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(54) Titre : COMPOSITION D'ADDITIF ANTI-USURE POUR COMPOSITIONS D'HUILES LUBRIFIANTESA FAIBLE TENEUR EN SOUFRE, EN CENDRES SULFATEES ET EN PHOSPHORE, UTILISEE DANS LES MOTEURS DIESELS DE GROSSE CYLINDRE

(54) Title: ANTI-WEAR ADDITIVE COMPOSITION FOR A LOW SULFUR, LOW SULFATED ASH AND LOW PHOSPHORUS LUBRICATING OIL COMPOSITION FOR HEAVY DUTY DIESEL ENGINES

(57) Abrégé/Abstract:
The present invention is directed to a low sulfur, low sulfated ash and low phosphorus lubricating oil composition for low emission heavy duty diesel engines comprising (a) a major amount of an oil of lubricating viscosity and (b) at least 2 weight percent of an anti-wear additive composition comprising a metal salt of a Mannich condensation product based on the total weight of the lubricating oil. The present invention is also directed to a low sulfur, low sulfated ash and low phosphorus lubricating oil concentrate comprising (a) an oil of lubricating viscosity and (b) at least 2 weight percent of an anti-wear additive composition comprising a metal salt of a Mannich condensation product based on the total weight of the lubricating oil.

ABSTRACT

The present invention is directed to a low sulfur, low sulfated ash and low phosphorus lubricating oil composition for low emission heavy duty diesel engines comprising (a) a major amount of an oil of lubricating viscosity and (b) at least 2 weight percent of an anti-wear additive composition comprising a metal salt of a Mannich condensation product based on the total weight of the lubricating oil. The present invention is also directed to a low sulfur, low sulfated ash and low phosphorus lubricating oil concentrate comprising (a) an oil of lubricating viscosity and (b) at least 2 weight percent of an anti-wear additive composition comprising a metal salt of a Mannich condensation product based on the total weight of the lubricating oil.

TITLE

ANTI-WEAR ADDITIVE COMPOSITION FOR A LOW SULFUR, LOW SULFATED ASH AND LOW PHOSPHORUS LUBRICATING OIL COMPOSITION FOR HEAVY DUTY DIESEL ENGINES

FIELD OF THE INVENTION

The present invention is directed to a low sulfur, low sulfated ash and low phosphorus lubricating oil composition for low emission heavy duty diesel engines comprising (a) a major amount of an oil of lubricating viscosity and (b) at least 2 weight percent of an anti-wear additive composition comprising a metal salt of a Mannich condensation product based on the total weight of the lubricating oil. The present invention is also directed to a low sulfur, low sulfated ash and low phosphorus lubricating oil concentrate comprising (a) an oil of lubricating viscosity and (b) at least 2 weight percent of an anti-wear additive composition comprising a metal salt of a Mannich condensation product based on the total weight of the lubricating oil.

BACKGROUND OF THE INVENTION

Heavy duty diesel internal combustion engines mounted on motor-driven vehicles, constructions machines and power generators are generally driven using gas oil or heavy oil (which is a fuel having a sulfur content of approximately 0.05 wt.% or more). Most lubricating oils for the diesel engines have a sulfur content of approximately 0.3 to 0.7 weight percent, a sulfated ash content of approximately 1.3 to 2.0 weight percent, and a phosphorus content of approximately 0.1 to 0.13 weight percent.

In order to reduce air pollution, vehicle manufacturers and petroleum companies are interested in developing lubricating oil systems that have low emissions and better fuel economy for heavy duty diesel engines. Environmental pollution caused by emissions from diesel engines may comprise particulates and carbon oxides, sulfur oxides and nitrogen oxides. Diesel engine manufacturers have started to equip diesel engines with exhaust after-

treatment devices containing particulate filters, oxidation catalysts and reduction catalysts to obviate environmental problems.

Both the fuel and the lubricating oil used to lubricate diesel engines contribute to particulates and oxides found in emissions from diesel engines. Conventionally used anti-wear agents and anti-oxidants, such as zinc di-alkyl di-thiophosphates, contribute to reduction in the activity of the oxidation catalysts, thus, reduction in phosphorus levels reduces the deactivation of the catalysts used in exhaust after-treatment devices. The zinc in zinc di-alkyl di-thiophosphates may also contribute to sulfated ash which may clog the particulate filters. Therefore, there is a need to decrease the phosphorus and zinc content in the lubricating oil to protect the oxidation catalysts from deterioration and to prevent the clogging of the particulate filters.

Another major concern is sulfated ash derived from the salts of alkali and alkaline earth metal detergent additives in lubricating oil. The non-combustible ash deposits in diesel engines become trapped in the channels of diesel engine exhaust gas particulate filters. Conventional lubricating oils used in diesel engines are also high in sulfur content, which originates in the additive components and the base oil. Sulfur in diesel fuels is converted to sulfuric acid and sulfates which emigrate to the exhaust gas cleaning devices and contribute to the particulates that clog the particulate filters in heavy duty diesel engine vehicles equipped with them. Sulfuric acid may also indirectly contribute to clogging the particulate filters by wetting the particulates, thus adding to their mass. The sulfuric acid and the sulfates also poison the oxidation catalysts in the exhaust gas cleaning devices which may also result in failure to meet emission requirements. Thus, for continued functioning of these particulate traps and oxidation catalysts, it is essential that the sulfur and sulfated ash content in the lubricating oil is lowered considerably compared to the conventional diesel engine lubricating oils.

