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TITLE

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

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FIELD OF THE INVENTION

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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.

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BACKGROUND OF THE INVENTION

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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.

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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-

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

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

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

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

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

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

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

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25 U. S. Patent No. 5,102,566 discloses a low sulfated ash lubricating oil
26 composition which comprises a base oil, at least about 2 weight percent of an
27 ashless nitrogen- or ester-containing dispersant, an oil-soluble antioxidant
28 material, and an oil soluble di-hydrocarbyl di-thiophosphate anti-wear
29 material, and which has a total sulfated ash level of 0.01 to 0.6 weight percent
30 and a weight ratio of total sulfated ash and the dispersant in the range of
31 0.01:1 to 0.2:2.

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

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

16 U. S. Patent No. 6,159,911 discloses a diesel engine oil composition
17 containing a lube oil base and one or more metallic detergents-dispersants
18 selected from among a perbasic alkaline earth metal sulfonate, phenolate and
19 salicylate. The total phosphorus content of the composition is suppressed to
20 100 parts per million by weight or less, to thereby provide diesel engine oil
21 compositions having oxidation stability and wear resistance.

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

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

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

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8 U. S. Patent Nos. 6,331,510 and 6,610,637 disclose a lubricant containing (a)
9 a synthetic base oil composition having an overall kinematic viscosity of at
10 least about $4.8 \times 10^{-6} \text{ m}^2/\text{s}$ (4.8 cSt) at 100°C and a viscosity index of at least
11 110; (b) a dispersant-viscosity modifier; and (c) a sulfur-free functionalized
12 hydrocarbyl-substituted phenol detergent provides improved valve train wear,
13 with longer drain intervals, to heavy duty diesel engines.

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

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

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

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

11
12 European Patent Application No. 01201752.1 (Publication No. EP 1 256 619
13 A1) deemed withdrawn as of March 5, 2005, and U.S. Patent Application NO.
14 10/142,513 (Publication No. US 2003/0096716 A1) disclose a lubricating oil
15 composition comprising: (A) an oil of lubricating viscosity, in a major amount
16 and added thereto: (B) a detergent composition comprising one or more metal
17 detergents which comprises metal salts or organic acids, in a minor amount,
18 wherein the detergent composition comprises more than 50 mole percent of a
19 metal salt of an aromatic carboxylic acid, based on the moles of the metal
20 salts of organic acids in the detergent composition, and (C) one or more co-
21 additives, in a minor amount; wherein the total amounts of phosphorus and
22 sulfur derived from (B) or (C) or both (B) and (C) are less than 0.1 mass p% of
23 phosphorus and at the most 0.5 mass % of sulfur, based on the mass of the
24 oil composition. It has been found that a detergent composition comprising
25 more than 50 mole % of a metal salt of an aromatic carboxylic acid improves
26 the reduction in wear in an engine.

27
28 U.S. Patent Application No. 10/430,594 (Publication No. US 2003/0216266
29 A1) discloses a lubricating oil composition employable in combination with a
30 low sulfur content fuel oil is preferably composed of a base oil having a sulfur
31 content of at most 0.2 weight percent, an ashless dispersant comprising an
32 alkenyl- or alkyl-succinimide or derivative thereof, a metal-containing
33 detergent containing an organic acid metal salt, a zinc di-alkyl di-

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

6
7 International Publication No. WO 2004/046283 A1 discloses the use of
8 lubricating oils with low sulfur content in combination with a low sulfur fuel to
9 reduce particulate emissions of a diesel engine equipped with a particulate
10 trap.

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12 SUMMARY OF THE INVENTION

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

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

26 In one aspect, there is provided the use of a metal salt of a Mannich
27 condensation product as an anti-wear agent in a low sulfur, low sulfated ash
28 and low phosphorus lubricating oil composition for low emission heavy duty
29 diesel engines, wherein the metal salt of a Mannich condensation product is

used in an amount of at least 2 weight percent based on the total weight of the lubricating oil composition, and wherein:

- (a) the sulfur content of the lubricating oil composition is in the range of 0.0 weight percent to 0.4 weight percent based on the total weight of the lubricating oil;
- (b) the sulfated ash content of the lubricating oil composition is in the range of 0.2 weight percent to 4.0 weight percent based on the total weight of the lubricating oil; and
- (c) the phosphorous content of the lubricating oil composition is in the range of 0.005 weight percent to 0.06 weight percent based on the total weight of the lubricating oil.

