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

(11) **EP 1 801 191 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
27.06.2007 Bulletin 2007/26

(21) Application number: **06255569.3**

(22) Date of filing: **30.10.2006**

(51) Int Cl.:
C10M 163/00 *(2006.01)* *C10N 10/02* *(2006.01)*
C10N 10/04 *(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: **20.12.2005 US 316105**

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(54) **A lubricating oil composition comprising a mixture of potassium overbased detergent and calcium overbased detergent**

(57) The present invention is directed to a lubricating oil composition comprising (a) a major amount of an oil of lubricating viscosity (b) a mixture of a potassium overbased detergent and a calcium overbased detergent (c) one or more anti-oxidants (d) one or more derivatized succinimide dispersants and (e) one or more anti-wear agents, wherein the lubricating oil composition contains no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a di-alkyl carboxylate. The present invention is also directed to a lubricating oil composition comprising (a) an oil of lubricating viscosity (b) a mixture of a potassium overbased mono-alkyl carboxylate and a calcium overbased alkylaryl sulfonate (c) an amine-containing anti-oxidant (d) an ethylene carbonate treated succinimide dispersant and (e) a phosphorus-containing anti-wear agent, wherein the lubricating oil composition contains no more than 0.1 weight percent of potassium and no more than 0.12 weight percent phosphorus and provided the lubricating oil composition does not contain a di-alkyl carboxylate. 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.

EP 1 801 191 A1

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) a mixture of a potassium overbased detergents and a calcium overbased detergent (c) one or more anti-oxidants (d) one or more derivatized succinimide dispersants and (e) one or more anti-wear agents, wherein the lubricating oil composition contains no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a di-alkyl carboxylate detergent. The present invention is also directed to a lubricating oil composition comprising (a) an oil of lubricating viscosity (b) a mixture of a potassium overbased mono-alkyl carboxylate and a calcium overbased alkylaryl sulfonate (c) one or more anti-oxidants (d) an ethylene carbonate treated succinimide dispersant and (e) one or more anti-wear agents, wherein the lubricating oil composition contains no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a di-alkyl carboxylate 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 mixtures of potassium overbased detergents and calcium overbased detergents. Catalyst poisoning measurements were performed with these experimental lubricating oils employing mixtures of potassium overbased mono-alkyl carboxylates and calcium overbased alkylaryl sulfonates in an internal combustion engine and the results unexpectedly showed reduction in catalyst poisoning compared to lubricating oils employing detergents other than those employed in the lubricating oil of the present invention. Since the phosphorus content of the lubricating oil of the present invention was twice the content of the comparative lubricating oils, this result was surprising because it showed that catalyst poisoning could be reduced while maintaining wear control if a mixture of a potassium overbased mono-alkyl carboxylate and a calcium overbased alkylaryl sulfonate was employed in the lubricating oil composition.

[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) a mixture of a potassium overbased mono-alkyl carboxylate and a calcium overbased alkylaryl sulfonate (c) one or more anti-oxidants (d) one or more derivatized succinimide dispersants and (e) one or more anti-wear agents. The lubricating oil of the present invention, 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 potassium 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. 03813288.2 (Publication No. EP 1 580 257 A1) discloses a lubricating oil additive and a lubricating oil composition wherein no precipitation is generated to exhibit a good storage stability even if a combination of a salicylate detergent and another metal detergent is used. Incorporated into the lubricant base oil are (A) an alkali metal or alkaline earth metal salicylate having at its 3 and 5-positions hydrocarbon groups having 1 to 40 carbon atoms and a perbasic salt, and (B) a metal detergent other than any salicylate detergent.

[0012] 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.

[0013] 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.

[0014] U. S. Patent Application No. 10/714,469 (Publication No. US 2004/0102339 A1) discloses a method of improving the brake and clutch capacity of a functional fluid comprising adding a friction-modifying amount of polyalkenyl sulfonate to the frictional fluid, wherein the polyalkenyl sulfonate is an alkali metal or alkaline earth metal salt of a polyalkylene sulfonic acid derived from a mixture of polyalkylenes comprising greater than about 20 mole percent alkyl vinylidene and 1,1-dialkyl isomers.

[0015] 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.

[0016] 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.