A number of patents and patent applications have discussed methods for reducing particulate emissions and low sulfur, low sulfated ash and low phosphorus lubricating oil compositions, but none have disclosed a low sulfur,

low sulfated ash and low phosphorus lubricating oil composition comprising an anti-wear additive composition comprising a Mannich condensation product for a low emission diesel engine, wherein the anti-wear additive composition is also providing detergency.

Canadian Patent No. 810120 discloses a lubricating oil composition comprising the low sulfated ash and low viscosity reaction product obtained by the neutralization with an alkaline earth metal oxide or hydroxide of a sulfurized alkylphenol in admixture with a Mannich base reacted with carbon dioxide.

U. S. Patent No. 4,089,791 discloses a lubricating oil composition comprising a major portion of a mineral lubricating oil and minor amounts of an overbased alkaline earth metal compound, of a tri-alkanolamine and a zinc di-hydrocarbyl di-thiophosphate for reduction of bearing weight loss in an internal combustion engine, while retaining the low ash and rust inhibition properties.

U. S. Patent No. 4,330,420 discloses low ash, low phosphorus motor oils having improved oxidation stability as a result of the addition of synergistic amounts of a di-alkyl di-phenylamine anti-oxidant and of a sulfurized polyolefin. The synergism between the two additives compensates for the decreased amount of phosphorus in the form of zinc di-thiophosphate such that the oils retain an SE quality rating.

U. S. Patent No. 5,102,566 discloses a low sulfated ash lubricating oil composition which comprises a base oil, at least about 2 weight percent of an ashless nitrogen- or ester-containing dispersant, an oil-soluble antioxidant material, and an oil soluble di-hydrocarbyl di-thiophosphate anti-wear material, and which has a total sulfated ash level of 0.01 to 0.6 weight percent and a weight ratio of total sulfated ash and the dispersant in the range of 0.01:1 to 0.2:2.

U. S. Patent No. 5,490,945 discloses lubricating oil compositions and concentrates containing alkali metal overbased salts of carboxylic acids and either magnesium overbased salts of acidic compounds having a metal ratio of at least 3 provided that the lubricating composition is free of calcium overbased salts of acidic compounds having a metal ratio greater than 3 provided that the lubricating composition is free of magnesium overbased salts having a metal ratio greater than 3.

U. S. Patent No. 6,114,288 discloses a lubricating oil composition for internal combustion engines having a high temperature shear viscosity of from 2.1 to less than 2.9 mPas, wherein the lubricating base oil comprises (1) a zinc di-alkyl di-thiophosphate, (2) a metallic detergent chosen from calcium alkylsalicylate and a mixture of calcium alkyl and magnesium alkylsalicylate and optionally (3) friction modifier. The lubricating oil composition overcomes the problems of scuffing and the wear resistance of moving parts under severe lubrication conditions.

U. S. Patent No. 6,159,911 discloses a diesel engine oil composition containing a lube oil base and one or more metallic detergents-dispersants selected from among a perbasic alkaline earth metal sulfonate, phenolate and salicylate. The total phosphorus content of the composition is suppressed to 100 parts per million by weight or less, to thereby provide diesel engine oil compositions having oxidation stability and wear resistance.

U. S. Patent No. 6,162,770 discloses an un-sulfurized, alkali metal-free, detergent-dispersant composition having from about 40% to 60% alkylphenol, from 10% to 40% alkaline earth alkylphenol, and from 20% to 40% alkaline earth single aromatic-ring alkylsalicylate. This composition may have an alkaline earth double aromatic-ring salicylates as long as the mole ratio of single-ring alkylsalicylate to double aromatic ring alkylsalicylate is at least 8:1.

U. S. Patent No. 6,277,794 discloses a marine diesel lubricant composition having a TBN of at least 10 and preferably a VI of at least 90, comprise a major amount of oil of lubricating viscosity, and admixed therewith, minor amounts of an ashless anti-wear additive and a metal detergent in the form of

(i) an overbased metal detergent having a TBN of at least 300, more preferably at least 400, and comprising a surfactant system derived from at least two surfactants, and/or (ii) a metal detergent other than (i); provided that, if detergent (ii) is present, the composition does not contain a minor amount of an extreme pressure additive, being up to 5.0 mass percent on the total mass of the composition.

U. S. Patent Nos. 6,331,510 and 6,610,637 disclose a lubricant containing (a) a synthetic base oil composition having an overall kinematic viscosity of at least about $4.8X10^{-6}$ m^2/s (4.8 cSt) at 100°C and a viscosity index of at least 110; (b) a dispersant-viscosity modifier; and (c) a sulfur-free functionalized hydrocarbyl-substituted phenol detergent provides improved valve train wear, with longer drain intervals, to heavy duty diesel engines.

U. S. Patent No. 6,376,434 discloses a lube composition which is suitably used for diesel engines which exhaust large amounts of sulfur dioxides. The composition exhibits corrosion/wear preventive properties against sulfur dioxides. The lube composition includes a lube base oil, a component (A) which is a compound selected from a group consisting of overbased sulfonates of alkaline earth metal, overbased phenates of alkaline earth metals and overbased salicylates of alkaline earth metals, and a component (B) which is a bis-type succinimide compound.

U. S. Patent No. 6,730,638 discloses a lubricating oil for internal combustion engines especially useful with fuels having less than 350 parts per million sulfur comprises a lubricating oil basestock, a boron containing ashless dispersant, a molybdenum containing friction reduction agent, a metal type detergent and zinc di-thiophosphate.

