

1 TITLE

2 DETERGENT COMPOSITION FOR A LOW SULFUR, LOW SULFATED ASH
3 AND LOW PHOSPHORUS LUBRICATING OIL FOR HEAVY DUTY DIESEL
4 ENGINES

5
6 FIELD OF THE INVENTION

7 The present invention is directed to a low sulfur, low sulfated ash and low
8 phosphorus lubricating oil composition for low emission heavy duty diesel
9 engines comprising (a) a major amount of an oil of lubricating viscosity and
10 (b) a detergent composition comprising (i) a mixture of a metal salt of an
11 alkyl hydroxyaromatic carboxylic acid and a metal salt of an alkyl phenol, and
12 (ii) a metal salt of a Mannich condensation product. The present invention is
13 also directed to a low sulfur, low sulfated ash and low phosphorus lubricating
14 oil concentrate comprising (a) an oil of lubricating viscosity and (b) a detergent
15 composition comprising (i) a mixture of a metal salt of an alkyl
16 hydroxyaromatic carboxylic acid and a metal salt of an alkyl phenol, and (ii) a
17 metal salt of a Mannich condensation product.

18 BACKGROUND OF THE INVENTION

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

26
27 In order to reduce air pollution, vehicle manufacturers and petroleum
28 companies are interested in developing lubricating oil systems that have low
29 emissions and better fuel economy for heavy duty diesel engines.

30 Environmental pollution caused by emissions from diesel engines may
31 comprise particulates and carbon oxides, sulfur oxides and nitrogen oxides.

32 Diesel engine manufacturers have started to equip diesel engines with

1 exhaust after-treatment devices containing particulate filters, oxidation
2 catalysts and reduction catalysts to obviate environmental problems.

3

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

22

23 Anti-wear and anti-oxidants, such as zinc di-alkyl di-thiophosphates, also
24 contribute to reduction in the activity of the oxidation catalysts. Increased
25 phosphorus levels in the lubricating oil enhance deactivation of the oxidation
26 catalysts used in exhaust gas cleaning devices. Therefore, there is a need to
27 decrease the phosphorus content in the lubricating oil to keep the oxidation
28 catalysts from deterioration. Furthermore, the zinc contributes to the sulfated
29 ash which cogs the particulate filters in the exhaust gas cleaning devices.

30

31 A number of patents and patent applications have discussed methods for
32 reducing particulate emissions and low sulfur, low sulfated ash and low

1 phosphorus lubricating oil compositions, but none have disclosed a low
2 emission lubricating oil of the present invention for diesel engines.
3 Canadian Patent No. 810120 discloses a lubricating oil composition
4 comprising the reaction product obtained by the neutralization with an alkaline
5 earth metal oxide or hydroxide of a sulfurized alkyl phenol in admixture with a
6 Mannich base reacted with carbon dioxide.

7
8 U. S. Patent No. 5,102,566 discloses a low sulfated ash lubricating oil
9 composition which comprises a base oil, at least about 2 weight percent of an
10 ashless nitrogen- or ester-containing dispersant, an oil-soluble antioxidant
11 material, and an oil soluble di-hydrocarbyl di-thiophosphate anti-wear
12 material, and which has a total sulfated ash level of 0.01 to 0.6 weight percent
13 and a weight ratio of total sulfated ash and the dispersant in the range of
14 0.01:1 to 0.2:2.

15
16 U. S. Patent Nos. 5,486,300 and 5,490,945 disclose a lubricating oil
17 composition comprising a major amount of an oil of lubricating viscosity; and
18 (A) an amount of at least one alkali metal overbased salt of an acidic organic
19 compound sufficient to provide at least about 0.005 equivalents of alkali metal
20 per 100 grams of lubricating composition; (B) at least about 1.13% by weight
21 of at least one dispersant; (C) at least one metal di-hydrocarbyl di-
22 thiophosphate; and (D) at least one anti-oxidant, provided that the lubricating
23 oil composition is free of calcium overbased sulfonate provided that the
24 composition contains less than about 0.08 % by weight calcium; and provided
25 that (C) and (D) are not the same.

26
27 U. S. Patent Nos. 5,562,864 and 5,614,480 disclose a lubricating oil
28 composition which comprises a major amount of an oil of lubricating viscosity
29 and (A) at least about 1% by weight of at least one carboxylic derivative
30 composition produced by reacting (A-1) at least one substituted succinic
31 acylating agent containing at least 50 carbon atoms in the substituent with
32 (A-2) from about 0.5 equivalents up to about 2 moles per equivalents of
33 acylating agent (A-1), or at least one amine compound characterized by the

1 presence within its structure of at least one HN<group; and (B) an amount of
2 at least one alkali metal overbased salt of a carboxylic acid or a mixture of a
3 carboxylic acid and an organic sulfonic acid sufficient to provide at least about
4 0.002 equivalent of alkali metal per 100 grams of the lubricating oil
5 composition provided that when the alkali metal salt comprises a mixture of
6 overbased alkali metal salts of hydrocarbyl -substituted carboxylic acids and
7 a hydrocarbyl-substituted sulfonic acid, then the carboxylic acid comprises
8 more than 50% of the acid equivalents of the mixture; and either; (C-1) at
9 least one magnesium overbased salt of an acidic organic compound provided
10 that the lubricating oil composition is free of calcium overbased salts of acidic
11 organic compounds; or (C-2) at least one calcium overbased salt of an acidic
12 organic compounds provided that the lubricating composition is free of
13 magnesium overbased salts of acidic organic compounds.

14 U. S. Patent No. 5,726,133 discloses a low ash natural gas engine oil which
15 contains an additive package including a particular combination of detergents
16 and also containing other standard additives such as dispersants, anti-
17 oxidants, anti-wear agents, metal deactivators, anti-foamants and pour point
18 depressants and viscosity index improvers. The low ash natural gas engine
19 oil exhibits reduced deposit formation and enhanced resistance to oil
20 oxidation and nitration.

21 U. S. Patent No. 6,140,282 discloses a long life lubricating oil as evidenced by
22 a reduction in viscosity increase, oxidation and nitration, comprising a major
23 amount of a base oil of lubricating viscosity and a minor amount of a mixture
24 of high TBN, medium TBN and low/neutral TBN detergents which in the metal
25 salicylate detergents is at least one of the medium or low/neutral TBN
26 detergents.

27 U. S. Patent No. 6,159,911 discloses a diesel engine oil composition
28 containing a lube oil base and one or more metallic detergents-dispersants
29 selected from among a perbasic alkaline earth metal sulfonate, phenolate and
30 salicylate. The total phosphorus content of the composition is suppressed to

1 100 parts per million by weight or less, to thereby provide diesel engine oil
2 compositions having oxidation stability and wear resistance.

3

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

10

11 U. S. Patent No. 6,277,794 discloses a marine diesel lubricant composition
12 having a TBN of at least 10 and preferably a VI of at least 90, comprise a
13 major amount of oil of lubricating viscosity, and admixed therewith, minor
14 amounts of an ashless anti-wear additive and a metal detergent in the form of
15 (i) an overbased metal detergent having a TBN of at least 300, more
16 preferably at least 400, and comprising a surfactant system derived from at
17 least two surfactants, and/or (ii) a metal detergent other than (i); provided that,
18 if detergent (ii) is present, the composition does not contain a minor amount of
19 an extreme pressure additive, being up to 5.0 mass percent on the total mass
20 of the composition.

21

22 U. S. Patent Nos. 6,331,510 and 6,610,637 disclose a lubricant containing (a)
23 a synthetic base oil composition having an overall kinematic viscosity of at
24 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
25 110; (b) a dispersant-viscosity modifier; and (c) a sulfur-free functionalized
26 hydrocarbyl-substituted phenol detergent provides improved valve train wear,
27 with longer drain intervals, to heavy duty diesel engines.