[0017] 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

[0018] The present invention is directed to a lubricating oil composition comprising (a) a major amount of an oil of lubricating viscosity (b) a mixture of a potassium overbased detergent and a calcium overbased detergent (c) one or more anti-oxidants (d) one or more derivatized succinimide dispersants and (e) one or more anti-wear agents, wherein the lubricating oil composition contains no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a di-alkyl carboxylate detergent. The present invention is also directed to a lubricating oil composition comprising (a) an oil of lubricating viscosity (b) a mixture of a potassium overbased mono-alkyl carboxylate and a calcium overbased alkylaryl sulfonate (c) one or more anti-oxidants (d) an ethylene carbonate treated succinimide dispersant and (e) one or more anti-wear agents, wherein the lubricating oil composition contains no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a di-alkyl carboxylate 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.

[0019] Specifically, the present invention is directed to a lubricating oil composition comprising:

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

(b) a mixture of a potassium overbased detergent and a calcium overbased detergent;

(c) one or more anti-oxidants;

(d) one or more derivatized succinimide dispersants; and

(e) one or more anti-wear agents;

wherein the lubricating oil composition contains no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a di-alkyl carboxylate detergent.

[0020] The ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present invention is in the range of from about 0.5:1.0 to about 10:1. Preferably the ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present invention is in the range of from about 1.0:1.0 to about 7. 5:1.0. More preferably ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present invention is in the range of from about 2.0: 1.0 to about 5.0:1.0. Most preferably ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present invention is 3.5:1.

[0021] In the above lubricating oil composition of the present invention, preferably the concentration of the potassium in the potassium overbased detergent is in the range of about 1.0 weight percent to about 10.0 weight percent based on the total weight of the potassium overbased detergent. More preferably the concentration of the potassium in the potassium overbased detergent is in the range of about 1.5 weight percent to about 7.5 weight percent based on the total weight of the potassium overbased detergent, even more preferably the concentration of the potassium in the potassium overbased detergent is in the range of about 2.0 weight percent to about 5.0 weight percent based on the total weight of the potassium overbased detergent. Most preferably the concentration of the potassium in the potassium overbased detergent is in the range of about 2.5 weight percent to about 3.0 weight percent based on the total weight of the potassium overbased detergent.

[0022] Preferably the concentration of the calcium in the calcium overbased detergent employed in the lubricating oil of the present invention is in the range of from about 1.0 weight percent to about 15.0 weight percent based on the total weight of the calcium overbased detergent. More preferably the calcium overbased detergent employed in the lubricating oil of the present invention is in the range of from about 2.0 weight percent to about 10.0 weight percent based on the total weight of the calcium overbased detergent, and even more preferably the calcium overbased detergent employed in the lubricating oil of the present invention is in the range of from about 3.0 weight percent to about 7.5 weight percent based on the total weight of the calcium overbased detergent. Most preferably the concentration of the potassium in the calcium overbased detergent is in the range of from about 4.0 weight percent to about 6.0 weight percent based on the total weight of the calcium overbased detergent.

[0023] 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.

[0024] Examples of the preferred medium overbased metal detergents that may be employed in the lubricating oil composition of the present invention are medium overbased alkylaryl sulfonates, mono-alkyl carboxylate/salicylates, sulfurized salicylates or Mannich condensation products of alkylphenols, aldehydes and amines. More preferred are medium overbased mono-alkyl carboxylates and alkylaryl sulfonates. Preferably they are alkali metal mono-alkyl carboxylates and alkaline earth metal alkylaryl sulfonates and more preferably the detergents are potassium medium overbased mono-alkyl carboxylates and calcium medium overbased alkylaryl sulfonates. Most preferred the detergent is a mixture of a potassium medium overbased mono-alkyl carboxylate and a calcium medium overbased alkylaryl sulfonate. The TBN of these detergents is greater than 1 and less than 200.

[0025] 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'-di-methylaminomethylphenol), 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.

[0026] Preferred dispersants that may be employed in the lubricating oil composition of the present invention are ashless dispersants. Examples of ashless dispersants are derivatized alkenyl succinimides and derivatized alkenyl succinamides. The can be derivatized 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.

[0027] 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.

[0028] 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 mixture of potassium mono-alkyl carboxylate and calcium overbased alkylaryl sulfonate;

(c) a amine-containing anti-oxidant;

(d) an ethylene carbonate treated succinimide dispersant; and

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

wherein the lubricating oil composition contains no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a di-alkyl carboxylate detergent.

[0029] 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 detergent is not a di-alkyl carboxylate, anti-oxidants different from those recited in (c), dispersants different from those recited in (d), provided they are derivatized succinimides or succinamides, 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.

[0030] 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 mixture of a potassium overbased detergent and a calcium overbased detergent;

(c) one or more anti-oxidants;

(d) one or more derivatized succinimides; and

(e) one or more anti-wear agents;

wherein the lubricating oil concentrate contains no more than 0.12 weight percent phosphorus, and provided the lubricating oil concentrate does not contain a di-alkyl carboxylate.