In one embodiment, 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

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

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

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

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

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

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

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

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

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

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

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

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

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

4 Preferably the sulfated ash content of the lubricating oil composition of the
5 present invention is in the range of 0.2 weight percent to about 4.0 weight
6 percent based on the total weight of the lubricating oil. More preferably the
7 sulfated ash content of the lubricating oil composition of the present invention
8 is in the range of 0.3 weight percent to about 2.0 weight percent based on the
9 total weight of the lubricating oil. Most preferably the sulfated ash content of
10 the lubricating oil composition of the present invention is in the range of 0.5
11 weight percent to about 1.2 weight percent based on the total weight of the
12 lubricating oil.

13 Preferably the phosphorus content of the lubricating oil composition of the
14 present invention is in the range of 0.005 weight percent to about 0.06 weight
15 percent based on the total weight of the lubricating oil. More preferably the
16 phosphorus content of the lubricating oil composition of the present invention
17 is in the range of 0.015 weight percent to about 0.05 weight percent based on
18 the total weight of the lubricating oil. Most preferably the phosphorus content
19 of the lubricating oil composition of the present invention is in the range of
20 0.03 weight percent to about 0.04 weight percent based on the total weight of
21 the lubricating oil.

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

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

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

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

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

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

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

23 Useful foam inhibitors are of the polysiloxane type.

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

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

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

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

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

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

11 DETAILED DISCRIPTION OF THE INVENTION

12 DEFINITIONS

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

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

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

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

1 The term "dispersants" as used herein refers to additives that keep soot and
2 combustion products in suspension in the body of the oil charge and therefore
3 prevent deposition as sludge or lacquer. Typically, the ashless dispersants
4 are nitrogen-containing dispersants formed by reacting alkenyl succinic acid
5 anhydride with an amine. Examples of such dispersants are alkenyl
6 succinimides and succinamides. These dispersants can be further modified
7 by reaction with, for example, boron or ethylene carbonate. Ester-based
8 ashless dispersants derived from long chain hydrocarbon-substituted
9 carboxylic acids and hydroxy compounds may also be employed. Preferred
10 ashless dispersants are those derived from polyisobutenyl succinic anhydride.
11 Dispersancy may also be controlled by dispersant viscosity modifiers, such as
12 polymethacrylates, alkylmethacrylate styrene copolymers,
13 polyalkylmethacrylates and olefin copolymers. A large number of dispersants
14 are commercially available.

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

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

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

1 Unless otherwise specified, all percentages are in weight percent.

2 LUBRICATING OIL COMPOSITION

3 It has been discovered that the a low sulfur, low sulfated ash and low
4 phosphorus lubricating oil composition comprising an anti-wear additive
5 composition comprising a metal salt of a Mannich condensation product
6 provides good wear control when used for low emission heavy duty diesel
7 engines. Wear control in conventional lubricating oil compositions is achieved
8 by the addition of metal salts of di-alkyl di-thiophosphates, for example zinc di-
9 alkyl di-thiophosphates, however, the metal in these anti-wear additives
10 contributes to an increase in sulfated ash in the lubricating oil and the
11 phosphorus causes inactivation of oxidation catalysts used in exhaust after-
12 treatment devices. The anti-wear additive composition employed in the
13 lubrication oil composition of the present invention provides good wear control
14 without contributing to an increase in sulfur and sulfated ash, and because it
15 does not contain any phosphorus, it does not inactivate the oxidation
16 catalysts.

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

22 Oil of Lubricating Viscosity

23 Oil of lubricating viscosity, or base oil as used herein refer to lubricating oils
24 which may be mineral oil or synthetic oils of lubricating viscosity and
25 preferably useful in the crankcase of an internal combustion engine.
26 Crankcase lubricating oils ordinarily have a viscosity of about 1300
27 centistokes at -17.8°C to 22.7 centistokes at 98.9°C. The lubricating oils may
28 be derived from synthetic or natural sources. Mineral oil for use as the base
29 oil in this invention includes paraffinic, naphthenic and other oils that are
30 ordinarily used in lubricating oil compositions. Synthetic oils include

1 hydrocarbon synthetic oils and synthetic esters. Useful synthetic hydrocarbon
2 oils include liquid polymers of alpha-olefins having the proper viscosity.
3 Especially useful are the hydrogenated liquid oligomers of C₆ to C₁₂ alpha-
4 olefins such as 1-decene trimer. Similarly, alkyl benzenes of proper viscosity,
5 such as didodecyl benzene, may be used. Useful synthetic esters include the
6 esters of both mono-carboxylic acids and polycarboxylic acids as well as
7 mono-hydroxy alkanols and polyols. Typical examples are didodecyl adipate,
8 pentaerthritol tetracapoate, di-2-ethylhexyl adipate, di-laurylsebacate and the
9 like. Complex esters prepared from mixtures of mono- and di-carboxylic acid
10 and mono- and di-hydroxy alkanols can also be used. Blends of hydrocarbon
11 oils and synthetic oils may also be used. For example, blends of 10 weight
12 percent to 25 weight percent hydrogenated 1-decene trimer with 75 weight
13 percent to 90 weight percent 683 centistokes at 37.8°C mineral oil gives an
14 excellent oil base. Fischer-Tropsch derived base oils may also be employed
15 in the lubricating oil composition of the present invention.