U. S. Patent No. 6,784,143 discloses the use of a minor amount of a detergent composition comprising one or more metal detergents which comprises metal salts of organic acids , wherein the detergent composition comprises more than 50 mole percent, based on the moles of the metal salts

of organic acids in the detergent composition, of: (I) a metal salt of an aromatic carboxylic acid, or (II) a metal salt of a phenol, or (III) both a metal salt of an aromatic carboxylic acid and a metal salt of a phenol, in a lubricating oil composition for improving oxidation resistance of the lubricating oil composition, wherein the amount of phosphorus and sulfur in the oil composition is less than 0.09 mass % and at the most 0.5 mass % respectively, based on the mass of the oil composition. It has also been found that a detergent composition comprising more than 50 mole % of a metal salt of an aromatic carboxylic acid improves the reduction in wear in an engine.

European Patent Application No. 01201752.1 (Publication No. EP 1 256 619 A1) deemed withdrawn as of March 5, 2005, and U.S. Patent Application NO. 10/142,513 (Publication No. US 2003/0096716 A1) disclose a lubricating oil composition comprising: (A) an oil of lubricating viscosity, in a major amount and added thereto: (B) a detergent composition comprising one or more metal detergents which comprises metal salts or organic acids, in a minor amount, wherein the detergent composition comprises more than 50 mole percent of a metal salt of an aromatic carboxylic acid, based on the moles of the metal salts of organic acids in the detergent composition, and (C) one or more co-additives, in a minor amount; wherein the total amounts of phosphorus and sulfur derived from (B) or (C) or both (B) and (C) are less than 0.1 mass p% of phosphorus and at the most 0.5 mass % of sulfur, based on the mass of the oil composition. It has been found that a detergent composition comprising more than 50 mole % of a metal salt of an aromatic carboxylic acid improves the reduction in wear in an engine.

U.S. Patent Application No. 10/430,594 (Publication No. US 2003/0216266 A1) discloses a lubricating oil composition employable in combination with a low sulfur content fuel oil is preferably composed of a base oil having a sulfur content of at most 0.2 weight percent , an ashless dispersant comprising an alkenyl- or alkyl-succinimide or derivative thereof, a metal-containing detergent containing an organic acid metal salt, a zinc di-alkyl di-

thiophosphate, a zinc di-alkylaryl di-thiophosphate, and an oxidation inhibitor selected from a group consisting of a phenol compound, an amine compound, and a molybdenum-containing compound, wherein a ratio of the phosphorus content of the zinc di-alkyl di-thiophosphate to the phosphorus content of the zinc di-alkylaryl di-thiophosphate is in the range of 20:1 to 2:1.

International Publication No. WO 2004/046283 A1 discloses the use of lubricating oils with low sulfur content in combination with a low sulfur fuel to reduce particulate emissions of a diesel engine equipped with a particulate trap.

SUMMARY OF THE INVENTION

The present invention is directed to a low sulfur, low sulfated ash and low phosphorus lubricating oil composition for low emission heavy duty diesel engines comprising (a) a major amount of an oil of lubricating viscosity and (b) at least 2 weight percent of an anti-wear additive composition comprising a metal salt of a Mannich condensation product based on the total weight of the lubricating oil. The present invention is also directed to a low sulfur, low sulfated ash and low phosphorus lubricating oil concentrate comprising (a) an oil of lubricating viscosity and (b) at least 2 weight percent of an anti-wear additive composition comprising a metal salt of a Mannich condensation product based on the total weight of the lubricating oil.

The Mannich condensation product employed in the anti-wear additive composition of the present invention surprisingly shows anti-wear performance while maintaining good detergency.

Specifically, the present invention is directed to a low sulfur, low sulfated ash and low phosphorus lubricating oil composition for low emission heavy duty diesel engines comprising:

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

(b) at least 2 weight percent of an anti-wear additive composition comprising a metal salt of a Mannich condensation product based on the total weight of the lubricating oil composition.

In the lubricating oil composition of the present invention, preferably the concentration of the Mannich condensation product is from about 2 weight percent to about 12 weight percent based on the total weight of the lubricating oil composition. More preferably the concentration of the Mannich condensation product is preferably from about 3 weight percent to about 9 weight percent based on the total weight of the lubricating oil composition, and most preferably the concentration of the Mannich condensation product is preferably from about 4 weight percent to about 7 weight percent based on the total weight of the lubricating oil composition.

The Mannich condensation product (b) in the anti-wear additive composition in the lubricating oil of the present invention is prepared from a formaldehyde or an aldehyde having one carbon atom to about 10 carbon atoms, a nitrogen base selected from ammonia, a lower alkyl amine, a polyamine and mixtures thereof, and an alkylphenol.

In the anti-wear composition (b), the Mannich condensation product is a condensation product of an aldehyde having one carbon atom to about 20 carbon atoms, a nitrogen base selected from ammonia, a lower alkyl amine, a polyamine and mixtures thereof, and an alkylphenol.

The alkyl group on the alkylphenol employed to prepare the Mannich condensation product in the anti-wear additive composition (b) is a linear chain or a branched chain alkyl group. Preferably the alkyl group on the alkylphenol employed to prepare the Mannich condensation product is a branched chain alkyl group.

Preferably the branched chain alkyl group on the alkylphenol employed to prepare the Mannich condensation product in the anti-wear additive composition (b) has from about 4 carbon atoms to about 60 carbon atoms. More preferably the alkyl group on the alkylphenol has from about 6 carbon atoms to about 40 carbon atoms. Most preferably the alkyl group on the alkylphenol has from about 8 carbon atoms to about 20 carbon atoms.

