Lubricant Compositions with Reduced Phosphorous Content for Engines having Catalytic Converters

FIELD OF THE INVENTION

The present invention relates to lubricant compositions, particularly, lubricant compositions for 4-stroke cycle marine engine applications requiring the use of catalytic converters capable of providing enhanced protection against rust and have reduced concentrations of phosphorus.

BACKGROUND OF THE INVENTION

Lubricant compositions are formulated from additive packages for use in crankcase fluids, automotive transmission fluids, lubricating fluids for leisure marine engines, etc. Leisure marine engine applications have traditionally included outboard engines, stern drive engines, and inboard engines. The specific chemical composition of any lubricant composition depends on its performance requirements. As performance requirements continue to change, new finished lubricant compositions will be required.

For example, the emissions requirements of leisure marine engines are continuing to tighten. Consequently, it is expected that these engines will start to incorporate catalytic converters to reduce emissions. It is well known in the art that lubricant compositions having lower levels of phosphorus extend the useful life of catalytic converters. It is also well known in the art to include one or more rust inhibitors in lubricant compositions for leisure marine engines to protect the engines from the harsh environments in which they operate.

The present invention provides a marine lubricant composition comprising (a) ashless dispersant (b) metal-containing detergent; (c) a phosphorus-containing compound; (d) rust inhibitor; and (e) base stock. The lubricant composition of the invention has a low phosphorus level and provides significant rust protection for lubricant compositions that will be used in leisure marine engines having catalytic converters. The lubricant compositions of the invention can be formulated to meet the requirements of the National Marine Manufacturers Association (NMMA) FC-W specification.

SUMMARY OF THE INVENTION

In a non-limiting embodiment, the present invention is a marine lubricant composition comprising: (a) ashless dispersant; (b) metal-containing detergent; (c) a phosphorous-containing compound; (d) rust inhibitor; and (e) base stock, wherein the concentration of phosphorus in the lubricant composition is equal to or less than 0.08 mass%.

In another non-limiting embodiment, the present invention is a marine lubricant composition comprising: (a) ashless dispersant; (b) metal-containing detergent; (c) a phosphorus-containing compound; (d) rust inhibitor; and (e) base stock, wherein the lubricant composition has a concentration of phosphorus equal to or less than to 0.08 mass% and is formulated to meet the requirements of the National Marine Manufacturers Association (NMMA) FC-W specification.

In yet another non-limiting embodiment, the present invention is a method for lubricating a catalyst-equipped, 4-stroke leisure marine engine comprising lubricating the engine with the lubricant composition described above.

DETAILED DESCRIPTION OF THE INVENTION

Unless otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, dimensions, physical characteristics, processing parameters, and the like, used in the specification and claims are to be understood as being modified in all instances by the term "about". Accordingly, unless indicated to the contrary, the numerical values set forth in the following specification and claims may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical value should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Moreover, all ranges disclosed herein are to be understood to encompass the beginning and ending range values and any and all subranges subsumed therein. For example, a stated range of "1 to 10" should be considered to include any and all subranges between (and inclusive of) the minimum value of 1 and the maximum value of 10; that is, all subranges beginning with a

minimum value of 1 or more and ending with a maximum value of 10 or less, e.g., 5.5 to 10.

Any mention of a U.S. Patent or patent document or literature reference in the following description also incorporates by reference that document herein and is to be understood to be incorporated in its entirety.

The present invention is a marine lubricant composition comprising (a) ashless dispersant (b) metal-containing detergent; (c) a phosphorus-containing compound; (d) rust inhibitor; and (e) diluent, wherein the concentration of phosphorus in the lubricant composition is equal to or less than 0.08 mass%..

