inhibitors	0 to 3.0	0.2 to 2.0	0.2 to 1.5
Friction Modifiers	0 to 1.0	0.05 to 0.75	0.1 to 0.5
Foam Inhibitors	0 to 3.0	0.2 to 2.0	0.2 to 1.5

EXAMPLES

[0068] The lubricating oil composition of the present invention was evaluated for its ability to reduce catalyst poisoning in formulations prepared as described in Example 1 and Table I below.

Example 1

[0069] Comparative Formulation A and Test Formulation B contained an amine-containing anti-oxidant, an ethylene

carbonate treated dispersant, a phosphorus-containing anti-wear agent, a viscosity index improver and an anti-foaming agent. Comparative Formulation A also contained a calcium medium overbased sulfurized phenate and Test Formulation B contained a lithium medium overbased sulfurized phenate. Base oil was used to make-up a 100 percent of each of Comparative Formulation A and Test Formulation B.

[0070] The reduction in catalyst poisoning using Test Formulation B containing a lithium medium overbased sulfurized phenate in addition to the other components given above was compared with Comparative Formulation A which contained a calcium medium overbased sulfurized phenate in addition to the other components given above.

[0071] Comparative Formulation A and Test Formulation B are described in more detail in Table II below. The amounts of the components in the lubricating oil formulations are given in Table II in weight percent active additive.

Table II

Component	Formulation (weight %)	
	Comparative Formulation A	Test formulation B
Base Oil	Balance	Balance
Lithium-containing Phenate	0	1.6
Calcium-containing Phenate	1.6	0
Amine-containing Anti-oxidant	0.5	0.5
Ethylene Carbonate treated Dispersant	2.4	2.4
Phosphorus-containing Anti-wear Agent	0.83	0.83
Foam Inhibitor	5 ppm	5 ppm

[0072] Table III below shows the amount of the phosphorus in Comparative Formulation A and Test Formulation B.

Table III

Component	(weight %)	
	Comparative Formulation A	Test Formulation B
Phosphorus	0.093	0.093

Example 2

Catalyst Poisoning

[0073] Reduction in catalyst poisoning in exhaust after treatment systems was determined for Test Formulation B was compared to Comparative Formulation A as described below.

[0074] Catalyst poisoning was determined using a Honda E5 generator set that is equipped with a 0.3 liter, 2-cylinder, OHC engine. The catalyst core was under-sized the engine valve guides were removed to accelerate aging of the catalyst. The catalyst core was placed far enough down stream to prevent sintering. After aging of the catalyst, the core was measured for conversion efficiency and for deposited additive metals using the synthetic gas reactor.

[0075] The gas reactor was operated under three different conditions, lean, rich and perturbated. The perturbated condition most closely simulates the environment of the engine by alternating the gas mixture between lean and rich conditions. The experiment consisted of measurement of conversion efficiency of hydrocarbons, carbon monoxide and nitrous oxides as a function of time and temperature given a pre-determined temperature increase. The temperature increase was designed to simulate the warm-up of the catalytic converter during start-up of the engine. The temperature was increased nonlinearly to a maximum of 425 °C from a baseline temperature of 150°C. After a given temperature is reached, conversion increased rapidly as the catalyst "lights-off." The temperature at which 50 percent conversion (T50) is observed provides a measure of light-off and catalyst poisoning. Thus, lower T50 is positively correlated with conversion and negatively correlated with catalyst poisoning.

[0076] The data reported were T50 at the end of the test. The results of the Catalyst Poisoning Test are summarized in Table IV below.

Table IV

Catalyst Poisoning Test	Comparative Formulation A	Test Formulation B
T50	314°C	294°C

[0077] The results obtained in the Catalyst Poisoning Test summarized above in Table IV show that catalyst poisoning determined by the temperature as the catalyst "lights-off" measured by T50 for Comparative Formulation A containing a calcium medium overbased sulfurized phenate was 314°C, while the T50 measured for Test Formulation B containing a lithium medium overbased sulfurized phenate was 294°C. The data show that the addition of a lithium medium overbased sulfurized phenate to Test Formulation B gave a 7 percent reduction in catalyst poisoning compared to the catalyst poisoning observed with Comparative Formulation A, which contained a calcium medium overbased sulfurized phenate, while maintaining comparable wear control.

[0078] The results of the catalyst poisoning test summarized in Table IV above show that Test Formulation B employing a lithium-containing phenate gave a reduction in catalyst poisoning compared to Comparative Formulation A which contained a calcium-containing phenate. This result was unexpected since the phosphorus content of Test Formulation B and Comparative Formulation A was the same. It is a conventionally known that phosphorus-containing additives in lubricating oils poison catalysts, what is not known is that lithium-containing phenates in lubricating oils are capable of reducing catalyst poisoning even in the presence of phosphorus. Based on conventional wisdom, this was a surprising result.

Claims

1. A lubricating oil composition comprising:

(a) a major amount of an oil of lubricating viscosity;
(b) a lithium-containing detergent;
(c) one or more detergents other than a lithium-containing detergent;
(d) one or more anti-oxidants;
(e) one or more dispersants; and
(f) one or more anti-wear agents;

wherein the lubricating oil composition contains no more than 0.1 weight percent of lithium and no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a calcium-containing detergent.