The aldehyde useful for the preparation of the Mannich condensation product is an aldehyde having one carbon atom to about 10 carbon atoms. Preferably the aldehyde is formaldehyde, and more preferably it is paraformaldehyde.

The nitrogen base is selected from ammonia, a lower alkyl amine, wherein the alkyl group has one carbon atom to about 10 carbon atoms, a poly amine having 2 to about 12 amine nitrogen atoms and 2 to about 40 carbon atoms.

Preferably the nitrogen base for the preparation of the Mannich condensation product is a lower alkyl amine, wherein the alkyl group has one carbon atom to about 10 carbon atoms. The lower alkyl amine is an alkyl mono-amine, such as mono-methyl amine, mono-ethyl amine, mono-propyl amine, mono-butyl amine and mono-pentyl amine. More preferably the alkyl mono-amine is mono-methyl amine.

The polyamine useful for the preparation of the Mannich condensation product includes mono-alkylene polyamines and polyalkylene polyamines.

In a preferred embodiment of the lubricating oil composition of the present invention, the Mannich condensation product in the anti-wear additive composition (b) is prepared from an alkylphenol wherein the alkyl group on the alkylphenol is a branched chain alkyl group having from about 8 carbon atoms to about 20 carbon atoms, paraformaldehyde and mono-methyl amine.

The metal in the metal salt of a Mannich condensation product may be an alkali metal or an alkaline earth metal. Preferably the metal is an alkaline earth metal, and more preferably the alkaline earth metal is calcium.

Preferably the sulfur content of the lubricating oil composition of the present invention is in the range of 0.0 weight percent to about 0.4 weight percent based on the total weight of the lubricating oil. More preferably the sulfur content of the lubricating oil composition of the present invention is in the range of 0.05 weight percent to about 0.3 weight percent based on the total weight of the lubricating oil. Most preferably the sulfur content of the

lubricating oil composition of the present invention is in the range of 0.1 weight percent to about 0.2 weight percent based on the total weight of the lubricating oil.

Preferably the sulfated ash content of the lubricating oil composition of the present invention is in the range of 0.2 weight percent to about 4.0 weight percent based on the total weight of the lubricating oil. More preferably the sulfated ash content of the lubricating oil composition of the present invention is in the range of 0.3 weight percent to about 2.0 weight percent based on the total weight of the lubricating oil. Most preferably the sulfated ash content of the lubricating oil composition of the present invention is in the range of 0.5 weight percent to about 1.2 weight percent based on the total weight of the lubricating oil.

Preferably the phosphorus content of the lubricating oil composition of the present invention is in the range of 0.005 weight percent to about 0.06 weight percent based on the total weight of the lubricating oil. More preferably the phosphorus content of the lubricating oil composition of the present invention is in the range of 0.015 weight percent to about 0.05 weight percent based on the total weight of the lubricating oil. Most preferably the phosphorus content of the lubricating oil composition of the present invention is in the range of 0.03 weight percent to about 0.04 weight percent based on the total weight of the lubricating oil.

The above lubricating oil composition further comprises one or more lubricating oil additives selected from detergents, dispersants, anti-oxidants, viscosity index improvers, corrosion inhibitors, anti-wear agents, friction modifiers, pour point depressants and foam inhibitors.

Preferably the above lubricating oil composition further comprises one or more dispersants. More preferably the dispersants are ashless dispersants. Most preferably the ashless dispersants are derivatives of succinic anhydride.

The lubricating oil composition of the present invention may also contain viscosity index improvers such as polyalkyl methacrylates, ethylene-propylene copolymers, styrene-butadiene copolymers and polyisoprene.

Corrosion inhibitors and anti-oxidants optionally contemplated for use in the lubricating oil of the present invention are metal di-alkyl di-thiophosphates and derivatives of di-phenyl amine.

Metal di-alkyl di-thiophosphates may also be included in the lubricating oil composition of the present invention to control wear. However, it may be advantageous to control the amount of these additives because their metal contributes to sulfated ash in the lubricating oil and the phosphorus will be harmful to the exhaust gas oxidation catalysts. Examples of metal di-alkyl di-thiophosphates are zinc and molybdenum salts of di-alkyl di-thiophosphates.

Typically, friction modifiers are used to impart the proper friction characteristics to the lubricating oil composition. Useful friction modifiers are fatty acid esters and amides and molybdenum compounds, such as amine-molybdenum complex compound and molybdenum di-thiocarbamates. However, it should be noted that the addition of molybdenum di-thiocarbamates will further contribute sulfur to the lubricating oil composition and sulfated ash to the exhaust system.

Pour point depressants lower the temperature at which the fluid will flow or can be poured. Additives that optimize the low temperature fluidity of the lubricating oil are various copolymers, such as polymethacrylates.

Useful foam inhibitors are of the polysiloxane type.

A low sulfur, low sulfated ash and low phosphorus lubricating oil concentrate for low emission heavy duty diesel engines comprising:

(a) about 10 weight percent to about 90 weight percent of an oil of lubricating viscosity based on the total weight of the lubricating oil concentrate; and

(b) at least 2 weight percent of an anti-wear additive composition comprising a metal salt of a Mannich condensation product based on the total weight of the lubricating oil composition.

A method for lubricating low emission heavy duty diesel engines, which comprises lubricating with a low sulfur, low sulfated ash and low phosphorus lubricating oil composition comprising:

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

(b) at least 2 weight percent of an anti-wear additive composition comprising a metal salt of a Mannich condensation product based on the total weight of the lubricating oil composition.