28

29 U. S. Patent No. 6,569,818 discloses a lubricating oil composition having a
30 low phosphorus content of 0.01 to 0.1 weight percent, and a sulfated ash of
31 0.1 to 1.0 weight percent, which is composed of a (a) major amount of mineral
32 base oil having a low sulfur content of at most 0.1 weight percent; (b) an

1 ashless alkenyl or alkyl-succinimide dispersant; (c) a metal-containing
2 detergent (non-sulfurized alkali metal or alkaline earth metal salt of an
3 alkylsalicylic acid and/or non-sulfurized alkali metal or alkaline earth metal salt
4 of an alkyl phenol having a Mannich base structure; (d) zinc di-alkyl di-
5 thiophosphate; (e) an oxidation inhibitor (phenol compound and/or amine
6 compound) and wherein the sulfur content is 0.01 to 0.3 weight percent. The
7 lubricating oil composition shows good high temperature detergency
8 notwithstanding its low sulfur, phosphorus and sulfated ash content, and is
9 favorably employable in diesel engines using fuel of a low sulfur content.

10

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

16

17 U. S. Patent No. 6,784,143 discloses the use of a minor amount of a
18 detergent composition comprising one or more metal detergents which
19 comprises metal salts of organic acids, wherein the detergent composition
20 comprises more than 50 mole percent, based on the moles of the metal salts
21 of organic acids in the detergent composition, of: (I) a metal salt of an
22 aromatic carboxylic acid, or (II) a metal salt of a phenol, or (III) both a metal
23 salt of an aromatic carboxylic acid and a metal salt of a phenol, in a lubricating
24 oil composition for improving oxidation resistance of the lubricating oil
25 composition, wherein the amount of phosphorus and sulfur in the oil
26 composition is less than 0.09 mass % and at the most 0.5 mass %
27 respectively, based on the mass of the oil composition. It has also been
28 found that a detergent composition comprising more than 50 mole % of a
29 metal salt of an aromatic carboxylic acid improves the reduction in wear in an
30 engine.

31

32 European Patent Application No. 01201752.1 (Publication No. EP 1 256 619
33 A1) deemed withdrawn as of March 5, 2005, and U.S. Patent Application NO.

1 10/142,513 (Publication No. US 2003/0096716 A1) disclose a lubricating oil
2 composition comprising: (A) an oil of lubricating viscosity, in a major amount
3 and added thereto: (B) a detergent composition comprising one or more metal
4 detergents which comprises metal salts or organic acids, in a minor amount,
5 wherein the detergent composition comprises more than 50 mole percent of a
6 metal salt of an aromatic carboxylic acid, based on the moles of the metal
7 salts of organic acids in the detergent composition, and (C) one or more co-
8 additives, in a minor amount; wherein the total amounts of phosphorus and
9 sulfur derived from (B) or (C) or both (B) and (C) are less than 0.1 mass p% of
10 phosphorus and at the most 0.5 mass % of sulfur, based on the mass of the
11 oil composition. It has been found that a detergent composition comprising
12 more than 50 mole % of a metal salt of an aromatic carboxylic acid improves
13 the reduction in wear in an engine.

14
15 U.S. Patent Application No. 10/430,594 (Publication No. US 2003/0216266
16 A1) discloses a lubricating oil composition employable in combination with a
17 low sulfur content fuel oil is preferably composed of a base oil having a sulfur
18 content of at most 0.2 weight percent, an ashless dispersant comprising an
19 alkenyl- or alkyl-succinimide or derivative thereof, a metal-containing
20 detergent containing an organic acid metal salt, a zinc di-alkyl di-
21 thiophosphate, a zinc di-alkylaryl di-thiophosphate, and an oxidation inhibitor
22 selected from a group consisting of a phenol compound, an amine compound,
23 and a molybdenum-containing compound, wherein a ratio of the phosphorus
24 content of the zinc di-alkyl di-thiophosphate to the phosphorus content of the
25 zinc di-alkylaryl di-thiophosphate is in the range of 20:1 to 2:1.

26 U.S. Patent Application No. 10/344,390 (Publication No. US 2004/0106527
27 A1) discloses a lubricating oil composition used in conjunction with a gasoline
28 fuel having a sulfur content of less than 10 parts per million by weight,
29 characterized in that said oil composition has a phosphorus content of no
30 more than 0.05 percent by weight.

31 International Publication No. WO 2004/046283 A1 discloses the use of
32 lubricating oils with low sulfur content in combination with a low sulfur fuel to

1 reduce particulate emissions of a diesel engine equipped with a particulate
2 trap.
3
4 U.S. Patent Application No. 10/630,026 (Publication No. US 2005/0026791
5 A1) discloses a low sulfur, low ash, and low phosphorus lubricant additive
6 package comprising at one amine salt of a di-alkyl mono-thiophosphate.
7 Further, the patent application discloses lubricating oils based on the lubricant
8 additive package and methods of use.

9 SUMMARY OF THE INVENTION

10 The present invention is directed to a low sulfur, low sulfated ash and low
11 phosphorus lubricating oil composition for low emission heavy duty diesel
12 engines comprising (a) a major amount of an oil of lubricating viscosity and (b)
13 a detergent composition comprising (i) a mixture of a metal salt of an alkyl
14 hydroxyaromatic carboxylic acid and a metal salt of an alkyl phenol, and (ii) a
15 metal salt of a Mannich condensation product. The present invention is also
16 directed to a low sulfur, low sulfated ash and low phosphorus lubricating oil
17 concentrate comprising (a) an oil of lubricating viscosity and (b) a detergent
18 composition comprising (i) a mixture of a metal salt of an alkyl
19 hydroxyaromatic carboxylic acid and a metal salt of an alkyl phenol, and (ii) a
20 metal salt of a Mannich condensation product.

21

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

- 25 (a) a major amount of an oil of lubricating viscosity;
- 26 (b) a detergent composition comprising (i) a mixture of a metal salt of
27 an alkyl hydroxyaromatic carboxylic acid and a metal salt of an
28 alkyl phenol, and (ii) a metal salt of a Mannich condensation
29 product.

1 In (b) in the above lubricating oil composition, preferably the ratio of (i) the
2 mixture of a metal salt of an alkyl hydroxyaromatic carboxylic acid and a metal
3 salt of an alkyl phenol to (ii) the metal salt of a Mannich condensation product
4 is in the range of about 80:20 weight percent to about 20:80 weight percent
5 based on the total weight of the detergent composition. Preferably the ratio of
6 (i) the mixture of a metal salt of an alkyl hydroxyaromatic carboxylic acid and
7 a metal salt of an alkyl phenol to (ii) the metal salt of a Mannich condensation
8 product is in the range of about 70:30 weight percent to about 30:70 weight
9 percent based on the total weight of the lubricating oil composition. More
10 preferably the ratio of (i) the mixture of a metal salt of an alkyl
11 hydroxyaromatic carboxylic acid and a metal salt of an alkyl phenol to (ii) the
12 metal salt of a Mannich condensation product is about 50:50 weight percent
13 based on the total weight of the lubricating oil composition.

14 In the mixture in (i) in the detergent composition of the above lubricating oil
15 composition the ratio of the metal salt of an alkyl hydroxyaromatic carboxylic
16 acid to the metal salt of an alkyl phenol is in the range of about 80:20 weight
17 percent to about 20:80 weight percent based on the total weight of (i). More
18 preferably the ratio of the metal salt of an alkyl hydroxyaromatic carboxylic
19 acid to the metal salt of an alkyl phenol is in the range of about 60:40 weight
20 percent to about 40:60 weight percent based on the total weight of (i). Most
21 preferably the ratio of the metal salt of an alkyl hydroxyaromatic carboxylic
22 acid and the metal salt of an alkyl phenol is about 50:50 weight percent based
23 on the total weight of (i).

