

5 **ULTRA-LOW SAPS LUBRICANTS FOR INTERNAL COMBUSTION ENGINES**

FIELD OF THE INVENTION

The present invention generally relates to Ultra-Low SAPS lubricants for Internal Combustion Engines.

10

BACKGROUND OF THE INVENTION

When formulating motor oils for use in an automotive engine, there are a number of seemingly conflicting drivers which must be balanced. On the one hand there is a desire to formulate with additives which contain metals, sulfur and phosphorus because they have a proven track record for performance. These additives are known to impart wear and corrosion resistance to the oil and reduce deposit formation in the engine. This resistance is necessary as the demand for long life lubricants increases. However, the use of these additives is constrained by environmental legislation.

During the 1950s and 1960s a number of studies were undertaken to determine the source of air pollution which was becoming a problem in metropolitan areas. Automotive exhaust was indicated as a contributing factor. As a result, laws were put in place at the national and state levels to regulate the allowable limits for emissions of certain regulated chemicals. In response to these regulations, engine manufacturers have introduced exhaust gas after-treatment devices to clean up the emitted exhaust gas of internal combustion engines. Commonly used on spark ignited engines are oxidation catalysts, and commonly used on compression ignition engines are Diesel Particulate Filters (DPF) combined with an oxidation catalyst, and NOx reduction catalysts. The oxidation catalysts are used to decrease carbon monoxide (CO) and hydrocarbon emissions by oxidation. The catalysts utilized can be poisoned when they interact with certain metals or phosphorus. Limitations on sulfated ash, phosphorus, and sulfur levels (SAPS) in motor oils have been put in place to enable the use of exhaust gas after-treatment devices.

Commercial lubricants for internal combustion engines are commonly formulated in such a way that the SAPS content of the lubricant falls just below those limits. It is assumed by those skilled in the art of formulating engine lubricants that lowering the treat rates of SAPS containing performance additives far below those restrictions causes the performance of the lubricant to deteriorate to the point of unacceptability.

5 In addition to the CO and particle limits on emissions, there are efforts being made to reduce carbon dioxide (CO₂) emissions from vehicles. As CO₂ is a product of the combustion of hydrocarbon based fuels, the most direct means to reduce CO₂ emissions is to reduce fuel consumption. Deterioration of exhaust gas after-treatment devices can lead to increased fuel consumption. Accumulation of sulfated ash in diesel particulate filters can lead to increased engine backpressure and consequent fuel consumption increase. Also, when NO_x [a generic
10 term for mono-nitrogen oxides NO and NO₂ (nitric oxide and nitrogen dioxide) reduction catalysts are poisoned by sulfur, regeneration requires additional fuel injections, causing the total fuel consumption to increase. For these reasons the question of how deterioration of exhaust gas after-treatment devices can be minimized is more important than ever.

15 In general, the following patent art teaches elements of the proposed invention, but none are capable of solving the complex problem of high temperature corrosion, wear and deposit formation which result when Sulfated Ash, Phosphorous, and Sulfur (SAPS) are taken to nearly zero levels.

U. S. Patent Application No. 20100152079 discloses a lubricant composition
20 containing an oil of lubricating viscosity, a N,N,N',N'-tetramethyl-naphthalene-1,8-diamine, and at least one additive selected from antioxidants, detergents, dispersants which together provide superior oxidation inhibition for automotive and truck crankcase lubricants.

U. S. Patent Application No. 20080139425 discloses an additive package, useful in a lubricant composition, which comprises: a diluent; and a hydrocarbyl substituted triazole
25 compound, with the proviso that the lubricant is substantially free of compounds containing phosphorus. This additive package is selected for its ability to protect lead and silver bearings found in medium speed diesel engines including railroad engines.

European Patent Application No. 0758016 discloses an additive combination comprising an aromatic amine anti-oxidant and a "B" compound. The combination contains 1
30 pt. wt. of boron per 250 pts. of nitrogen in the amine. The oils exemplified are blended with a standard additive package and are not essentially free of SAPS derived from the components.

U. S. Patent Application No. 20080020953 discloses a lubricating oil composition which contains lube base oil comprising mineral oil and/or synthetic oil, ash-free dispersant (in mass%) (0.01-0.14) based on nitrogen amount, antioxidant and sulfated ash (1.2 or less).
35 The antioxidant contains dialkyldiphenyl amine (0.3-5) and hindered phenol compound (0-2.5). The dispersant contains alkenyl- or alkyl-succinimide and/or boron compound

5 derivative (0.05 or less) in terms of nitrogen amount. All example oils contain approximately 1% Sulfated Ash (SASH).