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

22 Anti-wear Additives

23 Metal salt of Mannich condensation product

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

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

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

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

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

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

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

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

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

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

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

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

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

21 Other Additives

22 The lubricating oil composition of the present invention may also typically
23 contain, in addition to the detergent composition of the present invention,
24 other additives used to impart desirable properties to the lubricating oil
25 composition of the present invention. Thus, the lubricating oil may contain
26 one or more of additives, such as, dispersants, anti-oxidants, viscosity index
27 improvers, corrosion inhibitors, anti-wear agents, friction modifiers, pour point
28 depressants and foam inhibitors.

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

7 Low, Medium and High Overbased Metal Detergents

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

20 Dispersants

21 The lubricating oil composition of the present invention optionally contains
22 dispersants. Typically, the ashless dispersants are nitrogen-containing
23 dispersants formed by reacting alkenyl succinic acid anhydride with an amine.
24 Examples of such dispersants are alkenyl succinimides and succinamides.
25 These dispersants can be further modified by reaction with, for example,
26 boron or ethylene carbonate. Ester-based ashless dispersants derived from
27 long chain hydrocarbon-substituted carboxylic acids and hydroxy compounds
28 may also be employed. Preferred ashless dispersants are those derived from

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

3 Anti-oxidants

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

15 Viscosity Index Improvers

16 Viscosity index improvers are added to lubricating oil to regulate viscosity
17 changes due to the change in temperature. Some commercially available
18 examples of viscosity index improvers are olefin copolymers, polybutene,
19 polymethacrylates, vinylpyrrolidone and methacrylate copolymers.

20 Corrosion inhibitors

21 Corrosion inhibitors are included in lubricating oils to protect vulnerable metal
22 surfaces. Such corrosion inhibitors are generally used in very small amounts
23 in the range of from about 0.02 weight percent to about 1.0 weight percent.
24 The corrosion inhibitor should not be one that is itself corrosive to silver and
25 silver plated bearings, such as, metal di-thiophosphates. Examples of
26 corrosion inhibitors that may be used are sulfurized olefin corrosion inhibitor
27 and the co-sulfurized alkenyl ester/alpha olefin corrosion inhibitor.

1 In addition to the materials already described, lubricating oil composition of
2 the present invention may also include other additives, such as pour point
3 depressants and anti-foaming agents. The various additive materials or
4 classes of materials herein described are well known materials and can be
5 readily purchased commercially or prepared by known procedures or obvious
6 modification thereof.

7 EXAMPLES

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

12 Example 1

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

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

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

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

3 Comparative Formulation B contained:

4 (A) calcium salts of a mixture of:

5 (a) a mixture of:

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

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

14 (b) a mixture of:

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

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

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

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

26

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

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

1

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

2

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

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

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

7

8

9

1

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

2

3

Example 2

4

Modified 4-Ball Test

5 The anti-wear performance of Test Formulation C was compared to
 6 Comparative Formulations A and B was evaluated using a modification of the
 7 4-Ball Test. The modification of the Test involved preaging the samples of
 8 Formulations A-C. The Preaging was conducted to allow for the building of a
 9 protective layer of the anti-wear additive composition of the present invention
 10 and to account for the oxidation decomposition products' impact on an
 11 additive's anti-wear performance. Comparative Formulations A and B and
 12 Test Formulation C, approximately 10 milliliter samples, were preaged for 2
 13 days at 160°C in the presence of the metal balls. The test was started with a
 14 10 kilogram load, which was increased step-wise to a total of 90 kilograms.
 15 Oil temperature at the center of the three fixed balls, torque and displacement
 16 of the load lever arm were recorded during the test. A wear index was
 17 calculated at the end of the test based on the arm displacement data. This
 18 modification of the 4-Ball Test is described in a paper titled *Screening Test for*
 19 *Anti-Wear Additives on Modified 4-Ball Test* by J. Cazin, P. Tequi and Y.
 20 Lesieur, presented at the 10th International Colloquium on Tribology – Solving

1 Friction and Wear Problems, Technische Akademie Esslingen BRD, January
2 9-11, 1996, Proceedings Volume 3, 2063-2073.

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

6 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

7

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

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

1 hydroxyaromatic carboxylic acid and a calcium salt of an alkylphenol or
2 Comparative Formulation B containing both (i) a mixture of a calcium salt of
3 an alkyl hydroxyaromatic carboxylic acid and a calcium salt of an alkylphenol
4 and (ii) a calcium salt of a Mannich condensation product. Table III above
5 shows that in each of the four categories of the data collected Formulation C
6 performed significantly better than either Comparative Formulations A or B.