[0031] The above lubricating oil concentrate may also employ one or more additives selected from 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.

[0032] The ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil concentrate of the present invention is in the range of from about 0.5:1.0 to about 10:1. Preferably the ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil concentrate of the present invention is in the range of from about 1.0:1.0 to about 7. 5:1.0. More preferably ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil concentrate of the present invention is in the range of from about 2.0: 1.0 to about 5.0:1.0. Most preferably ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil concentrate of the present invention is 3.5:1.

[0033] 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 mixture of a potassium overbased mono-alkyl carboxylate and a calcium overbased alkylaryl sulfonate;

(c) an amine-containing anti-oxidant;

(d) an ethylene carbonate treated succinimide dispersant;

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

wherein the lubricating oil concentrate contains no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a di-alkyl carboxylate.

[0034] The above lubricating oil concentrate may further comprise one or more additives selected from one or more detergents, different from those recited in (b), provided the detergent is not a di-alkyl carboxylate, anti-oxidants different from those recited in (c), dispersants s different from those recited in (d), provided they are derivatized succinimides or succinamides, 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.

[0035] 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 potassium overbased mono-alkyl carboxylate and a calcium overbased alkylaryl sulfonate;

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

(d) an ethylene carbonate treated succinimide dispersant; and

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

wherein the lubricating oil composition contains no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a di-alkyl carboxylate detergent.

[0036] The ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present invention is in the range of from about 0.5:1.0 to about 10:1. Preferably the ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present invention is in the range of from about 1.0:1.0 to about 7. 5:1.0. More preferably ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present invention is in the range of from about 2.0: 1.0 to about 5.0:1.0. Most preferably ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present invention is 3.5:1.

[0037] In the above method for reducing catalyst poisoning in internal combustion engines the engines are diesel engines, gasoline engines and natural gas engines.

[0038] 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 detergent is not a di-alkyl carboxylate, antioxidants different from those recited in (c), dispersants different from those recited in (d), provided they are derivatized succinimides or succinamides, 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

[0039] As used herein, the following terms have the following meanings unless expressly stated to the contrary:

[0040] The term "alkali metal" as used herein refers to Group IA metals of the Periodic Table, including lithium, sodium or potassium, with potassium being preferred.

[0041] The term "alkaline earth metal" as used herein refers to Group II metals of the Periodic Table, including calcium, barium, magnesium and strontium, with calcium being preferred.

[0042] The term "aryl group" as used herein refers to a substituted or non-substituted phenyl group.

[0043] The term "derivatized succinimide" as used herein refers to derivatives of succinimides derived from alkenyl succinic anhydride, such as polyisobutenyl succinic anhydride, These dispersants can be further derivatized by reaction with, for example, boron or ethylene carbonate. The most preferred are ethylene carbonate treated polyisobutenyl succinic anhydride derived dispersants.

[0044] The term "hydrocarbyl" as used herein refers to an alkyl or alkenyl group.

[0045] The term "overbased" as used herein refers to alkali metal and alkaline earth metal alkylaryl 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 alkylaryl sulfonates having a Total Base Number (TBN) greater than 1 and less than 20, medium overbased refers to alkali metal or alkaline earth metal alkylaryl sulfonates having a TBN greater than 20 and less than 200. High overbased refers to alkali metal or alkaline earth metal alkylaryl sulfonates having a TBN greater than 200.

[0046] 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.

[0047] Unless otherwise specified, all percentages are in weight percent.

LUBRICATING OIL COMPOSITION

[0048] 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 twice the amount of phosphorus as the comparative examples. It is conventional wisdom that phosphorus-

containing additives in lubricating oil poison catalysts, what is not known is that a mixture of a potassium overbased mono-alkyl carboxylate and a calcium overbased alkylaryl sulfonate employed in the lubricating oil composition of the present invention is capable of reducing catalyst poisoning even in the presence of phosphorus.

[0049] 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

[0050] 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.

[0051] 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.

[0052] 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.

[0053] 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.

Medium Overbased Metal Detergents

[0054] Examples of the preferred low and medium overbased metal detergents that may be employed in the lubricating oil composition of the present invention are medium overbased alkylaryl sulfonates, carboxylates/salicylates, sulfurized salicylates or Mannich condensation products of alkylphenols, aldehydes and amines, provided the carboxylates/salicylates are not di-alkyl carboxylates/salicylates. More preferred are medium overbased mono-alkyl carboxylates and alkylaryl sulfonates. These detergents may be alkali metal detergents or alkaline earth metal detergents, provided the alkali metal is not lithium. Preferably they are alkali metal mono-alkyl carboxylates and alkaline earth metal alkylaryl sulfonates, and more preferably they are potassium medium overbased mono-alkyl carboxylates and calcium medium overbased alkylaryl sulfonates. Most preferably it is a mixture of a potassium medium overbased mono-alkyl carboxylate and calcium medium overbased alkylaryl sulfonate. The TBN of these detergents is greater than 1 and less than 200.