According to the present invention, the lubricant composition comprises ashless dispersant. Suitable ashless dispersants include, but are not limited to, hydrocarbyl succinimides, hydrocarbyl succinamides, mixed ester/amides of hydrocarbyl-substituted succinic acid, hydroxyesters of hydrocarbyl-substituted succinic acid, Mannich condensation products of hydrocarbyl-substituted phenols, formaldehyde and polyamines. Condensation products of polyamines and hydrocarbyl substituted phenyl acids are also suitable ashless dispersants. Mixtures of the abovementioned ashless dispersants can also be used.

The ashless dispersants used in the present invention are well known and methods of preparing them are described in the patent literature. Hydrocarbyl-substituted succinimides and succinamides and methods of preparing them are described in U.S. Patent Nos. 3,018,247; 3,018,250; 3,018,291; 3,361,673; and 4,234,435. Mixed ester-amides of hydrocarbyl-substituted succinic acids and methods of preparing them are described in U.S. Patent Nos. 3,576,743; 4,234,435; and 4,873,009. Mannich dispersants and methods of preparing them are described in U.S. Patent Nos. 3,368,972; 3,413,347; 3,539,633; 3,697,574; 3,725,277; 3,725,480; 3,726,882; 3,798,247; 3,803,039; 3,985,802; 4,231,759; and 4,142,980. Amine dispersants and methods of preparing them are described in U.S. Pat. Nos. 3,275,554; 3,438,757; and 3,565,804.

In a non-limiting embodiment of the invention, the ashless dispersant comprises an alkenyl succinimide and/or an alkenyl succinamide. The alkenyl succinimide and/or alkenyl succinamide dispersant can be prepared using methods which are well known in the art.

According to the present invention, the ashless dispersant can be post-treated with many reagents as is known to those skilled in the art. For example, the ashless dispersant can be treated with a borating agent as is well known in the art.

In a non-limiting embodiment of the invention, the ashless dispersant is present in an amount ranging from 1.1 to 18.5 weight percent, for example, 3.0 to 12.0 weight percent or 3.5 to 4.5 weight percent, based on the total weight of the lubricant composition. Unless noted otherwise, all weight percentages contained herein are on an active ingredient basis.

According to the present invention, the lubricant composition comprises a metal-containing detergent. Metal-containing detergents function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors thereby reducing wear and corrosion as well as extending engine life. The metal-containing detergents of the present invention generally comprise a compound having a polar head and long hydrophobic tail. The polar head can comprise a metal salt of an acid organic compound.

In a non-limiting embodiment of the invention, the salt contains a substantially stoichiometric amount of metal and has a total base number (TBN) ranging from 0 to 80 measured according to ASTM D-2896. Such salts are typically referred to as "normal" or "neutral" salts.

In another non-limiting embodiment of the invention, the metal-containing detergent is an overbased detergent formed by reacting an excess of a metal compound such as an oxide or hydroxide with an acid gas such as carbon dioxide. The overbased detergent comprises neutralized detergent as the outer layer of a metal base (e.g., carbonate) micelle. Such overbased detergents typically have a TBN of 150 or greater.

Suitable metal-containing detergents also include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal. For example, the metal can be an alkali or alkaline earth metal, e.g., sodium, potassium, lithium, calcium, and magnesium. In a non-limiting embodiment of the invention, the metal is calcium; magnesium; or a mixture of calcium and/or magnesium with sodium.

In a non-limiting embodiment of the invention, the metal-containing detergent is present in an amount ranging from 0.2 to 3.0 weight percent, for example, 0.8 to 2.0

weight percent or 1.0 to 1.4 percent, based on the total weight of the lubricant composition.

According to the present invention, the lubricant composition comprises a phosphorus-containing compound having anti-wear properties. In a non-limiting embodiment, the phosphorus-containing compound is a zinc dihydrocarbyl dithiophosphate (ZDDP). Examples of suitable ZDDPs include (a) those having the formula $Zn[SP(S)(OR^1)(OR^2)]_2$ wherein R^1 and R^2 contain from 1 to 18 carbon atoms and (b) a ZDDP which has more secondary alkyl groups than primary alkyl groups, for example a ZDDP which has at least 50 mass % of secondary alkyl groups, based on the mass of the total alkyl groups. ZDDP and methods of preparing ZDDP are well known in the art. See US Patent No. 6,642,188 which is hereby incorporated by reference.