24 The alkyl group on the alkyl hydroxyaromatic carboxylic acid in (i) in the
25 detergent composition of the above lubricating oil composition is a linear chain
26 or a branched chain alkyl group or mixtures thereof. Preferably the alkyl
27 group on the alkyl hydroxyaromatic carboxylic acid is a mixture of linear chain
28 and branched chain alkyl groups. More preferably the ratio of the linear chain
29 alkyl groups to the branched chain alkyl group in the mixture is in the range of
30 about 70:30 to about 30:70 based on the total alkyl groups on the alkyl
31 hydroxyaromatic carboxylic acid. Most preferably the ratio of the linear chain

1 alkyl groups to the branched chain alkyl group in the mixture is about 50:50
2 based on the total alkyl groups on the alkyl hydroxyaromatic carboxylic acid.

3 The alkyl group on the alkyl phenol in (i) in the detergent composition of the
4 above lubricating oil composition is a linear chain or a branched chain alkyl
5 group. Preferably the alkyl group on the alkyl phenol is a mixture of linear
6 chain and branched chain alkyl groups or mixtures thereof. More preferably
7 the ratio of the linear chain alkyl groups to the branched chain alkyl group in
8 the mixture is in the range of about 70:30 to about 30:70 based on the total
9 alkyl groups on the alkyl phenol. Most preferably the ratio of the linear chain
10 alkyl groups to the branched chain alkyl group in the mixture is about 50:50
11 based on the total alkyl groups on the alkyl phenol.

12 Preferably the branched chain alkyl group on the alkyl hydroxyaromatic
13 carboxylic acid in (i) in the detergent composition of the above lubricating oil
14 composition has from about 4 carbon atoms to about 60 carbon atoms. More
15 preferably the branched chain alkyl group on the alkyl hydroxyaromatic
16 carboxylic acid has from about 6 carbon atoms to about 40 carbon atoms.
17 Most preferably the branched chain alkyl group on the alkyl hydroxyaromatic
18 carboxylic acid has from about 8 carbon atoms to about 20 carbon atoms.

19 Preferably the linear chain alkyl group on the alkyl hydroxyaromatic carboxylic
20 acid in (i) in the detergent composition of the above lubricating oil composition
21 has from about 4 carbon atoms to about 60 carbon atoms. More preferably
22 the linear chain alkyl group on the alkyl hydroxyaromatic carboxylic acid has
23 from about 12 carbon atoms to about 40 carbon atoms. Most preferably the
24 alkyl group on the alkyl hydroxyaromatic carboxylic acid has from about 20
25 carbon atoms to about 30 carbon atoms.

26 Preferably the branched chain alkyl group on the alkyl phenol in (i) in the
27 detergent composition of the above lubricating oil composition has from about
28 4 carbon atoms to about 60 carbon atoms. More preferably the branched
29 chain alkyl group on the alkyl phenol has from about 6 carbon atoms to about
30 40 carbon atoms. Most preferably the branched chain alkyl group on the alkyl
31 phenol has from about 8 carbon atoms to about 20 carbon atoms.

1 Preferably the linear chain alkyl group on the alkyl phenol in (i) in the
2 detergent composition of the above lubricating oil composition has from about
3 4 carbon atoms to about 60 carbon atoms. More preferably the linear chain
4 alkyl group on the alkyl phenol has from about 12 carbon atoms to about 40
5 carbon atoms. Most preferably the linear chain alkyl group on the alkyl phenol
6 has from about 20 carbon atoms to about 30 carbon atoms.

7 The Mannich condensation product in (ii) in the detergent composition in the
8 lubricating oil of the present invention is prepared from a formaldehyde or an
9 aldehyde having one carbon atom to about 20 carbon atoms, a nitrogen base
10 selected from ammonia, a lower alkyl amine, a polyamine and mixtures
11 thereof, and an alkyl phenol.

12 Preferably the alkyl group on the alkyl phenol employed to prepare the
13 Mannich condensation product in (ii) in the detergent composition of the
14 present invention is a linear chain or a branched chain alkyl group or mixtures
15 thereof. Preferably the alkyl group on the alkyl phenol employed to prepare
16 the Mannich condensation product is a branched chain alkyl group.

17 Preferably the branched chain alkyl group on the alkyl phenol employed to
18 prepare the Mannich condensation product in (ii) in the detergent composition
19 of the present invention has from about 4 carbon atoms to about 60 carbon
20 atoms. Most preferably the branched chain alkyl group on the alkyl phenol
21 has from about 6 carbon atoms to about 40 carbon atoms. Most preferably
22 the branched chain alkyl group on the alkyl phenol has from about 8 carbon
23 atoms to about 20 carbon atoms.

24 Preferably the linear chain alkyl group on the alkyl phenol employed to
25 prepare the Mannich condensation product in (ii) in the detergent composition
26 of the present invention has from about 4 carbon atoms to about 60 carbon
27 atoms. Most preferably the linear chain alkyl group on the alkyl phenol has
28 from about 12 carbon atoms to about 40 carbon atoms. Most preferably the
29 branched chain alkyl group on the alkyl phenol has from about 20 carbon
30 atoms to about 30 carbon atoms.

1 In a preferred embodiment of the lubricating oil composition of the present
2 invention, in (i) the alkyl hydroxyaromatic carboxylic acid is an alkyl
3 hydroxybenzene carboxylic acid, wherein the alkyl group is a 50:50 mixture of
4 a branched chain C₁₂ alkyl group and a linear chain C₂₀ to C₃₀ alkyl group.
5 The alkyl group on the alkyl phenol in (i) is a 50:50 mixture of branched chain
6 C₁₂ alkyl group and linear chain C₂₀ to C₃₀ alkyl group. In (ii) the Mannich
7 condensation product is a condensation product of an alkyl phenol, wherein
8 the alkyl group is a branched chain C₁₂ alkyl group, paraformaldehyde and
9 mono-methyl amine.

10 The metal in the metal salt of an alkyl hydroxyaromatic carboxylic acid and the
11 metal salt of an alkyl phenol independently may be an alkali metal or an
12 alkaline earth metal. Preferably the metal is an alkaline earth metal. More
13 preferably the alkaline earth metal is calcium.

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

17 Preferably the sulfur content of the lubricating oil composition of the present
18 invention is in the range of 0.0 weight percent to about 0.4 weight percent
19 based on the total weight of the lubricating oil. More preferably the sulfur
20 content of the lubricating oil composition of the present invention is in the
21 range of 0.05 weight percent to about 0.3 weight percent based on the total
22 weight of the lubricating oil. Most preferably the sulfur content of the
23 lubricating oil composition of the present invention is in the range of 0.1
24 weight percent to about 0.2 weight percent based on the total weight of the
25 lubricating oil.

26 Preferably the sulfated ash content of the lubricating oil composition of the
27 present invention is in the range of 0.2 weight percent to about 4.0 weight
28 percent based on the total weight of the lubricating oil. More preferably the
29 sulfated ash content of the lubricating oil composition of the present invention
30 is in the range of 0.5 weight percent to about 2.0 weight percent based on the
31 total weight of the lubricating oil. Most preferably the sulfated ash content of

1 the lubricating oil composition of the present invention is in the range of 0.75
2 weight percent to about 1.2 weight percent based on the total weight of the
3 lubricating oil.

4 Preferably the phosphorus content of the lubricating oil composition of the
5 present invention is in the range of 0.005 weight percent to about 0.06 weight
6 percent based on the total weight of the lubricating oil. More preferably the
7 phosphorus content of the lubricating oil composition of the present invention
8 is in the range of 0.015 weight percent to about 0.05 weight percent based on
9 the total weight of the lubricating oil. Most preferably the phosphorus content
10 of the lubricating oil composition of the present invention is in the range of
11 0.03 weight percent to about 0.04 weight percent based on the total weight of
12 the lubricating oil.