[0055] Preferably the concentration of the potassium in the potassium overbased detergent employed in the lubricating oil of the present invention is in the range of from about 0.5 weight percent to about 5.0 weight percent based on the total weight of the potassium overbased detergent. More preferably the concentration of the potassium in the potassium overbased detergent is in the range of from about 1.0 weight percent to about 4.0 weight percent based on the total weight of the potassium overbased detergent. Most preferably the concentration of the potassium in the potassium overbased detergent is in the range of from about 1.5 weight percent to about 3.0 weight percent based on the total weight of the potassium overbased detergent.

[0056] Preferably the concentration of the calcium in the calcium overbased detergent employed in the lubricating oil of the present invention is in the range of from about 1.0 weight percent to about 9.0 weight percent based on the total weight of the calcium overbased detergent. More preferably the concentration of the calcium in the calcium overbased detergent is in the range of from about 2.0 weight percent to about 7.0 weight percent based on the total weight of the calcium overbased detergent. Most preferably the concentration of the calcium in the calcium overbased detergent is in the range of from about 3.0 weight percent to about 6.0 weight percent based on the total weight of the calcium overbased detergent.

[0057] The preferred detergent mixture, a mixture of a potassium medium overbased mono-alkyl carboxylate and a calcium medium overbased alkylaryl sulfonate, may be prepared using the procedures described in Example 9 in U.S.

Patent Application No. 10/745,125 (Publication No. 2005/0137098) and given below or by any procedure known to a person skilled in the art.

[0058] Preparation of a mixture of a potassium medium overbased mono-alkyl carboxylate and a calcium medium overbased alkylaryl sulfonate

1. Premixing
473.8 g of xylene was introduced into a four-neck reactor with stirring at 350 rpm under vacuum, followed by a lime slurry constituted by 568.6 g of xylene, 92.5 g of methanol (1) and 96.3 g of lime (1).
Total xylene (1) = 1042.4 g

2. Neutralization of Alkylaryl sulfonic Acid
120 g of alkylarylsulfonic acid, wherein the alkyl chain is a C_{20}-C_{24} linear alpha olefin marketed by Chevron Phillips Chemical Company (CPC) under the name Alpha Olefin C_{20}-C_{24} was introduced into the above obtained premixture. The reaction medium was preheated to 50°C over 20 minutes then left to homogenize for 15 minutes, until the temperature reached approximately 25°C.

3. Preparation and Addition of Potassium Alkylhydroxybenzoate
The process for the preparation of the potassium alkylhydroxybenzoate is described herein as follows.

A. Neutralization Step:

[0059] 1200 g of alkylphenol wherein the alkyl group is derived from a mixture of C_{20}-C_{28} linear alpha olefins, available from Chevron Phillips Chemical Company (CPC) and 632 g of ethylhexanol were charged with stirring into a four-necked reactor under vacuum.

[0060] The reaction mixture was heated from ambient temperature to 95°C over 25 minutes under 10^5 Pa (absolute pressure), then 311.8 g of an aqueous solution with 50 wt % of potassium hydroxide was introduced. The mixture was then taken to a temperature of 195°C over 3 hours 30 minutes. As purity of KOH is 86.4 wt % and water: 50 wt %; effective quantity of KOH is: 311.8 x 0.5 x 0.864 = 134.7 g [which corresponds to a CMR (KOH/alkylphenol) = 0.9]. Heating was continued progressively until reflex temperature was reached at 210°C, at which the temperature was maintained for 2 hours.

[0061] The temperature was then allowed to drop to 195°C while reducing the vacuum to $4X10^3$ Pa in order to distill the solvents. This temperature and pressure was maintained for 30 minutes with continued stirring at 600 rpm. At the end of the distillation operation, 554.2 g of a 100N dilution oil, having a viscosity of 100 SUS at 37.8°C, was slowly added. When the temperature reached 170°C, the vacuum was discontinued with nitrogen purging while continuing to add dilution oil.