In a non-limiting embodiment of the invention, the phosphorus-containing compound is present in an amount that will provide a phosphorus level in the finished oil ranging from 0.03 to 0.08 weight percent, for example, 0.05 to 0.08 or 0.07 to 0.08.

According to the present invention, the lubricant composition comprises one or more rust inhibitors. Suitable rust inhibitors include, but are not limited to the following: fatty acid, alkenyl succinate half ester, fatty acid soap, ester of fatty acid and polyhydric alcohol, ethoxylated amines, fatty acid amine, oxidized paraffin, alkyl polyoxyethylene ether, nonionic polyoxyalkylene polyols and esters thereof, other polyoxyalkylene phenols, anionic alkyl sulfonic acids, metal salts of alkyl naphthalene sulfonic acids such as "NA-SUL 129", available from King Industries, and dialkyl hydrogen phosphites or phosphates. Mixtures of rust inhibitors can also be used.

In a non-limiting embodiment of the invention, the rust inhibitor comprises a mixture of ethoxylated nonylphenol or C_4 -C_{18} alkyl phenol rust inhibitor containing about 2 to 10 moles of ethylene oxide per mol and tetrapropyl succinic acid.

In a non-limiting embodiment of the invention, the lubricant composition contains an amount of rust inhibitor capable of providing protection against rust that is equal to or better than the performance of NMMA reference oil 5973. Therefore, in this embodiment, the lubricant composition exhibits a NMMA FC-W Rust Test value less than that of NMMA reference oil 5973 when reference oil 5973 falls within the range of 20-40% rust.

In a non-limiting embodiment of the invention, the rust inhibitor is present in an amount ranging from 0.1 to 2.0 weight percent, for example, 0.2 to 1.0 or 0.2 to 0.6, based on the total weight of the lubricant composition.

According to the present invention, the lubricant composition comprises a base stock. The base stock comprises a Group I, Group II, Group III, Group IV and/or Group V base oil blend. The various base oil blends are defined in the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum Dec. 1, 1998. In a non-limiting embodiment of the invention, the base stock is present in an amount greater than or equal to 50 weight percent of the lubricant composition.

In a non-limiting embodiment of the present invention, the lubricant composition comprises a molybdenum-containing compound. Suitable molybdenum-containing compounds include every oil soluble organo-molybdenum compound. In a non-limiting embodiment of the invention, the molybdenum-containing compound comprises a dialkyldithiocarbamate, dialkyldithiophosphate, dialkyldithiophosphinate, xanthate, thioxanthate, carboxylate or mixtures thereof.

In a non-limiting embodiment of the invention, the molybdenum-containing compound is present in an amount to provide a concentration of molybdenum ranging from 0.001 to 1.0 weight percent, for example, 0.002 to 0.5 weight percent or 0.005 to 0.1 weight percent, based on the total weight of the lubricant composition.

According to the present invention, various optional compounds and materials can be added to the lubricant composition. These optional compounds and materials include, but are not limited to, friction modifiers, viscosity modifiers, stabilizers, oxidation inhibitors, demulsifiers, antifoam additives, tackifiers and pour depressants.

In a non-limiting embodiment of the present invention, the lubricant composition further comprises a viscosity modifier. Suitable viscosity modifiers include, but are not limited to, oil soluble polymers such as polyesters having a weight average molecular weights from about 10,000 to 1,000,000, preferably from about 20,000 to 500,000, as determined by gel permeation chromatography or light scattering methods. Representative examples of suitable viscosity modifiers are polyisobutylene, copolymers of ethylene and propylene and higher alpha-olefins, polymethacrylates, polyalkylmethacrylates, methacrylate copolymers, copolymers of

unsaturated dicarboxylic acid and vinyl compound, inter polymers of styrene and acrylic ester, and partially hydrogenated copolymers of styrene/isoprene, styrene/butadiene and isoprene/butadiene, as well as partially hydrogenated homopolymers of butadiene and isoprene and isoprene/divinylbenzene.