U. S. Patent No. 7,026,273 discloses a crankcase lubricating oil composition, for an internal combustion engine, which comprises an admixture of oil and boron-containing additive, and preset amounts of phosphorus and sulfur. This patent family teaches lubricating
10 oil compositions containing (a) a boron-containing additive and one or more co-additives, wherein the lubricating oil composition has greater than 200 ppm by mass of boron, less than 600 ppm by mass of phosphorus and less than 4000 ppm by mass of sulfur, based on the mass of the oil composition. All example lubricants contain approximately 1% SASH.

U. S. Patent Application No. 20060058200 discloses a lubricating oil composition for
15 internal combustion engines, which contains a major amount of oil of lubricating viscosity, (a) at least one nitrogen-containing dispersant, the dispersant providing to the oil a nitrogen content of at least 0.075 wt. % nitrogen, the dispersant having a polyalkenyl backbone which has a molecular weight range of about 900 to 3000, and (b) an oil soluble or oil dispersible source of boron, present in an amount so as to provide a ratio of wt. % nitrogen to wt. %
20 boron in the oil composition of about 3:1 to 5:1, wherein said lubricating oil composition has a sulfur content of up to 0.3 wt. %, a phosphorus content of up to 0.08 wt. %, a sulfated ash content of up to 0.80 wt. %. These oils are low SAPS, but not significantly below the current mandated levels. They still contain ZnDTP and metal detergents.

Japanese Patent No. 2922675 discloses a lubricating oil composition for coping with
25 strict regulation of exhaust gas which contains 0.5-8 wt.% a (3,5-di-tert-butyl-4-hydroxyphenol) carboxylic acid alkyl ester(s) as an ash-free cleaner, 3-12 wt.% succinimide type ash-free dispersant(s) and 0.1-3 wt.% phenol type ash-free antioxidant(s) in a lubricating base oil comprising a mineral and a synthetic oil(s). These lubricants are designed to not precipitate when in contact with methanol fuel.

30 U. S. Patent Application No. 20080020952 discloses a lubricant oil composition for contacting metal materials containing lead which comprises a lubricant base oil, an optional zinc dithiophosphate present in 0.08 wt% or less, and an additive selected from organic molybdenum compound excluding molybdenum thiophosphate, boric acid ester and/or derivatives, a mixture of the two, or organic molybdenum compound, boric acid modified
35 alkyl or alkenyl succinic acid imide. These oils are low in Zn salts, but still contain metallic detergents.

5 U. S. Patent Application No. 20060009366 discloses an oil composition for lubricating internal combustion engines which comprises base oil and at least 1.4 wt% of an aminic and/or phenolic antioxidant, wherein said lubricating oil composition is phosphorus free. These lubricants are formulated to be free of phosphorus antiwear additives, but are not free of metallic detergents. They are neither low ash nor low sulfur.

10 U. S. Patent Application No. 20040106527 discloses a lubricating oil composition for use in internal combustion engines, used along with a gasoline fuel having sulfur content of less than 10 ppm by weight, which has a phosphorous content of no more than 0.05 wt.%. These lubricants are again low P without limiting sulfur or ash.

Although some of these references address one problem that occurs when the SAPS
15 levels in a lubricant are limited, commercial lubricants must pass a battery of tests to be qualified. None of the references above address the multitude of high temperature corrosive wear and deposition issues which an oil needs to face in order to be qualified for sale. For a real solution to the problem of delivering low SAPS oils, it is desirable to be able to balance protection of the exhaust gas after treatment system with the performance expected of a
20 modern lubricant in order to be truly viable.

SUMMARY OF THE INVENTION

With the existing limitations of Low SAPS, all applicable emission requirements for modern engines can be met. The currently existing lubricants have Low SAPS restrictions
25 including: sulfated ash limits of <0.8 wt% for PCMO (Passenger Car Motor Oil) or <1.0 wt% for HDEO (Heavy Duty Engine Oil); phosphorus limits of <0.08 wt% for both PCMO and HDEO; and sulfur limits of <0.3 wt% for both PCMO and HDEO.

If exhaust gas after-treatment devices are harmed by sulfur, phosphorus and sulfated ash, then minimizing SAPS levels should maximize the lifetime of the exhaust gas after-
30 treatment devices. An evaluation was done to determine which lubrication performance gaps arise when a conventional fully formulated lubricant is stripped of all the performance enhancing additives that contribute to SAPS. As expected, the performance tests run on those SAPS free lubricants indicate clearly unacceptable performance. However, with the subsequent addition of alternative performance enhancing additives which do not contribute
35 to SAPS or only contribute minor amounts of SAPS, Ultra-Low SAPS experimental lubricants were created which, much to our surprise, gave acceptable performance. The resultant prototype lubricants consist of components which are built up of the elements H, O,

5 N, and C, with very minor amounts of other elements. In some embodiments, SAPS levels derived from the components in the additive package can be essentially zero.