B. Carboxylation Step:

[0062] The mixture resulting from the neutralization step described above was introduced into a stainless steel reactor with stirring under vacuum pressure. Carbon dioxide under a pressure of $3.5X10^5$ Pa was then introduced into the reactor at a temperature of 125°C to 130°C over 6 hours. The potassium alkylhydroxybenzoate (alkylsalicylate) was recovered having a C_{20}-C_{28} alkyl chain along with unreacted alkylphenol and potassium alkylphenate.
720 g of the potassium C_{20}-C_{28} alkylhydroxybenzoate was introduced into the reactor over 20 minutes.

4. Carbonation

[0063] 43.7 g (1) of carbon dioxide was introduced into the reactor over 90 minutes, at a temperature of 30°C to 40°C, then a lime slurry containing 260.7 g of xylene (2), 24.4 g of methanol (2) and 25 g of calcium hydroxide (2), was introduced into the reactor.

[0064] 13.1 g (2) of carbon dioxide was then introduced into the reactor over 45 minutes at a temperature of 35°C to 43°C.

5. Pre-distillation, Centrifugation and Final Distillation

[0065] The temperature of the mixture contained in the reactor was increased to between 110°C to 132°C. 181.9 g of 600N dilution oil and 259 g of xylene were added successively. Then, another 181.9 g of 600N oil and 259 g of xylene (3) were again successively added. The resulting mixture was centrifuged on an Alfa Laval Gyrotester® and heated to approximately 200°C in order to eliminate the xylene while under partial vacuum at $4x10^3$ Pa for 10 minutes.

[0066] Tables 1 and 2 below summarize the loads used and the analysis results obtained in the preparation of the

potassium medium overbased carboxylate and the calcium medium overbased alkylaryl sulfonate.

Table I

Loads	
Linear alkylphenols	
CPC (C20-C28 olefin derivatives)	100 %
Molar ratio KOH/alkylphenols	0.9
Lime (1) (g)	96.3
Lime (2) (g)	25
Methanol (1) (g)	92.5
Methanol (2) (g)	24.4
Xylene (1) (Premixing) (g)	1042.4
Xylene (2) (g)	260.7
Xylene (3) (g)	259
CO_2 (1) (g)	43.7
CO_2 (2) (g)	13.1
Sulfonic acid (g)	120
Potassium alkylsalicylate (g)	720
Dilution oil (600 N) (g)	181.9
Quantity produced (g)	1170.5
Total surfactant (after dialysis[1]) (g)	556
"Phenol" / total surfactant [2] (wt/wt)	0.106
"Phenol" + "Hydroxybenzoic acid" / total surfactant (wt/wt)	0.82
Total surfactant (% by weight)	47.50
TBN / % total surfactant	3.61

[1] In order to eliminate the unreacted alkylphenols.
[2] The carboxylates and sulfonates were assayed in acid form.

Table II

Analyses	
Linear alkylphenols	
CPC (C20-C28 olefin derivatives)	100 %
Molar ratio KOH/alkylphenols	0.9
OVERBASING PHASE	
Analyses	--
Potassium (wt %)	2.86
Calcium (wt % wt %)	5.12
% CaS ASTM D3712 (wt %)	0.401
TBN ASTM D2896 (mg KOH/g)	171.5
Salicylic acid[1] (mg KOH/g)	34.94
Viscosity at 100°C ASTM D445 (mm^2/s)	43.94
Appearance in oil (MAO 23)	1/0
Color (ASTM D1500)	2.6 DD
Crude sediments (ASTM D2273, vol %)	0.60
Final sediments (ASTM D2273, vol %)	0.02

[1] Expressed in mg KOH/g through ASTM D2896.

Anti-oxidants

[0067] 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'-di-methylaminomethylphenol), 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

[0068] 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, 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

[0069] 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

[0070] 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

[0071] 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

[0072] 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

[0073] Polymethyl methacrylate is an example of a pour point depressant useful for addition to the lubricating oil of the present invention.

Rust Inhibitors

[0074] 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

[0075] 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

[0076] 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

[0077] 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

[0078] 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

[0079] 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

[0080] Useful foam inhibitors for the present invention are alkyl methacrylate polymers, dimethyl silicone polymers and polysiloxane type foam inhibitors.

[0081] 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.

[0082] 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.

[0083] In Table III 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 III

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

[0084] 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 III below.

Example 1

[0085] Comparative Formulations A-C and Test Formulation D contained an amine-containing anti-oxidant, an ethylene carbonate treated succinimide 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, Comparative Formulation B contained a calcium overbased alkylaryl sulfonate, Comparative Formulation C contained a magnesium overbased alkylaryl sulfonate and Test Formulation D contained a mixture of a potassium medium overbased mono-alkyl carboxylate and a calcium overbased alkylaryl sulfonate in a ratio of 3.5 to 1.0. Base oil was used to make-up a 100 percent of each of Comparative Formulations A-C and Test Formulation D.