Suitable viscosity modifiers also include hydrogenated copolymers of a vinyl substituted aromatic compound and a conjugated diene. These hydrogenated styrene-isoprene block copolymers products are commercially available from Infineum USA L.P. (New Jersey) as Infineum SV140 and Infineum SV150.

In another non-limiting embodiment of the invention, the lubricant composition

further comprises one or more of the following: stabilizers, oxidation inhibitors, demulsifiers, antifoam additives and pour depressants as are well known in the art.

Examples of known oxidation inhibitors include hindered phenols, alkaline earth metal salts of alkylphenolthioesters having preferably C_5 to C_{12} alkyl side chains, calcium nonylphenol sulfide, ashless oil soluble phenates, sulfurized phenates, sulfurized hydrocarbons, metal thiocarbamates, aromatic amines having at least two aromatic groups attached directly to the nitrogen constitute and oil soluble copper compounds as described in U.S. Patent No. 4,867,890.

Examples of suitable demulsifiers include those described in EP 330,522. Examples of suitable pour point depressants include C_8 to C_{18} dialkyl fumarate/vinyl acetate copolymers, polyalkylmethacrylates, etc. Examples of suitable antifoam additives include a fluorosilicone and polysiloxane compounds such as silicone oil or polydimethyl siloxane.

The lubricant composition of the present invention can be formulated from the individual components described above using methods and techniques which are well known in the art. In a non-limiting embodiment of the invention, the lubricant compositions of the invention can be formulated to meet the requirements of the National Marine Manufacturers Association (NMMA) FC-W specification

The present invention also encompasses additive packages from which the described lubricant compositions are formulated.

In a non-limiting embodiment of the invention, when the lubricant composition is subjected to ASTM D4683, it exhibits a High Temperature, High Shear ("HTHS") viscosity equal to or greater than 3.3 cP at 150°C after being

subjected to 30 cycles of shear as described in ASTM D6278 Shear Stability test. ASTM D6278 simulates the type of shear an oil might experience in an engine. A minimum HTHS viscosity of 3.3 cP at 150°C ensures adequate viscosity for proper lubrication of the engine bearings.

The lubricant composition of the present invention has a phosphorus level equal to or less than 0.08 m% and provides improved rust protection. As a result, the lubricant composition is ideally suited for use in marine engines equipped with catalytic converters. Lubricant compositions with low phosphorus levels are known within the industry as contributing to extended catalyst life.

The present invention also encompasses a method for lubricating a catalyst-equipped 4-stroke leisure marine engine comprising lubricating the engine with the lubricant composition described above.

Examples

The present invention is illustrated by five non-limiting examples- Examples 1-5. Each of the Examples was prepared by mixing the specified components in the amounts indicated as in Table 1 below and blending. The oils in the examples were prepared using standard laboratory blending techniques and temperatures.

Table 1. Compositional Information for Examples 1-5

Component	Example 1 [wt% of active ingredient]	Example 2 [wt% of active ingredient]	Example 3 [wt% of active ingredient]	Example 4 [wt% of active ingredient]	Example 5 [wt% of active ingredient]
Alkenyl succinimide ashless dispersant	3.543	3.543	0.000	2.943	2.943
Borated alkenyl succinimide ashless dispersant	0.000	0.000	4.447	0.000	0.000
Borated alkenyl succinimide ashless dispersant	0.000	0.675	0.000	0.720	0.720
Overbased calcium sulfonate detergent	1.018	1.018	0.000	0.000	0.000
Overbased magnesium sulfonate detergent	0.000	0.000	0.726	0.719	0.719