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

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

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

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

26 Metal di-alkyl di-thiophosphates may also be included in the lubricating oil
27 composition of the present invention to provide anti-wear. However, it may be
28 advantageous to control the amount of this additive because of its metal and

1 phosphorus contribution to the lubricating oil. Examples of metal di-alkyl di-
2 thiophosphates are zinc and molybdenum salts of di-alkyl di-thiophosphates.

3 Typically, friction modifiers are used to impart the proper friction
4 characteristics to the lubricating oil composition. Useful friction modifiers are
5 fatty acid esters and amides and molybdenum compounds, such as amine-
6 molybdenum complex compound and molybdenum di-thiocarbamates.

7 However, it should be noted that the addition of molybdenum di-
8 thiocarbamates will further contribute sulfur to the lubricating oil composition.

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

12 Useful foam inhibitors are of the polysiloxane type.

13 A further embodiment of the present invention is directed to a low sulfur, low
14 sulfated ash and low phosphorus lubricating oil concentrate for low emission
15 heavy duty diesel engines comprising:

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

17 (b) a detergent composition comprising (i) a mixture of a metal salt of
18 an alkyl hydroxyaromatic carboxylic acid and a metal salt of an alkyl
19 phenol, and (ii) a metal salt of a Mannich condensation product.

20 Another embodiment of the present invention is directed to a method for
21 lubricating low emission heavy duty diesel engines using a low sulfur, low
22 sulfated ash and low phosphorus lubricating oil composition comprising:

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

24 (b) a detergent composition comprising (i) a mixture of a metal salt of
25 an alkyl hydroxyaromatic carboxylic acid and a metal salt of an alkyl
26 phenol, and (ii) a metal salt of a Mannich condensation product.

1 An additional embodiment of the invention is directed to the use of a low
2 sulfur, low sulfated ash and low phosphorus lubricating oil composition for
3 lubricating low emission heavy duty diesel engines comprising:

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

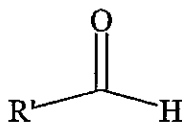
5 (d) a detergent composition comprising (i) a mixture of a metal salt of
6 an alkyl hydroxyaromatic carboxylic acid and a metal salt of an alkyl
7 phenol, and (ii) a metal salt of a Mannich condensation product.

8 DETAILED DISCRIPTION OF THE INVENTION

9 DEFINITIONS

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

12 The term "aldehydes" as used herein refer to formaldehyde or aldehydes
13 having the formula



15 wherein R' is branched or linear alkyl having from one carbon atom to about
16 10 carbon atoms, cycloalkyl having from about 3 carbon atoms to about 10
17 carbon atoms, aryl having from about 6 carbon atoms to about 10 carbon
18 atoms, alkaryl having from about 7 carbon atoms to about 20 carbon atoms,
19 or aralkyl having from about 7 carbon atoms to about 20 carbon atoms.

20 Aldehydes most preferred for use in the in the preparation of the Mannich
21 condensation products of the present invention are paraformaldehyde and
22 formalin.

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

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

5 The term "a nitrogen base" as used herein refers to a nitrogen base selected
6 from ammonia, a lower alkyl amine, having one carbon atom to about 10
7 carbon atoms, a polyamine having 2 amine nitrogen atoms to 12 amine
8 nitrogen atoms and 2 carbon atoms to about 40 carbon atoms, and mixtures
9 thereof.

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

17 The term "dispersants" as used herein refers to additives that keep soot and
18 combustion products in suspension in the body of the oil charge and therefore
19 prevent deposition as sludge or lacquer. Typically, the ashless dispersants
20 are nitrogen-containing dispersants formed by reacting alkenyl succinic acid
21 anhydride with an amine. Examples of such dispersants are alkenyl
22 succinimides and succinamides. These dispersants can be further modified
23 by reaction with, for example, boron or ethylene carbonate. Ester-based
24 ashless dispersants derived from long chain hydrocarbon-substituted
25 carboxylic acids and hydroxy compounds may also be employed. Preferred
26 ashless dispersants are those derived from polyisobutenyl succinic anhydride.
27 A large number of dispersants are commercially available.

28 The term "low sulfur" as used herein refers to the sulfur content of the
29 lubricating oil composition of the present invention. The sulfur content is in

1 the range of 0.0 weight percent to about 0.4 weight percent based on the total
2 weight of the lubricating oil composition.

3 The term "low phosphorus" as used herein refers to the phosphorus content of
4 the lubricating oil composition of the present invention. The phosphorus
5 content is in the range of about 0.005 weight percent to about 0.06 weight
6 percent based on the total weight of the lubricating oil composition.

7 The term "low sulfated ash" as used herein refers to the sulfated ash content
8 of the lubricating oil composition of the present invention. The sulfated ash
9 content is in the range of about 0.2 weight percent to about 4.0 weight percent
10 based on the total weight of the lubricating oil composition.

11 The term "Mannich condensation product" as used herein refers to the
12 condensation product of an alkyl phenol, a formaldehyde or an aldehyde
13 having one carbon atom to about 20 carbon atoms and a nitrogen base
14 selected from ammonia, a lower alkyl amine having one carbon atom to about
15 10 carbon atoms, a polyamine having 2 amine nitrogen atoms to about 12
16 amine nitrogen atoms and 2 carbon atoms to about 40 carbon atoms, and
17 mixtures thereof.

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

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

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

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

9 LUBRICATING OIL COMPOSITION

10 It has been discovered that the detergent composition comprising (i) a mixture
11 of a metal salt of an alkyl hydroxyaromatic carboxylic acid and a metal salt of
12 an alkyl phenol, and (ii) a metal salt of a Mannich condensation product in the
13 low sulfur, low sulfated ash and low phosphorus lubricating oil composition of
14 the present invention provides good detergency and deposit control when
15 used for low emission heavy duty diesel engines. The present invention is
16 also directed to a low sulfur, low sulfated ash and low phosphorus lubricating
17 oil concentrate comprising (a) a major amount of an oil of lubricating viscosity
18 and (b) a detergent composition. Thus, even though the lubricating oil
19 composition of the present invention has low sulfur contents, the detergent
20 composition, which is also low in sulfur content, maintains the functionality
21 and quality of the lubricating oil composition.

22 The low sulfur, low sulfated ash and low phosphorus lubricating oil
23 composition of the present invention comprises a major amount of an oil of
24 lubricating viscosity and a detergent composition comprising (i) a mixture of a
25 metal salt of an alkyl hydroxyaromatic carboxylic acid and a metal salt of an
26 alkyl phenol, and (ii) a metal salt of a Mannich condensation product. The
27 lubricating oil composition of the present invention may be prepared by simple
28 blending or mixing of the compounds described in more detail below. These
29 compounds may also be preblended as a concentrate or package with various

- 1 other additives in appropriate ratios to facilitate blending of a lubricating oil
- 2 composition containing the desired concentration of additives.