“Ultra-Low SAPS” lubricating oil compositions are defined as: lubricating oil compositions wherein Sulfur is present at less than 1000 ppm, Phosphorous is present at less than 300 ppm, and Sulfated Ash is present at less than 0.25 wt%. In some embodiments S
10 (Sulfur) is present at <1000 ppm, <800 ppm, <500 ppm, <300 ppm, <100 ppm, < 50 ppm, <10 ppm, and could be zero; P (Phosphorous) is present at <300 ppm, <200 ppm, <100 ppm, <50 ppm, <10 ppm, and could be zero; and Sulfated Ash is present as <0.25 wt%, <0.20 wt%, <0.15 wt%, <0.10 wt%, <0.05wt%, <0.01 wt% and could be 0 wt% in the finished lubricant.

15 In accordance with one embodiment of the present invention, there is provided an ultra-low SAPS lubricating oil composition comprising:
an oil of lubricating viscosity;
a borated dispersant supplying at least 500 ppm boron to said lubricating oil composition;
an ashless peroxide decomposer present at a treat rate of from about 0.4 to 5.0 wt%;
20 a metal deactivator wherein the metal deactivator is present at a treat rate of greater than 0.08 wt%;
wherein said lubricating oil composition contains less than 1000 ppm sulfur less than 300 ppm phosphorus and less than 0.25 wt% sulfated ash.

25 In accordance with another embodiment of the present invention, there is provided a method of lubricating an engine with an ultra-low SAPS lubricating oil composition comprising:
an oil of lubricating viscosity;
a borated dispersant supplying at least 500 ppm boron to said lubricating oil composition;
30 an ashless peroxide decomposer present at a treat rate of from about 0.4 to 5.0 wt%;
a metal deactivator wherein the metal deactivator is present at a treat rate of greater than 0.08 wt%;
wherein said lubricating oil composition contains less than 1000 ppm sulfur, less than 300 ppm phosphorus and <0.25 wt% sulfated ash.

35

5

DETAILED DESCRIPTION OF THE INVENTION

In general, provided herein is a process for preparing an ultra-low SAPS lubricating oil composition comprising:

an oil of lubricating viscosity;

a borated dispersant supplying at least 500 ppm boron to said lubricating oil composition;

10 an ashless peroxide decomposer present at a treat rate of from about 0.4 to 5.0 wt%;

a metal deactivator wherein the metal deactivator is present at a treat rate of greater than 0.08 wt%;

wherein said lubricating oil composition contains less than 1000 ppm sulfur, less than 300 ppm phosphorus and less than 0.25 wt% sulfated ash.

15

Also provided herein is a method of lubricating an engine with an ultra-low SAPS lubricating oil composition comprising:

an oil of lubricating viscosity;

a borated dispersant supplying at least 500 ppm boron to said lubricating oil composition;

20 an ashless peroxide decomposer present at a treat rate of from about 0.4 to 5.0 wt%;

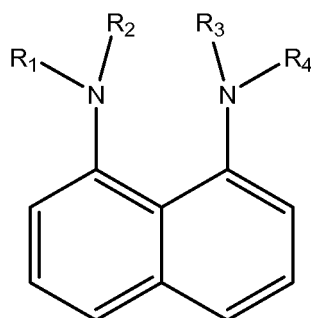
a metal deactivator wherein the metal deactivator is present at a treat rate of greater than 0.08 wt%;

wherein said lubricating oil composition contains less than 1000 ppm sulfur, less than 300 ppm phosphorus and less than 0.25 wt% sulfated ash.

25

In one embodiment, the oil soluble ashless peroxide decomposer is as described U. S. Patent Application No. 20100152079 which is incorporated in its entirety.

The oil soluble ashless peroxide is a compound according to formula I:



Formula I

30

5 wherein R₁ and R₂ and R₃ and R₄ are each independently selected from the group consisting of alkyl from 1 to 20 carbon atoms, more preferably alkyl from 1 to 10 carbon atoms and even more preferably lower alkyl from 1 to six carbon atoms. The alkyl groups above, can have either a straight chain or a branched chain, which are fully saturated hydrocarbon chain; for example, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl,
10 nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, and the like, and isomers and mixtures thereof. An example of a suitable hindered amine that may be used in the present invention is N,N,N',N'-tetramethyl-naphthalene-1,8-diamine and sold by Sigma-Aldrich as Proton-spongeTM. The N,N,N',N'-tetramethyl-naphthalene-1,8-diamine is a strained molecule due to the close proximity to the
15 dimethylamine groups. The free base is destabilized by the steric inhibition of resonance, van der Waals repulsions, and lone pair interactions. These strains are typically relieved by monoprotection and formation of an intramolecular hydrogen bond and thus can effectively alter the equilibrium constant of the hydroperoxide decomposition reaction. This imparts a high basicity relative to normal aliphatic amines or aromatic amines and which is necessary
20 to deprotonate a hydroperoxide. Deprotonation of the peroxide would render the oxygen-oxygen bond more stable toward decomposition into radicals. The strong basicity of the N,N,N',N'-tetramethyl-naphthalene-1,8-diamine can be ascribed to the operation of several factors, e.g. the steric inhibition of conjugation in the free base, relief of nonbonded repulsions, including a little lone pair/lone pair repulsion, stabilization of the cation by the
25 hydrogen bonding, etc. Clearly the N,N,N',N'-tetramethyl-naphthalene-1,8-diamine structure is compromise involving several factors including a twist in the naphthalene ring system, favorable lone pair/ π overlap, lone pair/methyl nonbonded interactions, and lone pair/lone pair repulsion.

 The compounds of formula I are selected with sufficient alkyl groups to be oil
30 soluble in the lubricating composition and thus the compound of formula I are combined with an oil of lubricating viscosity. The concentration of the compound of formula I in the lubricating composition can vary depending upon the requirements, applications and effect or degree of synergy desired. In a preferred embodiment of the invention, a practical N,N,N',N'-tetraalkyl-naphthalene-1,8-diamine use range in the lubricating composition is from about 0.4
35 to 10.0 wt % , and preferably from 0.5 to 3.0 wt%.based on the total weight of the lubricating oil composition. The N,N,N',N'-tetraalkyl-naphthalene-1,8-diamine compound of formula I can be used as a complete or partial replacement for commercially available antioxidants

5 currently used in lubricant formulations and can be in combination with other additives typically found in motor oils and fuels. When used in combination with other types of antioxidants or additives used in oil formulations, synergistic and/or additive performance effects may also be obtained with respect to improved antioxidancy, antiwear, frictional and detergency and high temperature engine deposit properties. Such other additives can be any
10 presently known or later-discovered additives used in formulating lubricating oil compositions. The lubricating oil additives typically found in lubricating oils are, for example, dispersants, detergents, corrosion/rust inhibitors, antioxidants, anti-wear agents, anti-foamants, friction modifiers, seal swell agents, emulsifiers, VI improvers, pour point depressants, and the like.

15 Inhibition of free radical-mediated oxidation is one of the most important reactions in organic substrates and is commonly used in rubbers, polymers and lubrication oils; namely, since these chemical products may undergo oxidative damage by the autoxidation process. Hydrocarbon oxidation is a three step process which comprises: initiation, propagation and termination. Oxidative degradation and the reaction mechanisms
20 are dependent upon the specific hydrocarbons, temperatures, operating conditions, catalysts such as metals, etc., which more detail can be found in Chapter 4 of Mortier R.M. et al., 1992, "Chemistry and Technology of Lubricants Initiation", VCH Publishers, Inc.; incorporated herein by reference in its entirety. Initiation involves the reaction of oxygen or nitrogen oxides (NO_x) on a hydrocarbon molecule. Typically, initiation starts by the
25 abstraction of hydrocarbon proton. This may result in the formation of hydrogen peroxide (HOOH) and radicals such as alkyl radicals ($\text{R}^\bullet$) and peroxy radicals ($\text{ROO}^\bullet$). During the propagation stage, hydroperoxides may decompose, either on their own or in the presence of catalysts such as metal ions, to alkoxy radicals ($\text{RO}^\bullet$) and peroxy radicals. These radicals can react with the hydrocarbons to form a variety of additional radicals and reactive oxygen
30 containing compounds such as alcohols, aldehydes, ketones and carboxylic acids; which again can further polymerize or continue chain propagation. Termination results from the self termination of radicals or by reacting with oxidation inhibitors.

The uncatalyzed oxidation of hydrocarbons at temperatures of up to about 120°C primarily leads to alkyl-hydroperoxides, dialkylperoxides, alcohols, ketones; as well as the
35 products which result from cleavage of dihydroperoxides such as diketones, keto-aldehydes hydroxyketones and so forth. At higher temperatures (above 120°C) the reaction rates are increased and cleavage of the hydroperoxides plays a more important role. Since autoxidation

5 is a free-radical chain reaction, it therefore, can be inhibited at the initiation and/or propagation steps. . Hydroperoxide decomposers convert the hydroperoxides into non-radical products and thus prevent the chain propagation reaction. Traditionally organosulfur and organophosphorous containing additives have been employed for this purpose typically eliminating hydroperoxides via acid catalyzed decomposition or oxygen transfer. However as
10 mentioned previously, increased concerns regarding total sulfur and/or phosphorous content in finished lubricating oil has led to efforts to reduce or eliminate sulfur and phosphorous in lubricant oil formulations. The oil soluble ashless peroxide decomposer according to formula I is a potent decomposer which converts hydroperoxides into non-radical products and thus prevent the chain propagation reaction.