2. The lubricating oil composition of claim 1, wherein the concentration of the lithium in the lubricating oil composition is less than 0.08 weight percent based on the total weight of the lubricating oil composition.

3. The lubricating oil composition of claim 2, wherein the concentration of the lithium in the lubricating oil composition is less than 0.07 weight percent based on the total weight of the lubricating oil composition.

4. The lubricating oil composition of claim 3, wherein the concentration of the lithium in the lubricating oil composition is 0.05 weight percent based on the total weight of the lubricating oil composition.

5. The lubricating oil composition of claim 1, wherein the phosphorus content is in the range of 0.03 weight percent to about 0.12 weight percent based on the total weight of the lubricating oil composition.

6. The lubricating oil composition of claim 5, wherein the phosphorus content is in the range of 0.05 weight percent to about 0.1 weight percent based on the total weight of the lubricating oil composition.

7. The lubricating oil composition of claim 6, wherein the phosphorus content is in the range of 0.07 weight percent to about 0.09 weight percent based on the total weight of the lubricating oil composition.

8. A lubricating oil composition comprising:

(a) a major amount of an oil of lubricating viscosity;

(b) a lithium-containing detergent;
(c) one or more detergents other than a lithium-containing detergent;
(d) an amine-containing anti-oxidant;
(e) an ethylene carbonate treated dispersant; and
(f) a phosphorus-containing anti-wear agent;

wherein the lubricating oil composition contains no more than 0.1 weight percent of lithium and no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a calcium-containing detergent.

9. The lubricating oil composition of claim 8, wherein the concentration of the lithium in the lubricating oil composition is less than 0.08 weight percent based on the total weight of the lubricating oil composition.

10. The lubricating oil composition of claim 9, wherein the concentration of the lithium in the lubricating oil composition is less than 0.07 weight percent based on the total weight of the lubricating oil composition.

11. The lubricating oil composition of claim 10, wherein the concentration of the lithium-containing detergents in the lubricating oil composition is 0.05 weight percent based on the total weight of the lubricating oil composition.

12. The lubricating oil composition of claim 8, wherein the phosphorus content is in the range of 0.03 weight percent to about 0.12 weight percent based on the total weight of the lubricating oil composition.

13. The lubricating oil composition of claim 12, wherein the phosphorus content is in the range of 0.05 weight percent to about 0.1 weight percent based on the total weight of the lubricating oil composition.

14. The lubricating oil composition of claim 13, wherein the phosphorus content is in the range of 0.07 weight percent to about 0.09 weight percent based on the total weight of the lubricating oil composition.

15. The lubricating oil composition of claim 8, wherein the lithium-containing detergent is a lithium overbased phenate, a lithium overbased sulfurized phenate, an lithium overbased salicylates or a lithium overbased carboxylate.

16. The lubricating oil composition of claim 15, wherein the lithium-containing detergent is a lithium overbased phenate, a lithium overbased sulfurized phenate.

17. The lubricating oil composition of claim 16, wherein the lithium-containing detergent is a lithium overbased sulfurized phenate.

18. The lubricating oil composition of claim 8, wherein the phosphorus-containing anti-wear agent is a metal di-alkyl di-thiophosphate.

19. The lubricating oil composition of claim 18, wherein the metal in the metal di-alkyl di-thiophosphate is zinc.

20. A lubricating oil concentrate comprising:

(a) from about 10 weight percent to about 90 weight percent an oil of lubricating viscosity based on the total weight of the lubricating oil concentrate;
(b) a lithium-containing detergent;
(c) one or more detergents other than a lithium-containing detergent;
(d) an amine-containing anti-oxidant;
(e) an ethylene carbonated treated dispersant; and
(f) a phosphorus-containing anti-wear agent;

wherein the lubricating oil concentrate contains no more than 0.1 weight percent of lithium and no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a calcium-containing detergent.

21. The lubricating oil composition of claim 20, wherein the lithium-containing detergent is a lithium overbased sulfurized phenate.

22. The lubricating oil composition of claim 20, wherein the phosphorus-containing anti-wear agent is zinc di-alkyl dithiophosphate.

23. A method for reducing catalyst poisoning in exhaust after treatment systems in internal combustion engines, which comprises operating the engine with a lubricating oil composition comprising:

(a) a major amount of an oil of lubricating viscosity;
(b) a lithium-containing detergent;
(c) one or more detergents other than a lithium-containing detergent;
(d) an amine-containing anti-oxidant and a phenolic anti-oxidant;
(e) an ethylene carbonate treated dispersant; and
(f) a phosphorus-containing anti-wear agent;

wherein the lubricating oil composition contains no more than 0.1 weight percent of lithium and no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a calcium-containing detergent.

24. The method of claim 23, wherein the internal combustion engines are diesel engines, gasoline engines and natural gas engines.

25. The lubricating oil composition of claim 23, wherein the lithium-containing detergent is a lithium overbased sulfurized phenate.

26. The lubricating oil composition of claim 23, wherein the phosphorus-containing anti-wear agent is zinc di-alkyl dithiophosphate.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 25 5465

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Place of search	Date of completion of the search	Examiner
Munich	19 March 2007	Glod, Guy

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X : particularly relevant if taken alone
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