3 Oil of Lubricating Viscosity

4 Oil of lubricating viscosity, or base oil as used herein refer to lubricating oils
5 which may be mineral oil or synthetic oils of lubricating viscosity and
6 preferably useful in the crankcase of an internal combustion engine.
7 Crankcase lubricating oils ordinarily have a viscosity of about 1300
8 centistokes at -17.8°C to 22.7 centistokes at 98.9°C. The lubricating oils may
9 be derived from synthetic or natural sources. Mineral oil for use as the base
10 oil in this invention includes paraffinic, naphthenic and other oils that are
11 ordinarily used in lubricating oil compositions. Synthetic oils include
12 hydrocarbon synthetic oils and synthetic esters. Useful synthetic hydrocarbon
13 oils include liquid polymers of alpha-olefins having the proper viscosity.
14 Especially useful are the hydrogenated liquid oligomers of C₆ to C₁₂ alpha-
15 olefins such as 1-decene trimer. Similarly, alkyl benzenes of proper viscosity,
16 such as didodecyl benzene, may be used. Useful synthetic esters include the
17 esters of both mono-carboxylic acids and polycarboxylic acids as well as
18 mono-hydroxy alkanols and polyols. Typical examples are didodecyl adipate,
19 pentaerthritol tetracapoate, di-2-ethylhexyl adipate, di-laurylsebacate and the
20 like. Complex esters prepared from mixtures of mono- and di-carboxylic acid
21 and mono- and di-hydroxy alkanols can also be used. Blends of hydrocarbon
22 oils and synthetic oils may also be used. For example, blends of 10 weight
23 percent to 25 weight percent hydrogenated 1-decene trimer with 75 weight
24 percent to 90 weight percent 683 centistokes at 37.8°C mineral oil gives an
25 excellent oil base. Fischer-Tropsch derived base oils may also be employed
26 in the lubricating oil composition of the present invention.

27 It is further contemplated that the oil of lubricating viscosity employed for
28 preparing the lubricating oil composition of the present invention is a low
29 sulfur base oil. Use of a low sulfur base oil will assist in obtaining a lubricating
30 oil composition which is ultra low in sulfur content. Sulfur content of base oils

1 is well known to persons skilled in the art, thus, selection of a low sulfur base
2 oil may be conveniently made for the purpose of the present invention.

3 Detergents

4 Detergents are used in lubricating oil to neutralize acid oxidation products,
5 such as sulfuric acid in the case of diesel fuel, and to control deposits.
6 Detergents conventionally used in heavy duty diesel lubricating oil
7 compositions are low, medium and high metal overbased sulfurized, and/or
8 carbonated alkyl phenols or metal overbased sulfonates. However,
9 lubricating oil compositions containing these detergents are high in sulfur and
10 metal content, 0.3 weight percent and 0.6 weight percent, respectively. On
11 combustion, these lubricating oils may yield 1.3 weight percent sulfated ash,
12 which leads to the formation of particulate matter with the resultant plugging
13 and malfunctioning of the exhaust gas after-treatment system and increased
14 emissions. The detergent composition of the present invention was
15 discovered in response to the need to find a detergent composition without
16 the high sulfur and metal content of conventional detergent compositions,
17 while maintaining good detergency.

18 Detergents used in the detergent composition of the low sulfur, low sulfated
19 ash and low phosphorus lubricating oil composition of the present invention
20 do not contain high metal overbased sulfurized, and/or carbonated alkyl
21 phenols or metal overbased sulfonates. Although, small amounts of low
22 and/or medium overbased detergents may be included in the detergent
23 composition of the present invention, detergents mainly employed are (i) a
24 mixture of a metal salt of an alkyl hydroxyaromatic carboxylic acid and a metal
25 salt of an alkyl phenol, and (ii) a metal salt of a Mannich condensation
26 product.

27 Metal salts of the alkyl hydroxyaromatic carboxylic acids

28 Alkyl hydroxyaromatic carboxylic acids used for preparing the metal salts may
29 be single ring, double ring or fused ring alkyl hydroxyaromatic carboxylic

1 acids. Preferably the alkyl hydroxyaromatic carboxylic acids are single ring
2 alkyl hydroxyaromatic carboxylic acids, more preferably the alkyl
3 hydroxyaromatic carboxylic acids are alkyl hydroxybenzene carboxylic acids,
4 wherein the alkyl group may be a branched chain alkyl group containing from
5 about 4 carbon atoms to about 60 carbon atoms or linear chain alkyl group
6 containing 4 carbon atoms to 60 carbon atoms, or mixtures thereof. Most
7 preferably the alkyl group on the alkyl hydroxybenzene is a 50:50 weight
8 percent mixture of branched chain alkyl group containing about 8 carbon
9 atoms to about 20 carbon atoms and linear chain alkyl group containing from
10 about 20 carbon atoms to about 30 carbon atoms. Preferably the branched
11 chain alkyl group and the linear chain alkyl group is independently attached to
12 the hydroxybenzene in a position para or ortho to the hydroxyl group on the
13 hydroxybenzene moiety.

14 More preferably the ratio of the attachment of the linear chain alkyl group in
15 the ortho-position to para-position is 70:30 based on the total alkyl
16 hydroxybenzene and most preferably the ratio of the attachment of the linear
17 chain alkyl group in the ortho-position to hydroxy-position is 60:40 based on
18 the total alkyl hydroxybenzene. More preferably the ratio of the attachment of
19 the branched chain alkyl group in the ortho-position to para-position is 20:80
20 based on the total alkyl hydroxybenzene, and most preferably the ratio of the
21 attachment of the branched chain alkyl group in the ortho-position to para-
22 position is 5:95 based on the total alkyl hydroxybenzene.

23 The carboxylic acid moiety on the alkyl hydroxyaromatic carboxylic acid may
24 be attached directly or indirectly to the hydroxybenzene. Preferably carboxylic
25 acid moiety is attached directly to the alkyl hydroxyaromatic moiety.

26 The metal employed to make the salts of the alkyl hydroxyaromatic carboxylic
27 acid may be an alkali metal or an alkaline earth metal. Preferably the metal is
28 an alkaline earth metal and more preferably the metal is calcium.

1 The method for preparation of the metal salts of alkyl hydroxyaromatic
2 carboxylic acids are well known in the art. Generally, the alkyl
3 hydroxyaromatic carboxylic acids are prepared by carboxylation of the
4 corresponding alkyl hydroxyaromatic compounds using carbon dioxide. The
5 metal salts are prepared using the oxides, hydroxide or alkoxides of the
6 desired metal. For example, the alkyl hydroxyaromatic carboxylic acids may
7 be prepared as described in U.S. patent No. 6,162,770.

8 Metal salt of an alkyl phenol

9 The alkyl group on the alkyl phenol may be a branched chain alkyl group
10 containing from about 4 carbon atoms to about 60 carbon atoms or linear
11 chain alkyl group containing 6 carbon atoms to 60 carbon atoms, or mixtures
12 thereof. More preferably the alkyl group on the alkyl phenol is a 50:50 weight
13 percent mixture of branched chain alkyl group containing about 8 carbon
14 atoms to about 20 carbon atoms and linear chain alkyl group containing from
15 about 20 carbon atoms to about 30 carbon atoms. The linear chain alkyl
16 group and the branched chain alkyl group is independently attached to the
17 hydroxybenzene in a position ortho or para to the hydroxyl group on the
18 benzene moiety.

19 More preferably the ratio of the attachment of the linear chain alkyl group in
20 the ortho-position to para-position is 70:30 based on the total alkyl
21 hydroxybenzene and most preferably the ratio of the attachment of the linear
22 chain alkyl group in the ortho-position to para-position is 60:40 based on the
23 total alkyl hydroxybenzene. More preferably the ratio of the attachment of the
24 branched chain alkyl group in the ortho-position to para-position is 20:80
25 based on the total alkyl hydroxybenzene and most preferably the ratio of the
26 attachment of the branched chain alkyl group in the ortho-position to para-
27 position is 5:95 based on the total alkyl hydroxybenzene.

1 The metal employed to make the salts of the alkyl phenol may be an alkali
2 metal or an alkaline earth metal. Preferably the metal is an alkaline earth
3 metal and more preferably the metal is calcium.

4 The method for preparation of the metal salts of alkyl phenols are well known
5 in the art. Typically, the metal salt of the alkyl phenol is prepared by first
6 alkylating the phenol and then preparing the metal salt using the oxides,
7 hydroxide or the alkoxides of the desired metal, for example as described in
8 U.S. Patent No. 5,292,968.