15 The oil soluble ashless peroxide decomposer compound according to formula I is effective by itself when employed in a lubricating oil composition. The oil soluble ashless peroxide decomposer compound according to formula I can function as an antioxidant and can also be employed in combination with other free radical antioxidants.

In one embodiment sulfur is present in the lubricating oil composition at less than
20 1000 ppm, less than 800 ppm, less than 500 ppm, less than 300 ppm, less than 100 ppm less than 50 ppm, less than 10 ppm, and 0 ppm.

In one embodiment phosphorous is present in the lubricating oil composition at less than 300 ppm, less than 200 ppm, less than 100 ppm, less than 50 ppm, less than 10 ppm, and 0 ppm.

25 In one embodiment sulfated ash is present in the lubricating oil composition at less than 0.25 wt%, less than 0.20 wt%, less than 0.15wt%, less than 0.10 wt%, less than 0.05 wt%, less than 0.01 wt%., and 0 wt.

In one embodiment of the present invention the lubricating oil composition contains less than 800 ppm sulfur, less than 200 ppm phosphorous, and less than 0.20 wt% sulfated
30 ash.

In one embodiment of the present invention the lubricating oil composition contains less than 500 ppm sulfur, less than 100 ppm phosphorous, and less than 0.15 wt% sulfated ash.

In one embodiment of the present invention the lubricating oil composition contains
35 less than 300 ppm sulfur, less than 50 ppm phosphorous, and less than 0.10 wt% sulfated ash.

In one embodiment of the present invention the lubricating oil composition contains less than 100 ppm sulfur, 0 ppm phosphorous, and less than 0.05 wt% sulfated ash.

5 In one embodiment of the present invention the lubricating oil composition contains less than 50 ppm sulfur, 0 ppm phosphorous, and less than 0.05 wt% sulfated ash.

 In another embodiment, the lubricating oil composition comprises an ashless metal deactivator. Some non-limiting examples of suitable metal deactivators include disalicylidene propylenediamine, triazole derivatives, thiadiazole derivatives, and
10 mercaptobenzimidazoles.

 The ashless metal deactivator component of the present invention is preferably an aromatic triazole or an alkyl-substituted aromatic triazole; for example, benzotriazole, tolyltriazole, or mixtures thereof. The most preferred triazole for use is tolyltriazole. The metal deactivator is employed at concentrations of about 0.1 – 0.5 wt %; preferably about 0.1
15 – 0.4 wt. %; preferably about 0.1 – 0.3 wt. %; and more preferably about 0.1 – 0.2 wt. %. Metal deactivators are useful in improving the corrosion protection of copper and copper alloys.

 In another embodiment, the borated dispersant supplying at least 500 ppm boron is a
20 borated succinimide.

 Examples of borated ashless dispersants are the borated ashless hydrocarbyl succinimide dispersants prepared by reacting a hydrocarbyl succinic acid or anhydride with an amine. Preferred hydrocarbyl succinic acids or anhydrides are those where the hydrocarbyl group is derived from a polymer of a C.sub.3 or C.sub.4 monoolefin, especially a
25 polyisobutylene wherein the polyisobutenyl group has a number average molecular weight (Mn) of from 700 to 5,000, more preferably from 900 to 2,500. Such dispersants generally have at least 1, preferably 1 to 2, more preferably 1.1 to 1.8, succinic groups for each polyisobutenyl group.

 Preferred amines for reaction to form the succinimide are polyamines having from 2
30 to 60 carbon atoms and from 2 to 12 nitrogen atoms per molecule, and particularly preferred are the polyalkyleneamines represented by the formula



 wherein n is 2 to 3 and m is 0 to 10. Illustrative are ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, tetrapropylene pentamine, pentaethylene
35 hexamine and the like, as well as the commercially available mixtures of such polyamines. Amines including other groups such as hydroxy, alkoxy, amide, nitride and imidazoline

5 groups may also be used, as may polyoxyalkylene polyamines. The amines are reacted with the alkenyl succinic acid or anhydride in conventional ratios of about 1:1 to 10:1, preferably 1:1 to 3:1, moles of alkenyl succinic acid or anhydride to polyamine, and preferably in a ratio of about 1:1, typically by heating the reactants to from 100.degree. to 250.degree. C., preferably 125.degree. to 175.degree. C. for 1 to 10, preferably 2 to 6, hours.