In accordance with another aspect, there is provided a low sulfur, low sulfated ash, low phosphorus and low emission heavy duty diesel engine lubricating oil composition comprising:

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

(b) about 3 weight percent to about 12 weight percent of a metal salt of a Mannich condensation product, based on the total weight of the lubricating oil composition.

In accordance with another aspect, there is provided a low sulfur, low sulfated ash, low phosphorus and low emission heavy duty diesel engine lubricating oil concentrate comprising:

(a) from about 10 weight percent to about 90 weight percent of an oil of lubricating viscosity based on the total weight of the lubricating oil concentrate; and

(b) about 3 weight percent to about 12 weight percent of a metal salt of a Mannich condensation product, based on the total weight of the lubricating oil composition.

In accordance with another aspect, there is provided a method for lubricating low emission heavy duty diesel engines, which comprises lubricating with a low sulfur, low sulfated ash, low phosphorus, and low emission heavy duty diesel engine lubricating oil composition comprising:

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

(b) about 3 weight percent to about 12 weight percent of a Mannich condensation product, based on the total weight of the lubricating oil composition.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

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

The term "alkali metal" as used herein refers to Group I metals of the Periodic Table, such as sodium, potassium and lithium.

The term "alkaline earth metal" as used herein refers to Group II metals of the Periodic Table, such as calcium and magnesium.

The term "detergents" as used herein refers to additives designed to hold the acid-neutralizing compounds in solution in the oil. They are usually alkaline and react with the strong acids (sulfuric and nitric) which form during the combustion of the fuel and which would cause corrosion to the engine parts if left unchecked. Suitable detergents for use in the present invention are alkyl sulfonates, alkyl phenates and Mannich base condensation products. Numerous detergents are commercially readily available

The term "dispersants" as used herein refers to additives that keep soot and combustion products in suspension in the body of the oil charge and therefore prevent deposition as sludge or lacquer. Typically, the ashless dispersants are nitrogen-containing dispersants formed by reacting alkenyl succinic acid anhydride with an amine. Examples of such 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. Preferred ashless dispersants are those derived from polyisobutenyl succinic anhydride. Dispersancy may also be controlled by dispersant viscosity modifiers, such as polymethacrylates, alkylmethacrylate styrene copolymers, polyalkylmethacrylates and olefin copolymers. A large number of dispersants are commercially available.

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

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

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.

Unless otherwise specified, all percentages are in weight percent.

LUBRICATING OIL COMPOSITION

It has been discovered that the a low sulfur, low sulfated ash and low phosphorus lubricating oil composition comprising an anti-wear additive composition comprising a metal salt of a Mannich condensation product provides good wear control when used for low emission heavy duty diesel engines. 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 metal in these anti-wear additives contributes to an increase in sulfated ash in the lubricating oil and the phosphorus causes inactivation of oxidation catalysts used in exhaust after-treatment devices. The anti-wear additive composition employed in the lubrication oil composition of the present invention provides good wear control without contributing to an increase in sulfur and sulfated ash, and because it does not contain any phosphorus, it does not inactivate the oxidation catalysts.

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

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. 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 di-carboxylic acid and mono- and di-hydroxy alkanols can also be used. 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.

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.

Anti-wear Additives

Metal salt of Mannich condensation product

The Mannich condensation product may be prepared using an alkylphenol, an aldehyde and a nitrogen base selected from ammonia, a lower amine, a polyamine and mixtures thereof.

The alkyl group on the alkylphenol employed to prepare the Mannich condensation product in the anti-wear additive composition (b) is a linear chain or a branched chain alkyl group. Preferably the alkyl group on the

alkylphenol employed to prepare the Mannich condensation product is a branched chain alkyl group.

The alkyl group on the alkylphenol used for the preparation of the Mannich condensation product may be a branched chain alkyl group containing from about 4 carbon atoms to about 60 carbon atoms or a linear chain alkyl group containing from about 6 carbon atoms to about 60 carbon atoms. Preferably the alkyl group on the alkylphenol is a branched chain alkyl group containing from about 8 carbon atoms to about 20 carbon atoms. Preferably the alkyl group is attached to the alkylphenol moiety at the ortho-position or the para-position to the hydroxyl group.

More preferably the ratio of the attachment of the alkyl group in the ortho-position to para-position is 20:80 based on the total alkylphenol, and most preferably the ratio of the attachment of the alkyl group in the ortho-position to para-position is 5:95 based on the total alkylphenol.

The aldehyde useful for the preparation of the Mannich condensation product is an aldehyde having one carbon atom to about 10 carbon atoms. Preferably the aldehyde is formaldehyde, and more preferably it is paraformaldehyde.

The nitrogen base is selected from ammonia, a lower alkyl amine, wherein the alkyl group has one carbon atom to about 10 carbon atoms, a polyamine having 2 to about 12 amine nitrogen atoms and 2 to about 40 carbon atoms.

Preferably the nitrogen base for the preparation of the Mannich condensation product is a lower alkyl amine, wherein the alkyl group has one carbon atom to about 10 carbon atoms. The lower alkyl amine is an alkyl mono-amine, such as mono-methyl amine, mono-ethyl amine, mono-propyl amine, mono-butyl amine and mono-pentyl amine. More preferably the alkyl mono-amine is mono-methyl amine.

The polyamines useful for preparation of the Mannich condensation product employed in the anti-wear additive composition of the present invention

include mono-alkylene polyamines and polyalkylene polyamines. Examples of mono-alkyl polyamines include ethylene di-amine, ethylene tri-amines and ethylene tetra-amines, propylene di-amine and propylene tri-amine. Examples of polyalkylene polyamines include di-ethylene di-amine, di-(tri-methylene) tri-amine, di-propylene tri-amines and tri-ethylene tetra-amine.