Carbonated low base number calcium sulphurized phenate detergent	0.230	0.230	0.487	0.483	0.483
Alkenyl succinic anhydride	0.360	0.360	0.000	0.144	0.144
Phosphorus-containing compound [Zinc dihydrocarbyl dithiophosphate]	0.698	0.698	0.705	0.705	0.705
Antioxidant [Nonyl alkylated diphenyl amines]	0.600	0.600	0.000	0.625	0.625
Antioxidant [$C_7 - C_9$ hindered phenol]	0.000	0.000	0.339	0.335	0.335
Demulsifier	0.000	0.000	0.003	0.000	0.000
Molybdenum-containing compound [Molybdenum Dialkyldithiocarbamate]	0.042	0.042	0.042	0.023	0.023
60,000 cSt silicone antifoam additive	0.000	0.000	0.000	0.002	0.002
Polydimethyl-siloxane antifoam additive	0.001	0.001	0.000	0.000	0.000
12,500 cSt silicone antifoam additive	0.000	0.000	0.001	0.000	0.000
Glycerol mono oleate (GMO)friction modifier	0.200	0.200	0.200	0.200	0.000
Ethoxylated nonyl phenol rust inhibitor	0.360	0.360	0.120	0.150	0.200
Tetrapropyl succinic acid rust inhibitor	0.252	0.252	0.084	0.105	0.200
Dialkyl fumarate/vinyl acetate copolymer pour point depressant	0.300	0.300	0.000	0.000	0.300
Pour Point Depressant [LZ6662A from Lubrizol]	0.000	0.000	0.200	0.200	0.000
Viscosity Modifier [Lubegard 2004]	0.000	0.000	8.550	11.000	0.000
Viscosity Modifier [Infineum SV205]	0.000	0.000	0.000	0.000	6.000
Group V base stock [TMP ester]	2.000	2.000	0.000	0.000	0.000
Group IV base stock [Poly alpha olefin]	8.000	8.000	0.000	0.000	0.000
Group II base stock	0.000	0.000	35.900	30.000	0.000
Group I base stock	82.396	81.721	48.196	51.646	86.601
Phosphorus concentration[1]	0.075	0.075	0.075	0.075	0.075

[1] Calculated value based on the amount of ZDDP in the compositions.

Examples 1-4 were subjected to a modification of the NMMA FC-W rust test. The NMMA FC-W rust test provides a standard method for making a qualitative evaluation of the corrosion protection performance of engine oils. The NMMA FC-W rust test procedure utilizes NMMA-approved steel coupons (cut from actual cylinder liners) hung in a humid salt environment for 24 hours. In this modification of the test, the NMMA FC-W rust test procedure was explicitly followed except that two coupons per oil were used for screening purposes rather than four coupons per oil.

Example 5 was run per the NMMA FC-W procedure using four coupons per oil. One of the coupons was dropped as a statistical outlier, per the procedure.

See Table 2 below for the results of the modified NMMA FC-W rust test. Table 2 shows the average rust test value for the coupons and the individual rust test values for the coupons. The individual rust test values are in parentheses. Rust test values for the NMMA 5973 reference oil during the tests is also shown to support the validity of all the tests.

Table 2. Modified NMMA FC-W Rust Test results

	Example 1	Example 2	Example 3	Example 4	Example 5
Avg. Rust Test Value	14 (15 and 12)	17 (20 and 14)	35 (33 and 37)	36 (23 and 48)	25 (30, 24 and 22)
Avg. Rust Test Value for NMMA 5973	39 (38 and 39)	21 (22 and 20)	40 (40 and 40)	37 (38 and 36)	38 (40, 40, 38 and 36)
Result	Pass	Pass	Pass	Pass	Pass

In order to pass the NMMA FC-W Rust Test, an example must exhibit rust performance that is equal to or better than that of a concurrent reference oil, identified as NMMA 5973. Additionally, in order for the results of the NMMA FC-W rust test to be valid, NMMA 5973 must fall within the range of 20-40% rust. As shown in Table 2, all of the examples according to the present invention passed the test.