9 Alternately, the metal salts of the alkyl hydroxyaromatic carboxylic acid and
10 the alkyl phenol may be prepared by making the desired mixture of the alkyl
11 hydroxyaromatic carboxylic acid and the alkyl phenol and subsequently
12 making the metal salts using the desired metal oxides, hydroxides or the
13 alkoxides.

14 Metal salt of Mannich condensation product

15 The Mannich condensation product employed in the detergent composition of
16 the present invention may be prepared using an alkyl phenol, a formaldehyde
17 or an aldehyde and a nitrogen base selected from ammonia, a lower alkyl
18 amine, a polyamine and mixtures thereof.

19 The alkyl group on the alkyl phenol used for the preparation of the Mannich
20 condensation product may be a branched chain alkyl group, a linear chain
21 alkyl group or mixtures thereof. Preferably the alkyl group is a branched chain
22 alkyl group containing from about 4 carbon atoms to about 60 carbon atoms.
23 More preferably 6 carbon atoms to about 40 carbon atoms and most
24 preferably from about 8 carbon atoms to about 20 carbon atoms.

25 Preferably the linear chain alkyl group contains from about 4 carbon atoms to
26 about 60 carbon atoms. More preferably the linear chain alkyl group contains
27 from about 12 carbon atoms to about 40 carbon atoms and most preferably

1 the linear chain alkyl group contains from about 20 carbon atoms to about 30
2 carbon atoms.

3 The alkyl group is attached to the phenol moiety at the position ortho or para
4 to the hydroxyl group.

5 More preferably the ratio of the attachment of the branched chain alkyl group
6 in the ortho-position to para-position is 20:80 based on the total alkyl phenol,
7 and most preferably the ratio of the attachment of the branched chain alkyl
8 group in the ortho-position to para-position is 5:95 based on the total alkyl
9 phenol.

10 Preferably the ratio of the attachment of the linear chain alkyl group in the
11 ortho-position to para-position is 70:30 based on the total alkyl
12 hydroxybenzene and most preferably the ratio of the attachment of the linear
13 chain alkyl group in the ortho-position to hydroxy-position is 60:40 based on
14 the total alkyl hydroxybenzene.

15 The aldehyde useful for the preparation of the Mannich condensation product
16 may be a formaldehyde or an aldehyde having one carbon atom to about 20
17 carbon atoms. Preferably the formaldehyde or the aldehyde is an aldehyde,
18 and more preferably it is paraformaldehyde.

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

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

1 Metal salts of the Mannich condensation product employed in the lubricating
2 oil composition of the present invention may be prepared by any method
3 known to a person skilled in the art. Generally, the Mannich condensation
4 product is prepared by reaction of the alkylphenol, a formaldehyde or an
5 aldehyde and a nitrogen base selected from ammonia, a lower alkyl amine, a
6 polyamine, and mixtures thereof, in the presence of a metal hydroxide and a
7 diluent.

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

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

18 Other Additives

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

26 For best overall results in terms of affording the properties desired in a
27 conventional lubricating oil composition for a heavy duty diesel engine
28 lubricating oil, the lubricating oil contains a compatible combination of
29 additives of each of the above classes of additives in effective amounts as

1 well as the detergent composition of the present invention in the amount
2 needed to provide the desired neutralization capacity.

3 Low and Medium Overbased Metal Detergents

4 Small quantities of low or medium overbased metal detergents may optionally
5 be employed in the lubricating oil composition of the present invention.
6 Examples of the low and medium overbased metal detergents are low or
7 medium overbased sulfonic acids, salicylic acids, carboxylic acids, or phenols
8 or Mannich condensation products of phenols, aldehydes and amines. These
9 detergents may be alkali metal detergents or alkaline metal detergents.
10 Preferably they are alkaline earth metal detergents and more preferably they
11 are calcium detergents. The TBN of these detergents is greater than 1 and
12 less than 200. However, it is worth noting that a further addition of detergents,
13 such as those described above, may contribute to the sulfur and/or sulfated
14 ash content of the lubricating oil. These detergents are well known in the art
15 and are commercially available.

16 Dispersants

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

27

28

1 Anti-oxidants

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

13 Viscosity Index Improvers

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

18 Corrosion inhibitors

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

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

1 classes of materials herein described are well known materials and can be
2 readily purchased commercially or prepared by known procedures or obvious
3 modification thereof.

4 EXAMPLES

5 The detergent composition employed in the low sulfur, low sulfated ash and
6 low phosphorus lubricating oil composition of the present invention were
7 evaluated for their detergency performance in formulations prepared as
8 described in Example 1 and Table I below.

9 Example 1

10 A mixture of a metal salt of an alkyl hydroxyaromatic carboxylic acid and a
11 metal salt of an alkyl phenol was prepared as described in U.S. patent No.
12 6,162,770 and a metal salt of a Mannich condensation product was prepared
13 as in described U.S. patent No. 5,370,805 for determining the detergency
14 performance of the detergent composition employed in the low sulfur, low
15 sulfated ash and low phosphorus lubricating oil composition of the present
16 invention.

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

23 The detergency performance of Test Formulation C containing the detergent
24 composition of the present invention comprising Detergent (i) a mixture of a
25 metal salt of an alkyl hydroxyaromatic carboxylic acid and a metal salt of an
26 alkyl phenol, and Detergent (ii) a metal salt of a Mannich condensation product
27 was compared with Comparative Formulation A containing only (i) a mixture
28 of a metal salt of an alkyl hydroxyaromatic carboxylic acid and a metal salt of

1 an alkyl phenol and Comparative Formulation B containing only (ii) a metal
2 salt of a Mannich condensation product.

3 Comparative Formulation A contained Detergent (i) calcium salts of a mixture
4 of two alkyl hydroxy benzene carboxylic acids, wherein the alkyl group on one
5 alkyl hydroxy benzene carboxylic acid was a branched chain alkyl group
6 containing 12 carbon atoms and the alkyl group on the other alkyl hydroxy
7 benzene carboxylic acid was a linear chain alkyl group containing 20 carbon
8 atoms to 28 carbon atoms, and calcium salts of a mixture of two alkyl phenols,
9 where in the alkyl group on one alkyl phenol was a branched chain alkyl group
10 containing 12 carbon atoms and the alkyl group on the other alkyl phenol was
11 a linear chain alkyl group containing 20 carbon atoms to 28 carbon atoms.
12 The calcium salt of alkyl hydroxybenzene carboxylic acids and the calcium
13 salt of the alkyl phenols were present in a ratio of 3:2.

14 Comparative Formulation B contained Detergent (ii) a calcium salt of the
15 Mannich condensation product of an alkyl phenol, paraformaldehyde and
16 mono-methyl amine. The alkyl group on the alkyl phenol was a branched
17 chain alkyl group containing 12 carbon atoms.

18 Test Formulation C contained the detergent composition of the present
19 invention comprising Detergent (i) and Detergent (ii) as described for
20 Comparative Formulations A and B above in addition to the additives
21 described above. Thus, Test Formulation C contained the detergent mixture
22 in Formulation A plus the detergent in Formulation B.

23

24

25

26

Table I

Component	Formulation (weight %)		
	Comparative A	Comparative B	Test C
Base Oil	92.01	84.24	89.23
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
Anti-wear Agent	0.36	0.36	0.36
Foam Inhibitor	0.0025	0.0025	0.0025
Detergent (i) *	3.16		2.01
Detergent (ii) **		11.00	4.00

2

3 * calcium salts of a mixture of two alkyl hydroxy benzene carboxylic acids,
4 wherein the alkyl group on one alkyl hydroxy benzene carboxylic acid
5 was a branched chain alkyl group containing 12 carbon atoms and the
6 alkyl group on the other alkyl hydroxy benzene carboxylic acid was a
7 linear chain alkyl group containing 20 carbon atoms to 28 carbon atoms,
8 and calcium salts of a mixture of two alkyl phenols, where in the alkyl
9 group on one alkyl phenol was a branched chain alkyl group containing
10 12 carbon atoms and the alkyl group on the other alkyl phenol was a
11 linear chain alkyl group containing 20 carbon atoms to 28 carbon atoms.