10 The boration of alkenyl succinimide dispersants is also well known in the art as disclosed in U.S. Pat. Nos. 3 087 936 and 3 254 025. The succinimide may for example be treated with a boron compound selected from the group consisting of boron, boron oxides, boron halides, boron acids and esters thereof, in an amount to provide from 0.1 atomic proportion of boron to 10 atomic proportions of boron for each atomic proportion of nitrogen
15 in the dispersant.

The borated product will generally contain 0.1 to 2.0, preferably 0.2 to 0.8 weight per cent boron based upon the total weight of the borated dispersant. Boron is considered to be present as dehydrated boric acid polymers attaching at the metaborate salt of the imide. The boration reaction is readily carried out adding from 1 to 3 weight per cent (based on the
20 weight of dispersant) of said boron compound, preferably boric acid, to the dispersant as a slurry in mineral oil and heating with stirring from 135.degree. C. to 165.degree. C. for 1 to 5 hours followed by nitrogen stripping filtration of the product. Alternatively boric acid may be added to the hot reaction mixture of succinic acid or anhydride and amine while removing water.

25 In one embodiment, the borated dispersant supplies at least 500 ppm boron to the lubricating oil composition. In one embodiment, the borated dispersant supplies from 500 to 3000 ppm boron to the lubricating oil composition. In one embodiment, the borated dispersant supplies from 500 to 2500 ppm boron to the lubricating oil composition. In one embodiment, the borated dispersant supplies from 500 to 2000 ppm boron to the lubricating
30 oil composition. In one embodiment, the borated dispersant supplies from 500 to 1500 ppm boron to the lubricating oil composition. In one embodiment, the borated dispersant supplies from 600 to 1200 ppm boron to the lubricating oil composition.

THE OIL OF LUBRICATING VISCOSITY

35 The base oil of lubricating viscosity for use in the lubricating oil compositions of this invention is typically present in a major amount, e.g., an amount of greater than 50 wt. %, preferably greater than about 70 wt. %, more preferably from about 80 to about 99.5 wt. %

5 and most preferably from about 85 to about 98 wt. %, based on the total weight of the composition. The expression "base oil" as used herein shall be understood to mean a base stock or blend of base stocks which is a lubricant component that is produced by a single manufacturer to the same specifications (independent of feed source or manufacturer's location); that meets the same manufacturer's specification; and that is identified by a unique
10 formula, product identification number, or both. The base oil for use herein can be any presently known or later-discovered base oil of lubricating viscosity used in formulating lubricating oil compositions for any and all such applications, e.g., engine oils, marine cylinder oils, functional fluids such as hydraulic oils, gear oils, transmission fluids, etc. Additionally, the base oils for use herein can optionally contain viscosity index improvers,
15 e.g., polymeric alkylmethacrylates; olefinic copolymers, e.g., an ethylene-propylene copolymer or a styrene-butadiene copolymer; and the like and mixtures thereof.

As one skilled in the art would readily appreciate, the viscosity of the base oil is dependent upon the application. Accordingly, the viscosity of a base oil for use herein will ordinarily range from about 2 to about 2000 centistokes (cSt) at 100° Centigrade (C).
20 Generally, individually the base oils used as engine oils will have a kinematic viscosity range at 100°C of about 2 cSt to about 30 cSt, preferably about 3 cSt to about 16 cSt, and most preferably about 4 cSt to about 12 cSt and will be selected or blended depending on the desired end use and the additives in the finished oil to give the desired grade of engine oil, e.g., a lubricating oil composition having an SAE Viscosity Grade of 0W, 0W-16, 0W-20,
25 0W-30, 0W-40, 0W-50, 0W-60, 5W, 5W-20, 5W-30, 5W-40, 5W-50, 5W-60, 10W, 10W-20, 10W-30, 10W-40, 10W-50, 15W, 15W-20, 15W-30, 15W-40, 20W-40 or 20W-50. Oils used as gear oils can have viscosities ranging from about 2 cSt to about 2000 cSt at 100°C.