What Is Claimed Is:

1. A lubricant composition comprising:

a. ashless dispersant;

b. metal-containing detergent;

c. a phosphorus-containing compound;

d. rust inhibitor; and

e. base stock, wherein the lubricant composition has a concentration of phosphorus equal to or less than to 0.08 mass%.

2. The lubricant composition according to claim 1, wherein the rust inhibitor is present in an amount capable of providing protection against rust that is equal to or better than the performance of NMMA reference oil 5973 in the NMMA FC-W Rust Test when reference oil 5973 is within the range of 20-40% rust.

3. The lubricant composition according to claim 2, wherein the rust inhibitor is present in an amount ranging from 0.1 to 2.0 weight percent, based on the total weight of the lubricant composition.

4. The lubricant composition according to claim 1 wherein the ashless dispersant is selected from the group comprising of hydrocarbyl succinimides, hydrocarbyl succinamides, mixed ester/amides of hydrocarbyl-substituted succinic acid, hydroxyesters of hydrocarbyl-substituted succinic acid, Mannich condensation products of hydrocarbyl-substituted phenols, formaldehyde, polyamines and mixtures thereof.

5. The lubricant composition according to claim 1 wherein the ashless dispersant is present in an amount ranging from 1.1 to 18.5 weight percent based on the total weight of the lubricant composition.

6. The lubricant composition according to claim 1 wherein the metal-containing detergent is selected from the group comprising oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates, other oil-soluble carboxylates of a metal and mixtures thereof.

7. The lubricant composition according to claim 1 wherein the metal-containing detergent is present in an amount ranging from 0.2 to 3.0 weight percent, based on the total weight of the lubricant composition.

8. The lubricant composition according to claim 1 wherein the basestock is selected from the group comprising Group I blended oils, Group II blended oils, Group III blended oils, Group IV blended oils, Group V blended oils and mixtures thereof.

9. The lubricant composition according to claim 1 further comprising a molybdenum-containing compound.

10. The lubricant composition according to claim 9 wherein the molybdenum-containing compound is present in an amount to provide a concentration of molybdenum ranging from 0.001 to 1.0 weight percent, based on the total weight of the lubricant composition.

11. The lubricant composition according to claim 1 wherein the phosphorus-containing compound is ZDDP.

12. The lubricant composition according to claim 1 further comprising one or more of the following: friction modifiers, viscosity modifiers, stabilizers, oxidation inhibitors, demulsifiers, antifoam additives, tackifiers and pour depressants.

13. A marine lubricant composition comprising:

a. ashless dispersant;
b. metal-containing detergent;

c. a phosphorus-containing compound;

d. rust inhibitor; and

e. base stock, wherein the lubricant composition has a concentration of phosphorus equal to or less than 0.08 mass% and is formulated to meet the requirements of the National Marine Manufacturers Association (NMMA) FC-W specification.

14. The marine lubricant composition according to claim 13 further comprising a molybdenum-containing compound.

15. The marine lubricant composition according to claim 14 wherein the molybdenum-containing compound is present in an amount to provide a concentration of molybdenum ranging from 0.001 to 1.0 weight percent, based on the total weight of the lubricant composition.

16. The marine lubricant composition according to claim 13 wherein when the lubricant composition is subjected to ASTM D4683, it exhibits an HTHS viscosity equal to or greater than 3.3 cP at 150°C after being subjected to 30 cycles of shear as described in ASTM D6278 Shear Stability test.

17. A method for lubricating a catalyst-equipped, 4-stroke marine engine comprising:

lubricating the engine with a lubricant composition comprising ashless dispersant; metal-containing detergent; a phosphorus-containing compound; rust inhibitor; and base stock, wherein the lubricant composition has a concentration of phosphorus less than or equal to 0.08 mass%.