[0086] The reduction in catalyst poisoning using Test Formulation D containing a potassium medium overbased mono-alkyl carboxylate and an calcium medium overbased alkylaryl sulfonate in addition to the other components given above was compared with Comparative Formulations A-C which contained only calcium or magnesium phenates or alkylaryl sulfonates in addition to the other components given above.

[0087] Comparative Formulations A-C and Test Formulation D are described in more detail in Table IV below. The amounts of the components in the lubricating oil formulations are given in Table IV in weight percent active additive.

Table IV

Component	Formulation (weight %)			
	Comparative Formulation A	Comparative Formulation B	Comparative Formulation C	Test formulation D
Base Oil	Balance	Balance	Balance	Balance

(continued)

Component	Formulation (weight %)			
	Comparative Formulation A	Comparative Formulation B	Comparative Formulation C	Test formulation D
Potassium Overbased Mono-alkyl Carboxylate + Calcium Overbased Alkylaryl Sulfonate *	0	0	0	10.5 +36.5
Calcium Overbased Sulfurized Phenate *	1.6	0	0	0
Calcium Overbased Alkylaryl Sulfonate *	0	0.9	0	0
Magnesium Overbased Alkylaryl Sulfonate *	0	0	0.7	0
Amine-containing Anti-oxidant	0.5	0.5	0.5	0.5
Ethylene Carbonate treated Succinimide Dispersant	2.4	2.4	2.4	2.4
Phosphorus-containing Anti-wear Agent	0.83	0.83	0.83	0.83
Foam Inhibitor	5 ppm	5 ppm	5 ppm	5 ppm
Phosphorus	0.045	0.09	0.09	0.09
* The concentration of the detergents employed in Comparative Examples A-C and Test Example D was kept the same in millimolar quantity, 55 millimolar for obtaining a better comparison.				

Example 2

Catalyst Poisoning

[0088] Reduction in catalyst poisoning in exhaust after treatment systems was determined for Test Formulation B was compared to Comparative Formulation A as described below.

[0089] 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.

[0090] 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 non-linearly 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.

[0091] The data reported were T50 at the end of the test. The results of the Catalyst Poisoning Test are summarized in Table V below.

Table V

Component	Formulation			
	Comparative Formulation A	Comparative Formulation B	Comparative Formulation C	Test formulation D
T50	314°C	306°C	310°C	273°C

[0092] The results obtained in the Catalyst Poisoning Test summarized above in Table V show that catalyst poisoning determined by the temperature as the catalyst "lights-off' measured by T50 for Comparative Formulations A-C and Test Formulation D. The results show that Comparative Formulation A containing a calcium medium overbased sulfurized phenate, Comparative Formulation B containing a calcium overbased alkylaryl sulfonate, Comparative Formulation C containing a magnesium overbased alkylaryl sulfonate gave T50 of 314°C, 306°C and 310°C respectively, while the T50 measured for Test Formulation D containing a mixture of a potassium medium overbased mono- alkyl carboxylate and a calcium overbased alkylaryl sulfonate was 273°C. The data show that the addition of a mixture of a potassium medium overbased mono-alkyl carboxylate and a calcium medium overbased alkylaryl sulfonate to Test Formulation D containing twice the amount of phosphorus gave a 13.1, 10.8 and 11.9 percent reduction in catalyst poisoning compared to the catalyst poisoning observed with Comparative Formulations A-C, respectively, The data appear to show that addition of a mixture of a potassium medium overbased mono-alkyl carboxylate and a calcium medium overbased alkylaryl sulfonate to Test Formulation D protects against catalyst poisoning while providing wear control.

[0093] The results of the catalyst poisoning test summarized in Table V above show that Test Formulation B employing a mixture of a potassium medium overbased carboxylate and a calcium medium overbased alkylaryl sulfonate gave a reduction in catalyst poisoning compared to Comparative Formulations A-C which did not contain a mixture of a potassium medium overbased carboxylate and a calcium medium overbased alkylaryl sulfonate, but contained half the amount of phosphorus in the formulations. It is conventionally known that phosphorus-containing additives in lubricating oils poison catalysts. Thus, the results obtained in the catalyst poisoning test were unexpected, since the phosphorus content of Test Formulation D was twice as high as Comparative Formulations A-C. Based on conventional wisdom, protection against catalyst poisoning observed a lubricating oil formulation containing a mixture of a potassium medium overbased carboxylate and a calcium medium overbased alkylaryl sulfonate is employed, even in the presence of phosphorus, was a surprising result.