Base stocks may be manufactured using a variety of different processes including, but not limited to, distillation, solvent refining, hydrogen processing, oligomerization,
30 esterification, and rerefining. Rerefined stock shall be substantially free from materials introduced through manufacturing, contamination, or previous use. The base oil of the lubricating oil compositions of this invention may be any natural or synthetic lubricating base oil. Suitable hydrocarbon synthetic oils include, but are not limited to, oils prepared from the polymerization of ethylene or from the polymerization of 1-olefins to provide polymers such
35 as polyalphaolefin or PAO oils, or from hydrocarbon synthesis procedures using carbon monoxide and hydrogen gases such as in a Fischer-Tropsch process. For example, a suitable

5 base oil is one that comprises little, if any, heavy fraction; e.g., little, if any, lube oil fraction of viscosity 20 cSt or higher at 100°C.

The base oil may be derived from natural lubricating oils, synthetic lubricating oils or mixtures thereof. Suitable base oil includes base stocks obtained by isomerization of synthetic wax and slack wax, as well as hydrocracked base stocks produced by hydrocracking
10 (rather than solvent extracting) the aromatic and polar components of the crude. Suitable base oils include those in all API categories I, II, III, IV and V as defined in API Publication 1509, 14th Edition, Addendum I, Dec. 1998. Group IV base oils are polyalphaolefins (PAO). Group V base oils include all other base oils not included in Group I, II, III, or IV. Although Group II, III and IV base oils are preferred for use in this invention, these base oils may be
15 prepared by combining one or more of Group I, II, III, IV and V base stocks or base oils.

Useful natural oils include mineral lubricating oils such as, for example, liquid petroleum oils, solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types, oils derived from coal or shale, animal oils, vegetable oils (e.g., rapeseed oils, castor oils and lard oil), and the like.

20 Useful synthetic lubricating oils include, but are not limited to, hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins, e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes), and the like and mixtures thereof; alkylbenzenes such as dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)-benzenes, and the like; polyphenyls such as biphenyls, terphenyls, alkylated
25 polyphenyls, and the like; alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivative, analogs and homologs thereof and the like.

Other useful synthetic lubricating oils include, but are not limited to, oils made by polymerizing olefins of less than 5 carbon atoms such as ethylene, propylene, butylenes,
30 isobutene, pentene, and mixtures thereof. Methods of preparing such polymer oils are well known to those skilled in the art.

Additional useful synthetic hydrocarbon oils include liquid polymers of alpha olefins having the proper viscosity. Especially useful synthetic hydrocarbon oils are the hydrogenated liquid oligomers of C₆ to C₁₂ alpha olefins such as, for example, 1-decene
35 trimer.

Another class of useful synthetic lubricating oils include, but are not limited to, alkylene oxide polymers, i.e., homopolymers, interpolymers, and derivatives thereof where

5 the terminal hydroxyl groups have been modified by, for example, esterification or etherification. These oils are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and phenyl ethers of these polyoxyalkylene polymers (e.g., methyl poly propylene glycol ether having an average molecular weight of 1,000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1000, diethyl
10 ether of polypropylene glycol having a molecular weight of 1,000-1,500, etc.) or mono- and polycarboxylic esters thereof such as, for example, the acetic esters, mixed C₃-C₈ fatty acid esters, or the C₁₃ oxo acid diester of tetraethylene glycol.

Yet another class of useful synthetic lubricating oils include, but are not limited to, the esters of dicarboxylic acids e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl
15 succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acids, alkyl malonic acids, alkenyl malonic acids, etc., with a variety of alcohols, e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, etc. Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl)sebacate, di-n-hexyl fumarate, dioctyl
20 sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid and the like.

Esters useful as synthetic oils also include, but are not limited to, those made from
25 carboxylic acids having from about 5 to about 12 carbon atoms with alcohols, e.g., methanol, ethanol, etc., polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, tripentaerythritol, and the like.

Silicon-based oils such as, for example, polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxy-siloxane oils and silicate oils, comprise another useful class of synthetic
30 lubricating oils. Specific examples of these include, but are not limited to, tetraethyl silicate, tetra-isopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-hexyl)silicate, tetra-(p-tert-butylphenyl)silicate, hexyl-(4-methyl-2-pentoxo)disiloxane, poly(methyl)siloxanes, poly(methylphenyl)siloxanes, and the like. Still yet other useful synthetic lubricating oils include, but are not limited to, liquid esters of phosphorous containing acids, e.g., tricresyl
35 phosphate, trioctyl phosphate, diethyl ester of decane phosphonic acid, etc., polymeric tetrahydrofurans and the like.