Metal salts of the Mannich condensation product employed in the lubricating oil composition of the present invention may be prepared by any method known to a person skilled in the art. Generally, the Mannich condensation product is prepared by reaction of the alkylphenol, formaldehyde and mono-alkyl amine in the presence of a metal hydroxide and a diluent.

The preparation of Mannich condensation product is well known to persons skilled in the art. The Mannich condensation product may be prepared using an alkylphenol, an aldehyde and an amine by any method known to a person skilled in the art. For example, the Mannich condensation product may be prepared as described in U.S. Patent 5,370,805.

The metal salt of the Mannich condensation product may be prepared by any well know process using a metal oxide, metal hydroxide or a metal alkoxides. The metal may be an alkali metal or an alkaline earth metal. Preferably the metal is an alkaline earth metal, and more preferably the alkaline earth metal is calcium.

<u>Other Additives</u>

The lubricating oil composition of the present invention may also typically contain, in addition to the detergent composition of the present invention, 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, dispersants, anti-oxidants, viscosity index improvers, corrosion inhibitors, anti-wear agents, friction modifiers, pour point depressants and foam inhibitors.

For best overall results in terms of affording the properties desired in a conventional lubricating oil composition for a heavy duty diesel engine lubricating oil, the lubricating oil contains a compatible combination of additives of each of the above classes of additives in effective amounts as well as the detergent composition of the present invention in the amount needed to provide the desired neutralization capacity.

Low, Medium and High Overbased Metal Detergents

Small quantities of low or medium overbased metal detergents may optionally be employed in the lubricating oil composition of the present invention. Examples of the low and medium overbased metal detergents are low or medium overbased sulfonic acids, salicylic acids, carboxylic acids, or phenols or Mannich condensation products of alkylphenols, aldehydes and amines. These detergents may be alkali metal detergents or alkaline metal detergents. Preferably they are alkaline earth metal detergents and more preferably they are calcium detergents. The TBN of these detergents is greater than 1 and about 500, or more. However, it is worth noting that a further addition of detergents, such as those described above, may contribute to the sulfur and/or sulfated ash content of the lubricating oil. These detergents are well known in the art and are commercially available.

Dispersants

The lubricating oil composition of the present invention optionally contains dispersants. Typically, the ashless dispersants are nitrogen-containing dispersants formed by reacting alkenyl succinic acid anhydride with an amine. Examples of such 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. Preferred ashless dispersants are those derived from

polyisobutenyl succinic anhydride. A large number of dispersants are commercially available.

Anti-oxidants

Anti-oxidants are used in lubricating oils for inhibition of decomposition processes that occur naturally in lubricating oils as they age or oxidize in the presence of air. These oxidation processes may cause formation of gums, lacquers and sludge resulting in an increase in acidity and viscosity. Examples of useful anti-oxidants are hindered phenols, alkylated and non-alkylated aromatic amines, alkyl or aryl phosphates, esters of thiodicarboxylic acids, salts of carbamic or di-thiophosphoric acids. Molybdenum compounds, such as amine-molybdenum complex compound and molybdenum di-thiocarbamates may also be used as anti-oxidants. However, it should be noted that the addition of molybdenum di-thiocarbamates will further contribute sulfur and sulfated ash to the lubricating oil composition.

Viscosity Index Improvers

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, polybutene, polymethacrylates, vinylpyrrolidone and methacrylate copolymers.

Corrosion inhibitors

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. The corrosion inhibitor should not be one that is itself corrosive to silver and silver plated bearings, such as, metal di-thiophosphates. Examples of corrosion inhibitors that may be used are sulfurized olefin corrosion inhibitor and the co-sulfurized alkenyl ester/alpha olefin corrosion inhibitor.

In addition to the materials already described, lubricating oil composition of the present invention may also include other additives, such as pour point depressants and anti-foaming agents. 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.

EXAMPLES

The anti-wear additive composition employed in the low sulfur, low sulfated ash and low phosphorus lubricating oil composition of the present invention were evaluated for their anti-wear performance in formulations prepared as described in Example 1 and Table I below.

Example 1

Comparative Formulations A and B and Test Formulation C contained an ashless dispersant, an anti-oxidant, a viscosity index improver, a medium overbased alkyl phenate, an anti-wear agent and a foam inhibitor. Base oil was used to make-up a 100 percent of each of Comparative Formulations A and B and Test Formulation C. Comparative Formulations A and B and Test Formulation C are given in more detail in Table I below.

The weight percent calcium concentration based on the total weight of the lubricating oil in each of the Comparative Formulations A and B and Test Formulation C was kept constant, and it is shown in Table II below.

The anti-wear performance of Test Formulation C containing the anti-wear additive composition of the present invention comprising, a calcium salt of a Mannich condensation product, was compared with Comparative Formulation A containing only a mixture of a calcium salt of an alkyl hydroxyaromatic carboxylic acid and a calcium salt of an alkylphenol, and Comparative Formulation B containing a mixture of a calcium l salt of an alkyl

hydroxyaromatic carboxylic acid and a calcium salt of an alkylphenol and a calcium salt of a Mannich condensation product.