Claims

1. A lubricating oil composition comprising:

(a) a major amount of an oil of lubricating viscosity;
(b) a mixture of a potassium overbased detergent and a calcium overbased detergent;
(c) one or more anti-oxidants;
(d) one or more derivatized succinimide dispersants; and
(e) one or more anti-wear agents;

wherein the lubricating oil composition contains no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a di-alkyl carboxylate.

2. The lubricating of claim 1, wherein the ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present is in the range of from about 0.5:1.0 to about 10.0:1.0.

3. The lubricating of claim 2, wherein the ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present is in the range of from about 1.0:1.0 to about 7.5:1.0.

4. The lubricating of claim 3, wherein the ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present is in the range of from about 2.0:1.0 to about 5.0:1.0.

5. The lubricating of claim 4, wherein the ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present is 3.5:1.0.

6. The lubricating oil composition of claim 1, wherein the concentration of the potassium in the potassium overbased detergent is in the range of about 1.0 weight percent to about 10.0 weight percent based on the total weight of the potassium overbased detergent.

7. The lubricating oil composition of claim 6, wherein the concentration of the potassium in the potassium overbased detergent is in the range of about 1.5 weight percent to about 7.5 weight percent based on the total weight of the potassium overbased detergent.

8. The lubricating oil composition of claim 7, wherein the concentration of the potassium in the potassium overbased detergent is in the range of about 2.0 weight percent to about 5.0 weight percent based on the total weight of the potassium overbased detergent.

9. The lubricating oil composition of claim 8, wherein the concentration of the potassium in the potassium overbased detergent is in the range of about 2.5 weight percent to about 3.0 weight percent based on the total weight of the potassium overbased detergent.

10. The lubricating oil composition of claim 1, wherein the concentration of the calcium in the calcium overbased detergent is in the range of about 1.0 weight percent to about 15.0 weight percent based on the total weight of the calcium overbased detergent.

11. The lubricating oil composition of claim 10, wherein the concentration of the calcium in the calcium overbased detergent is in the range of about 2.0 weight percent to about 10.0 weight percent based on the total weight of the calcium overbased detergent.

12. The lubricating oil composition of claim 11, wherein the concentration of the calcium in the calcium overbased detergent is in the range of about 3.0 weight percent to about 7.5 weight percent based on the total weight of the calcium overbased detergent.

13. The lubricating oil composition of claim 12, wherein the concentration of the calcium in the calcium overbased detergent is in the range of about 4.0 weight percent to about 6.0 weight percent based on the total weight of the calcium overbased detergent.

14. 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.

15. The lubricating oil composition of claim 14, 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.

16. The lubricating oil composition of claim 15, 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.

17. A lubricating oil composition comprising:

(a) a major amount of an oil of lubricating viscosity;
(b) a mixture of a potassium overbased mono-alkyl carboxylate and a calcium overbased alkylaryl sulfonate;
(c) an amine-containing anti-oxidant;
(d) an ethylene carbonate treated succinimide dispersant; and
(e) a phosphorus-containing anti-wear agent;

wherein the lubricating oil composition no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a di-alkyl carboxylate detergent.

18. The lubricating oil composition of claim 17, wherein the ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present is in the range of from about 0.5:1.0 to about 10.0:1.0.

19. The lubricating oil composition of claim 18, wherein the ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present is in the range of from about 1.0:1.0 to about

7.5:1.0.

20. The lubricating oil composition of claim 19, wherein the ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present is in the range of from about 2.0:1.0 to about 5.0:1.0.

21. The lubricating oil composition of claim 20, wherein the ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present is 3.5:1.0.

22. The lubricating oil composition of claim 17, wherein the concentration of the potassium in the potassium overbased detergent is in the range of about 1.0 weight percent to about 10.0 weight percent based on the total weight of the potassium overbased detergent.

23. The lubricating oil composition of claim 22, wherein the concentration of the potassium in the potassium overbased detergent is in the range of about 1.5 weight percent to about 7.5 weight percent based on the total weight of the potassium overbased detergent.

24. The lubricating oil composition of claim 23, wherein the concentration of the potassium in the potassium overbased detergent is in the range of about 2.0 weight percent to about 5.0 weight percent based on the total weight of the potassium overbased detergent.

25. The lubricating oil composition of claim 24, wherein the concentration of the potassium in the potassium overbased detergent is in the range of about 2.5 weight percent to about 3.0 weight percent based on the total weight of the potassium overbased detergent.