1 ** a calcium salt of the Mannich condensation product of an alkyl phenol,
2 paraformaldehyde and mono-methyl amine. The alkyl group on the alkyl
3 phenol was a branched chain alkyl group containing 12 carbon atoms.

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

Table II

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

Example 2

Panel Coker Test

10 The Panel Coker Test was used to evaluate the tendency of Test Formulation
11 C compared to Comparative Formulations A and B to form carbon deposits
12 when in contact with a metallic surface at high temperature. Samples, 300
13 grams, of Comparative Formulations A and B and Test Formulation C were
14 heated in a sump and intermittently projected by means of a rotating oil stirrer
15 on an aluminum test plate heated at high temperature. The amount of deposit
16 was weighed at the end of the test. The lower the number the better the
17 detergent. Viscosity increase at 40°C and varnish rating were also recorded.
18 The results of the Panel Coker Test are summarized in Table III below.

1

Table III

Panel Coker Test	Formulation		
	Comparative A	Comparative B	Test C
Deposit (mg)	66	64	9
Carbon (%)	36	27	2
Varnish (Rating)	3.6	6.3	8.6
Increase in Viscosity at 40°C (%)	31	45	21

2

3 The results obtained in the Panel Coker Test summarized above in Table III
4 show that the Test Formulation C containing the detergent composition of the
5 present invention comprising (i) a mixture of a metal salt of an alkyl
6 hydroxyaromatic carboxylic acid and a metal salt of an alkyl phenol, and (ii) a
7 metal salt of a Mannich condensation product gave better detergency
8 performance than Comparative Formulation A containing only (i) a mixture of
9 a metal salt of an alkyl hydroxyaromatic carboxylic acid and a metal salt of an
10 alkyl phenol or Comparative Formulation B containing only (ii) a metal salt of a
11 Mannich condensation product. In each of the four categories of the data
12 collected Test Formulation C performed significantly better than either of
13 Comparative Formulations A or B.

14

1 What is claimed:

2 1. A low sulfur, low sulfated ash and low phosphorus lubricating oil
3 composition for low emission heavy duty diesel engines comprising:

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

5 (b) a detergent composition comprising (i) a mixture of a metal salt
6 of an alkyl hydroxyaromatic carboxylic acid and a metal salt of
7 an alkyl phenol, and (ii) a metal salt of a Mannich condensation
8 product.

9 2. The lubricating oil composition of claim 1, wherein in the detergent
10 composition in (b), the ratio of (i) the mixture of a metal salt of an alkyl
11 hydroxyaromatic carboxylic acid and a metal salt of an alkyl phenol to
12 (ii) the metal salt of a Mannich condensation product is in the range of
13 about 80:20 weight percent to about 20:80 weight percent based on the
14 total weight of the detergent composition.

15 3. The lubricating oil composition of claim 2, wherein the ratio of (i) the
16 mixture of a metal salt of an alkyl hydroxyaromatic carboxylic acid and
17 a metal salt of an alkyl phenol to (ii) the metal salt of a Mannich
18 condensation product is in the range of about 70:30 weight percent to
19 about 30:70 weight percent based on the total weight of the detergent
20 composition.

21 4. The lubricating oil composition of claim 3, wherein the ratio of (i) the
22 mixture of a metal salt of an alkyl hydroxyaromatic carboxylic acid and
23 a metal salt of an alkyl phenol to (ii) the metal salt of a Mannich
24 condensation product is about 50:50 weight percent based on the total
25 weight of the detergent composition.

26 5. The lubricating oil composition of claim 1, wherein in (b)(i), the ratio of
27 the metal salt of an alkyl hydroxyaromatic carboxylic acid to the metal
28 salt of an alkyl phenol is in the range of about 80:20 weight percent to
29 about 20:80 weight percent based on the total weight of (i).

- 1 6. The lubricating oil composition of claim 5, wherein in (b)(i) the ratio of
2 the metal salt of an alkyl hydroxyaromatic carboxylic acid to the metal
3 salt of an alkyl phenol is in the range of about 60:40 weight percent to
4 about 40:60 weight percent based on the total weight of (i).
- 5 7. The lubricating oil composition of claim 6, wherein in (b)(i) the ratio of
6 the metal salt of an alkyl hydroxyaromatic carboxylic acid and the metal
7 salt of an alkyl phenol is about 50:50 weight percent based on the total
8 weight of (i).
- 9 8. The lubricating oil composition of any one of the preceding claims,
10 wherein in the detergent composition (b), the alkyl group on the alkyl
11 hydroxyaromatic carboxylic acid in (i) is a linear chain or a branched
12 chain alkyl group or mixtures thereof.
- 13 9. The lubricating oil composition of claim 8, wherein the ratio of the linear
14 chain alkyl groups to the branched chain alkyl groups on the alkyl
15 hydroxyaromatic carboxylic acid in the mixture is in the range of about
16 70:30 to about 30:70 based on the total alkyl groups on the alkyl
17 hydroxyaromatic carboxylic acid.
- 18 10. The lubricating oil composition of claim 9, wherein the ratio of the linear
19 chain alkyl groups to the branched chain alkyl groups on the alkyl
20 hydroxyaromatic carboxylic acid in the mixture is about 50:50 based on
21 the total alkyl groups on the alkyl hydroxyaromatic carboxylic acid.
- 22 11. The lubricating oil composition of any one of the preceding claims,
23 wherein in the detergent composition (b), the alkyl group on the alkyl
24 phenol in (i) is a linear chain or a branched chain alkyl group or
25 mixtures thereof.
- 26 12. The lubricating oil composition of claim 11, wherein the ratio of the
27 linear chain alkyl groups to the branched chain alkyl groups on the alkyl
28 phenol in the mixture is in the range of about 70:30 to about 30:70
29 based on the total alkyl groups on the alkyl phenol.

- 1 13. The lubricating oil composition of claim 12, wherein the ratio of the
2 linear chain alkyl groups to the branched chain alkyl group on the alkyl
3 phenol in the mixture is about 50:50 based on the total alkyl groups on
4 the alkyl phenol.
- 5 14. The lubricating oil composition of any one of the preceding claims,
6 wherein in the detergent composition (b), the branched chain alkyl
7 group on the alkyl hydroxyaromatic carboxylic acid in (i) has from about
8 4 carbon atoms to about 60 carbon atoms.
- 9 15. The lubricating oil composition of claim 14, wherein the branched chain
10 alkyl group on the alkyl hydroxyaromatic carboxylic acid has from about
11 6 carbon atoms to about 40 carbon atoms.
- 12 16. The lubricating oil composition of claim 15, wherein the branched chain
13 alkyl group on the alkyl hydroxyaromatic carboxylic acid has from about
14 8 carbon atoms to about 20 carbon atoms.
- 15 17. The lubricating oil composition of any one of claims 1 to 13, wherein in
16 the detergent composition (b), the linear chain alkyl group on the alkyl
17 hydroxyaromatic carboxylic acid in (i) has from about 4 carbon atoms
18 to about 60 carbon atoms.
- 19 18. The lubricating oil composition of claim 17, wherein the linear chain
20 alkyl group on the alkyl hydroxyaromatic carboxylic acid has from about
21 12 carbon atoms to about 40 carbon atoms.
- 22 19. The lubricating oil composition of claim 18, wherein the linear chain
23 alkyl group on the alkyl hydroxyaromatic carboxylic acid has from about
24 20 carbon atoms to about 30 carbon atoms.
- 25 20. The lubricating oil composition of any one of the preceding claims,
26 wherein in the detergent composition (b), the branched chain alkyl
27 group on the alkyl phenol in (i) has from about 4 carbon atoms to about
28 60 carbon atoms.