Comparative Formulation B contained:

(A) calcium salts of a mixture of:

(a) a mixture of:

(i) an alkyl hydroxy benzene carboxylic acid, wherein the alkyl group on the alkyl hydroxy benzene carboxylic acid was a branched chain alkyl group containing 12 carbon atoms, and

(ii) an alkyl hydroxy benzene carboxylic acid, wherein the alkyl group on the alkyl hydroxy benzene carboxylic acid was a linear chain alkyl group containing 20 carbon atoms to 28 carbon atoms, and

(b) a mixture of:

(i) a calcium salt of an alkylphenol, where in the alkyl group on the alkylphenol was a branched chain alkyl group containing 12 carbon atoms, and

(ii) a calcium salt of an alkylphenol, wherein the alkyl group on the other alkylphenol was a linear chain alkyl group containing 20 carbon atoms to 28 carbon atoms.

The calcium salt of (a) and (b) were present in a ratio of 3:2, and

(B) a calcium salt of the Mannich condensation product of an alkyl phenol, paraformaldehyde and mono-methyl amine. The Alkyl group on the alkylphenol was a branched chain alkyl group containing 10 carbon atoms to 20 carbon atoms.

Comparative Formulation A contained only (A), shown above in Comparative Formulation B. The calcium salt of (a) and (b) were present in a ratio of 3:2.

Test Formulation C contained only (B), shown above in Comparative Formulation B, the anti-wear additive composition of the present invention.

Table I

Component	Formulation (weight %)		
	Comparative A	Comparative B	Test C
Base Oil	92.08	91.47	90.40
Ashless Dispersant	3.4	3.4	3.4
Anti-oxidant	0.5	0.5	0.5
Viscosity Index Improver	0.28	0.28	0.28
Medium Overbased Phenate	0.22	0.22	0.22
Additional Anti-wear Agent	0.36	0.36	0.36
Foam Inhibitor	0.0025	0.0025	0.0025
(A)*	3.16	2.01	
(B)**		1.76	4.84

* (A) is described starting on page 19, line 19 and ending on page 20, line 7.

** (B) is described on page 20, lines 8-12.

Table II below shows the amount of the sulfur, sulfated ash, phosphorus and calcium in Comparative Formulations A and B and Test Formulation C.

Table II

Component	Formulation (weight %)		
	Comparative A	Comparative B	Test C
Sulfur	0.0992	0.1002	0.1007
Sulfated Ash	1.06	1.06	1.06
Phosphorus	0.0378	0.0378	0.0378
Calcium	0.296	0.296	0.296

Example 2

Modified 4-Ball Test

The anti-wear performance of Test Formulation C was compared to Comparative Formulations A and B was evaluated using a modification of the 4-Ball Test. The modification of the Test involved preaging the samples of Formulations A-C. The Preaging was conducted to allow for the building of a protective layer of the anti-wear additive composition of the present invention and to account for the oxidation decomposition products' impact on an additive's anti-wear performance. Comparative Formulations A and B and Test Formulation C, approximately 10 milliliter samples, were preaged for 2 days at 160°C in the presence of the metal balls. The test was started with a 10 kilogram load, which was increased step-wise to a total of 90 kilograms. Oil temperature at the center of the three fixed balls, torque and displacement of the load lever arm were recorded during the test. A wear index was calculated at the end of the test based on the arm displacement data. This modification of the 4-Ball Test is described in a paper titled *Screening Test for Anti-Wear Additives on Modified 4-Ball Test* by J. Cazin, P. Tequi and Y. Lesieur, presented at the 10th International Colloquium on Tribology – Solving

Friction and Wear Problems, Technische Akademie Esslingen BRD, January 9-11, 1996, Proceedings Volume 3, 2063-2073.

The data reported were wear index, oil temperature and torque at the end of the test and seizure. The results of the Modified 4-Ball Test are summarized in Table III below.

Table III

Modified 4-Ball Test	Formulation		
	A	B	C
Wear Index*	276	325	30
Temperature (°C)	134	131	113
Torque (deca-Newton)	0.246	0.243	0.159
Seizure	Yes	Yes	No

* Wear Index is obtained by normalizing the actual distance modification on the surface of the balls due to loss of metal because of wear in the Modified 4-Ball Test. The actual distance is measured in micrometers in the Modified 4-Ball Test, but for ease in reporting the numbers obtained in the Test are multiplied by 10.

The results obtained in the Modified 4-Ball Test summarized above in Table III show that the Test Formulation C containing the anti-wear additive composition of the present invention comprising a calcium salt of a Mannich condensation product gave better anti-wear performance than Comparative Formulation A containing only a mixture of a calcium salt of an alkyl

hydroxyaromatic carboxylic acid and a calcium salt of an alkylphenol or Comparative Formulation B containing both (i) a mixture of a calcium salt of an alkyl hydroxyaromatic carboxylic acid and a calcium salt of an alkylphenol and (ii) a calcium salt of a Mannich condensation product. Table III above shows that in each of the four categories of the data collected Formulation C performed significantly better than either Comparative Formulations A or B. The data show that Comparative Formulation B, even though it contained some calcium salt of a Mannich condensation product, as in Test Formulation C, Comparative Formulation B did not have anti-wear performance comparable to Test Formulation C. The presence of the mixture of a calcium salt of an alkyl hydroxyaromatic carboxylic acid and a calcium salt of an alkylphenol in Comparative Formulation B, even though Comparative Formulation B contained the calcium salt of a Mannich condensation, appears to have a negative effect on anti-wear performance compared to Test Formulation C, which contained only the calcium salt of a Mannich condensation product of an alkylphenol. This result was unexpected.

What is claimed:

1. A low sulfur, low sulfated ash, low phosphorus and low emission heavy duty diesel engine lubricating oil composition comprising:

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

(b) about 3 weight percent to about 12 weight percent of a metal salt of a Mannich condensation product, based on the total weight of the lubricating oil composition.