26. The lubricating oil composition of claim 17, wherein the concentration of the calcium in the calcium overbased detergent is in the range of about 1.0 weight percent to about 15.0 weight percent based on the total weight of the calcium overbased detergent.

27. The lubricating oil composition of claim 26, wherein the concentration of the calcium in the calcium overbased detergent is in the range of about 2.0 weight percent to about 10.0 weight percent based on the total weight of the calcium overbased detergent.

28. The lubricating oil composition of claim 27, wherein the concentration of the calcium in the calcium overbased detergent is in the range of about 3.0 weight percent to about 7.5 weight percent based on the total weight of the calcium overbased detergent.

29. The lubricating oil composition of claim 28, wherein the concentration of the calcium in the calcium overbased detergent is in the range of about 4.0 weight percent to about 6.0 weight percent based on the total weight of the calcium overbased detergent.

30. The lubricating oil composition of claim 17, 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.

31. The lubricating oil composition of claim 30, 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.

32. The lubricating oil composition of claim 31, 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.

33. The lubricating oil composition of claim 17, wherein the phosphorus-containing anti-wear agent is a metal di-alkyl di-thiophosphate.

34. The lubricating oil composition of claim 33, wherein the metal in the metal di-alkyl di-thiophosphate is zinc.

35. A lubricating oil concentrate comprising:

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

(b) a mixture of a potassium overbased detergent and a calcium overbased detergent;
(c) one or more anti-oxidants;
(d) one or more derivatized succinimides; and
(e) one or more anti-wear agents;

wherein the lubricating oil concentrate contains no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a di-alkyl carboxylate.

36. The lubricating oil concentrate of claim 35, wherein the phosphorus-containing anti-wear agent is zinc di-alkyl di-thiophosphate.

37. 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 mixture of a potassium overbased mono-alkyl carboxylate and a calcium overbased alkylaryl sulfonate;
(c) an amine-containing anti-oxidant;
(d) an ethylene carbonate treated succinimide dispersant; and
(e) a phosphorus-containing anti-wear agent;

wherein the lubricating oil concentrate contains no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a di-alkyl carboxylate detergent.

38. The lubricating oil concentrate of claim 37, wherein the ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present is in the range of from about 0.5:1.0 to about 10.0:1.0.

39. The lubricating oil concentrate of claim 38, wherein the ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present is in the range of from about 1.0:1.0 to about 7.5:1.0.

40. The lubricating oil concentrate of claim 39, wherein the ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present is in the range of from about 2.0:1.0 to about 5.0:1.0.

41. The lubricating oil concentrate of claim 40, wherein the ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present is 3.5:1.0.

42. The lubricating oil concentrate of claim 37, wherein the phosphorus-containing anti-wear agent is zinc di-alkyl di-thiophosphate.

43. 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) about 10 weight percent to about 90 weight percent of an oil of lubricating viscosity;
(b) a mixture of a potassium overbased detergent and a calcium overbased detergent;
(c) one or more anti-oxidants;
(d) one or more derivatized succinimides; and
(e) one or more anti-wear agents;

wherein the lubricating oil concentrate contains no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a di-alkyl carboxylate.

44. The method of claim 43, wherein the internal combustion engines are diesel engines, gasoline engines and natural gas engines.

45. The method of claim 43, wherein the phosphorus-containing anti-wear agent is zinc di-alkyl di-thiophosphate.

46. 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 mixture of a potassium overbased mono-alkyl carboxylate and a calcium overbased alkylaryl sulfonate;
(c) an amine-containing anti-oxidant and a phenolic anti-oxidant;
(d) an ethylene carbonate treated succinimide dispersant; and
(e) a phosphorus-containing anti-wear agent;

wherein the lubricating oil composition contains no more than 0.12 weight percent phosphorus, and provided the lubricating oil composition does not contain a di-alkyl carboxylate detergent.

47. The method of claim 46, wherein the ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present is in the range of from about 0.5:1.0 to about 10.0:1.0.

48. The method of claim 47, wherein the ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present is in the range of from about 1.0:1.0 to about 7.5:1.0.

49. The method of claim 48, wherein the ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present is in the range of from about 2.0:1.0 to about 5.0:1.0.

50. The method of claim 49, wherein the ratio of the potassium overbased detergent to the calcium overbased detergent in the lubricating oil composition of the present is 3.5:1.0.

51. The method of claim 46, wherein the internal combustion engines are diesel engines, gasoline engines and natural gas engines.

52. The method of claim 46, wherein the phosphorus-containing anti-wear agent is zinc di-alkyl di-thiophosphate.

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EUROPEAN SEARCH REPORT

Application Number
EP 06 25 5569

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