7 The data show that Comparative Formulation B, even though it contained
8 some calcium salt of a Mannich condensation product, as in Test Formulation
9 C, Comparative Formulation B did not have anti-wear performance
10 comparable to Test Formulation C. The presence of the mixture of a calcium
11 salt of an alkyl hydroxyaromatic carboxylic acid and a calcium salt of an
12 alkylphenol in Comparative Formulation B, even though Comparative
13 Formulation B contained the calcium salt of a Mannich condensation, appears
14 to have a negative effect on anti-wear performance compared to Test
15 Formulation C, which contained only the calcium salt of a Mannich
16 condensation product of an alkylphenol. This result was unexpected.

What is claimed:

1. Use of a metal salt of a Mannich condensation product as an anti-wear agent in a low sulfur, low sulfated ash and low phosphorus lubricating oil composition for low emission heavy duty diesel engines, wherein the metal salt of a Mannich condensation product is used in an amount of at least 2 weight percent based on the total weight of the lubricating oil composition, and wherein:
 - (a) the sulfur content of the lubricating oil composition is in the range of 0.0 weight percent to 0.4 weight percent based on the total weight of the lubricating oil;
 - (b) the sulfated ash content of the lubricating oil composition is in the range of 0.2 weight percent to 4.0 weight percent based on the total weight of the lubricating oil; and
 - (c) the phosphorous content of the lubricating oil composition is in the range of 0.005 weight percent to 0.06 weight percent based on the total weight of the lubricating oil.
2. Use according to claim 1, wherein the concentration of the Mannich condensation product is in the range of from about 2 weight percent to about 12 weight percent based on the total weight of the lubricating oil composition.
3. Use according to claim 1 or 2, 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.
4. Use according to any one of the preceding claims, 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.
5. Use according to any one of the preceding claims, wherein in the anti-wear additive 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.
6. Use according to claim 5, 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.

7. Use according to claim 6, wherein the alkyl group on the alkylphenol of the Mannich condensation product is a branched chain alkyl group.
- 5 8. Use according to any one of claims 5 to 7, wherein in the Mannich condensation product the alkyl group on the alkylphenol has from about 4 carbon atoms to about 60 carbon atoms.
9. Use according to any one of claims 5 to 8, wherein the alkyl group on the alkylphenol of the Mannich condensation product has from about 6 carbon atoms to about 40 carbon atoms.
- 10 10. Use according to any one of claims 5 to 9, wherein the alkyl group on the alkylphenol of the Mannich condensation product has from about 8 carbon atoms to about 20 carbon atoms.
11. Use according to any one of claims 5 to 10, wherein the alkyl group on the lower alkyl amine has from one carbon atom to about 10 carbon atoms and the polyamine has from 2 amine nitrogen atoms to about 12 amine nitrogen atoms and 2 carbon atoms to about 40 carbon atoms.
- 15 12. Use according to any one of claims 5 to 11, 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 about 10 carbon atoms.
13. Use according to claim 12, wherein the lower alkyl amine is an alkyl mono-amine.
- 20 14. Use according to any one of claims 5 to 13, wherein the polyamine is a mono-alkylene polyamine, polyalkylene polyamine or mixtures thereof.

15. Use according to any one of claims 5 to 14, wherein the aldehyde used to prepare the Mannich condensation product is formaldehyde.
- 5 16. Use according to any one of claims 5 to 15, wherein the aldehyde used to prepare the Mannich condensation product is paraformaldehyde.
- 10 17. Use according to any one of the preceding claims, 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 about 8 carbon atoms to about 20 carbon atoms, paraformaldehyde and mono-methyl amine.
18. Use according to any one of the preceding claims, wherein the metal in the metal salt of Mannich condensation product is an alkali metal or an alkaline earth metal.
19. Use according to claim 18, wherein the metal is an alkaline earth metal.
20. Use according to claim 19, wherein the alkaline earth metal is calcium.
- 15 21. Use according to any one of the preceding claims, 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.
- 20 22. Use according to any one of the preceding claims, 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. Use according to any one of the preceding claims, 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.
- 5 24. Use according to any one of the preceding claims, 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.
- 10 25. Use according to any one of the preceding claims, 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.
26. Use according to any one of the preceding claims, wherein the phosphorus content is in the range of 0.03 weight percent to about 0.04 weight
- 15 27. Use according to any one of the preceding claims, wherein the 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.