2. The lubricating oil composition of claim 1, wherein the concentration of the Mannich condensation product is in the range of from about 3 weight percent to about 9 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 Mannich condensation product is in the range of from about 4 weight percent to about 7 weight percent based on the total weight of the lubricating oil composition.

4. The lubricating oil composition of claim 1, wherein in the anti-wear additive composition (b), the Mannich condensation product is a condensation product of an aldehyde having one carbon atom to 20 carbon atoms, a nitrogen base selected from the group consisting of ammonia, a lower alkyl amine, a polyamine and mixtures thereof, and an alkylphenol.

5. The lubricating oil composition of claim 4, wherein the alkyl group on the alkylphenol of the Mannich condensation product is a linear chain or a branched chain alkyl group or mixtures thereof.

6. The lubricating oil composition of claim 5, wherein the alkyl group on the alkylphenol of the Mannich condensation product is a branched chain alkyl group.

7. The lubricating oil composition of claim 4, wherein in the Mannich condensation product the alkyl group on the alkylphenol has from 4 carbon atoms to 60 carbon atoms.

8. The lubricating oil composition of claim 7, wherein the alkyl group on the

alkylphenol of the Mannich condensation product has from 6 carbon atoms to 40 carbon atoms.

9. The lubricating oil composition of claim 8, wherein the alkyl group on the alkylphenol of the Mannich condensation product has from 8 carbon atoms to 20 carbon atoms.

10. The lubricating oil composition of claim 4, wherein the alkyl group on the lower alkyl amine has from one carbon atom to 10 carbon atoms and the polyamine has from 2 amine nitrogen atoms to 12 amine nitrogen atoms and 2 carbon atoms to 40 carbon atoms.

11. The lubricating oil composition of claim 10, wherein the nitrogen base for the preparation of the Mannich condensation product is a lower alkyl amine, wherein the alkyl group has one carbon atom to 10 carbon atoms.

12. The lubricating oil composition of claim 11, wherein the lower alkyl amine is an alkyl mono-amine.

13. The lubricating oil composition of claim 10, wherein the polyamine is a mono-alkylene polyamine, polyalkylene polyamine or mixtures thereof.

14. The lubricating oil composition of claim 4, wherein the aldehyde used to prepare the Mannich condensation product is formaldehyde.

15. The lubricating oil composition of claim 4, wherein the aldehyde used to prepare the Mannich condensation product is paraformaldehyde.

16. The lubricating oil composition of claim 4, wherein in the anti-wear additive composition (b) the Mannich condensation product is prepared from an alkylphenol, wherein the alkyl group on the alkylphenol is a branched chain alkyl group having from 8 carbon atoms to 20 carbon atoms, paraformaldehyde and mono-methyl amine.

17. The lubricating oil composition of claim 1, wherein the metal in the metal salt of Mannich condensation product is an alkali metal or an alkaline earth metal.

18. The lubricating oil composition of claim 17, wherein the metal is an alkaline earth metal.

19. The lubricating oil composition of claim 18, wherein the alkaline earth metal is calcium.

20. The lubricating oil composition of claim 1, wherein the sulfur content is in the range of 0.0 weight percent to about 0.4 weight percent based on the total weight of the lubricating oil.

21. The lubricating oil composition of claim 20, wherein the sulfur content is in the range of 0.05 weight percent to about 0.3 weight percent based on the total weight of the lubricating oil.

22. The lubricating oil composition of claim 21, wherein the sulfur content is in the range of 0.1 weight percent to about 0.2 weight percent based on the total weight of the lubricating oil.

23. The lubricating oil composition of claim 1, wherein the sulfated ash content is in the range of 0.2 weight percent to about 4.0 weight percent based on the total weight of the lubricating oil.

24. The lubricating oil composition of claim 23, wherein the sulfated ash content is in the range of 0.3 weight percent to about 2.0 weight percent based on the total weight of the lubricating oil.

25. The lubricating oil composition of claim 24, wherein the sulfated ash content is in the range of 0.5 weight percent to about 1.2 weight percent based on the total weight of the lubricating oil.

26. The lubricating oil composition of claim 1, wherein the phosphorus content is in the range of 0.005 weight percent to about 0.06 weight percent based on the total weight of the lubricating oil.

27. The lubricating oil composition of claim 26, wherein the phosphorus content is in the range of 0.015 weight percent to about 0.05 weight percent based on the total weight of the lubricating oil.

28. The lubricating oil composition of claim 27, wherein the phosphorus content is in the range of 0.03 weight percent to about 0.04 weight.

29. The lubricating oil composition of claim 1, wherein the lubricating oil composition further comprises one or more lubricating oil additives selected from the group consisting of detergents, dispersants, anti-oxidants, viscosity index improvers, corrosion inhibitors, additional anti-wear agents, friction modifiers, pour point depressants and foam inhibitors.

30. A low sulfur, low sulfated ash, low phosphorus and low emission heavy duty diesel engine lubricating oil concentrate comprising:

(a) from about 10 weight percent to about 90 weight percent of an oil of lubricating viscosity based on the total weight of the lubricating oil concentrate; and

(b) about 3 weight percent to about 12 weight percent of a metal salt of a Mannich condensation product, based on the total weight of the lubricating oil composition.

31. A method for lubricating low emission heavy duty diesel engines, which comprises lubricating with a low sulfur, low sulfated ash, low phosphorus, and low emission heavy duty diesel engine lubricating oil composition comprising:

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

(b) about 3 weight percent to about 12 weight percent of a metal salt of a Mannich condensation product, based on the total weight of the lubricating oil composition.