- 1 21. The lubricating oil composition of claim 20, wherein the branched chain
2 alkyl group on the alkyl phenol has from about 6 carbon atoms to about
3 40 carbon atoms.
- 4 22. The lubricating oil composition of claim 21, wherein the branched chain
5 alkyl group on the alkyl phenol has from about 8 carbon atoms to about
6 20 carbon atoms.
- 7 23. The lubricating oil composition of any one of claims 1 to 19, wherein in
8 the detergent composition (b), the linear chain alkyl group on the alkyl
9 phenol in (i) has from about 4 carbon atoms to about 60 carbon atoms.
- 10 24. The lubricating oil composition of claim 23, wherein the linear chain
11 alkyl group on the alkyl phenol has from about 12 carbon atoms to
12 about 40 carbon atoms.
- 13 25. The lubricating oil composition of claim 24, wherein the linear chain
14 alkyl group on the alkyl phenol has from about 20 carbon atoms to
15 about 30 carbon atoms.
- 16 26. The lubricating oil composition of any one of the preceding claims,
17 wherein in the detergent composition (b), the Mannich condensation
18 product in (ii) is a condensation product of a formaldehyde or an
19 aldehyde having one carbon atom to about 20 carbon atoms, a
20 nitrogen base selected from ammonia, a lower alkyl amine, polyamine
21 and mixtures thereof, and an alkyl phenol.
- 22 27. The lubricating oil composition of claim 26, wherein the lower alkyl
23 amine has from one carbon atom to about 10 carbon atoms and the
24 polyamine has from 2 amine nitrogen atoms to about 12 amine
25 nitrogen atoms and 2 carbon atoms to about 40 carbon atoms.
- 26 28. The lubricating oil composition of any one of the preceding claims,
27 wherein in the detergent composition (b), the Mannich condensation
28 product in (ii) the alkyl group on the alkyl phenol is a linear chain or a
29 branched chain alkyl group or mixtures thereof.

- 1 29. The lubricating oil composition of claim 28, wherein the alkyl group on
2 the alkyl phenol of the Mannich condensation product is a branched
3 chain alkyl group.
- 4 30. The lubricating oil composition of claim 29, wherein in the detergent
5 composition (b), the Mannich condensation product in (ii) the branched
6 chain alkyl group on the alkyl phenol has from about 4 carbon atoms to
7 about 60 carbon atoms.
- 8 31. The lubricating oil composition of claim 30, wherein the branched chain
9 alkyl group on the alkyl phenol of the Mannich condensation product
10 has from about 6 carbon atoms to about 40 carbon atoms.
- 11 32. The lubricating oil composition of claim 31, wherein the branched chain
12 alkyl group on the alkyl phenol of the Mannich condensation product
13 has from about 8 carbon atoms to about 20 carbon atoms.
- 14 33. The lubricating oil composition of claim 28, wherein in the detergent
15 composition (b), the Mannich condensation product in (ii) the linear
16 chain alkyl group on the alkyl phenol has from about 4 carbon atoms to
17 about 60 carbon atoms.
- 18 34. The lubricating oil composition of claim 33, wherein the linear chain
19 alkyl group on the alkyl phenol of the Mannich condensation product
20 has from about 12 carbon atoms to about 40 carbon atoms.
- 21 35. The lubricating oil composition of claim 34, wherein the linear chain
22 alkyl group on the alkyl phenol of the Mannich condensation product
23 has from about 20 carbon atoms to about 30 carbon atoms.
- 24 36. The lubricating oil composition of any one of the preceding claims,
25 wherein in (i) the alkyl hydroxyaromatic carboxylic acid is an alkyl
26 hydroxybenzene carboxylic acid, wherein the alkyl group is a 50:50
27 mixture of a branched chain C₁₂ alkyl group and a linear chain C₂₀ to
28 C₃₀ alkyl group.

- 1 37. The lubricating oil composition of any one of the preceding claims,
2 wherein in (i) the alkyl group on the alkyl phenol is a 50:50 mixture of a
3 branched chain C₁₂ alkyl group and a linear chain C₂₀ to C₃₀ alkyl
4 group.
- 5 38. The lubricating oil composition of any one of the preceding claims,
6 wherein in (ii) the Mannich condensation product is a condensation
7 product of an alkyl phenol, wherein the alkyl group is a branched chain
8 C₁₂ alkyl group, paraformaldehyde and mono-methyl amine.
- 9 39. The lubricating oil composition of any one of the preceding claims,
10 wherein the metal salt in each of the alkyl hydroxyaromatic carboxylic
11 acid, the alkyl phenol and the Mannich condensation product is
12 independently an alkali metal or an alkaline earth metal.
- 13 40. The lubricating oil composition of claim 39, wherein the alkaline earth
14 metal is calcium.
- 15 41. The lubricating oil composition of any one of the preceding claims,
16 wherein the sulfur content is in the range of 0.0 weight percent to about
17 0.4 weight percent based on the total weight of the lubricating oil.
- 18 42. The lubricating oil composition of claim 41, wherein the sulfur content is
19 in the range of about 0.05 weight percent to about 0.3 weight percent
20 based on the total weight of the lubricating oil.
- 21 43. The lubricating oil composition of claim 42, wherein the sulfur content is
22 in the range of about 0.1 weight percent to about 0.2 weight percent
23 based on the total weight of the lubricating oil.
- 24 44. The lubricating oil composition of any one of the preceding claims,
25 wherein the sulfated ash content is in the range of about 0.2 weight
26 percent to about 4.0 weight percent based on the total weight of the
27 lubricating oil.

- 1 45. The lubricating oil composition of claim 44, wherein the sulfated ash
2 content is in the range of about 0.5 weight percent to about 2.0 weight
3 percent based on the total weight of the lubricating oil.
- 4 46. The lubricating oil composition of claim 45, wherein the sulfated ash
5 content is in the range of about 0.75 weight percent to about 1.2 weight
6 percent based on the total weight of the lubricating oil.
- 7 47. The lubricating oil composition of any one of the preceding claims,
8 wherein the phosphorus content is in the range of about 0.005 weight
9 percent to about 0.06 weight percent based on the total weight of the
10 lubricating oil.
- 11 48. The lubricating oil composition of claim 47, wherein the phosphorus
12 content is in the range of about 0.015 weight percent to about 0.05
13 weight percent based on the total weight of the lubricating oil.
- 14 49. The lubricating oil composition of claim 48, wherein the phosphorus
15 content is in the range of about 0.03 weight percent to about 0.04
16 weight percent based on the total weight of the lubricating oil.
- 17 50. The lubricating oil composition of any one of the preceding claims,
18 wherein the lubricating oil composition further comprises one or more
19 lubricating oil additives selected from dispersants, anti-oxidants,
20 viscosity index improvers, corrosion inhibitors and foam inhibitors.
- 21 51. A low sulfur, low sulfated ash and low phosphorus lubricating oil
22 concentrate for low emission heavy duty diesel engines comprising:
- 23 (a) a major amount of an oil of lubricating viscosity;
- 24 (b) a detergent composition comprising (i) a mixture of a metal salt of
25 an alkyl hydroxyaromatic carboxylic acid and a metal salt of an
26 alkyl phenol, and (ii) a metal salt of a Mannich condensation
27 product.
- 28

- 1 52. A method for lubricating low emission heavy duty diesel engines using
2 a low sulfur, low sulfated ash and low phosphorus lubricating oil
3 composition comprising:
- 4 (a) a major amount of an oil of lubricating viscosity;
- 5 (b) a detergent composition comprising (i) a mixture of a metal salt of
6 an alkyl hydroxyaromatic carboxylic acid and a metal salt of an
7 alkyl phenol, and (ii) a metal salt of a Mannich condensation
8 product.