5 The lubricating oil may be derived from unrefined, refined and rerefined oils, either natural, synthetic or mixtures of two or more of any of these of the type disclosed hereinabove. Unrefined oils are those obtained directly from a natural or synthetic source (e.g., coal, shale, or tar sands bitumen) without further purification or treatment. Examples of unrefined oils include, but are not limited to, a shale oil obtained directly from retorting
10 operations, a petroleum oil obtained directly from distillation or an ester oil obtained directly from an esterification process, each of which is then used without further treatment. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. These purification techniques are known to those of skill in the art and include, for example, solvent extractions, secondary
15 distillation, acid or base extraction, filtration, percolation, hydrotreating, dewaxing, etc. Rerefined oils are obtained by treating used oils in processes similar to those used to obtain refined oils. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

20 Lubricating oil base stocks derived from the hydroisomerization of wax may also be used, either alone or in combination with the aforesaid natural and/or synthetic base stocks. Such wax isomerase oil is produced by the hydroisomerization of natural or synthetic waxes or mixtures thereof over a hydroisomerization catalyst.

 Natural waxes are typically the slack waxes recovered by the solvent dewaxing of
25 mineral oils; synthetic waxes are typically the wax produced by the Fischer-Tropsch process.

LUBRICATING OIL ADDITIVES

 The lubricating oil compositions of the present invention may also contain other conventional additives for imparting auxiliary functions to give a finished lubricating oil
30 composition in which these additives are dispersed or dissolved. For example, the lubricating oil compositions can be blended with antioxidants, anti-wear agents, ashless dispersants, detergents, rust inhibitors, dehazing agents, demulsifying agents, metal deactivating agents, friction modifiers, pour point depressants, antifoaming agents, co-solvents, package compatibilisers, corrosion-inhibitors, dyes, extreme pressure agents and the like and mixtures
35 thereof. A variety of the additives are known and commercially available. These additives, or their analogous compounds, can be employed for the preparation of the lubricating oil compositions of the invention by the usual blending procedures.

5 Examples of antioxidants include, but are not limited to, aminic types, e.g., diphenylamine, phenyl-alpha-naphthyl-amine, N,N-di(alkylphenyl) amines; and alkylated phenylene-diamines; phenolics such as, for example, BHT, sterically hindered alkyl phenols such as 2,6-di-tert-butylphenol, 2,6-di-tert-butyl-p-cresol and 2,6-di-tert-butyl-4-(2-octyl-3-propanoic) phenol; and mixtures thereof. The antioxidants of the present invention can be
10 aminic, phenolic, or mixtures thereof.

 Examples of antiwear agents include, but are not limited to, zinc dialkyldithiophosphates and zinc diaryldithiophosphates, e.g., those described in an article by Born et al. entitled "Relationship between Chemical Structure and Effectiveness of Some Metallic Dialkyl- and Diaryl-dithiophosphates in Different Lubricated Mechanisms",
15 appearing in Lubrication Science 4-2 January 1992, see for example pages 97-100; aryl phosphates and phosphites, sulfur-containing esters, phosphosulfur compounds, metal or ash-free dithiocarbamates, xanthates, alkyl sulfides and the like and mixtures thereof.

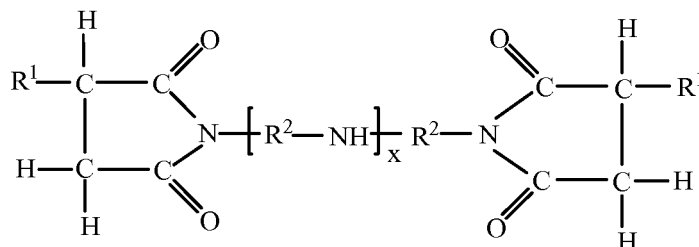
 Representative examples of ashless dispersants include, but are not limited to, amines, alcohols, amides, or ester polar moieties attached to the polymer backbones via bridging
20 groups. An ashless dispersant of the present invention may be, for example, selected from oil soluble salts, esters, amino-esters, amides, imides, and oxazolines of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of long chain hydrocarbons, long chain aliphatic hydrocarbons having a polyamine attached directly thereto; and Mannich condensation products formed by condensing a long chain
25 substituted phenol with formaldehyde and polyalkylene polyamine.

 Carboxylic dispersants are reaction products of carboxylic acylating agents (acids, anhydrides, esters, etc.) comprising at least about 34 and preferably at least about 54 carbon atoms with nitrogen containing compounds (such as amines), organic hydroxy compounds (such as aliphatic compounds including monohydric and polyhydric alcohols, or aromatic
30 compounds including phenols and naphthols), and/or basic inorganic materials. These reaction products include imides, amides, and esters.

 Succinimide dispersants are a type of carboxylic dispersant. They are produced by reacting hydrocarbyl-substituted succinic acylating agent with organic hydroxy compounds, or with amines comprising at least one hydrogen atom attached to a nitrogen atom, or with a
35 mixture of the hydroxy compounds and amines. The term "succinic acylating agent" refers to a hydrocarbon-substituted succinic acid or a succinic acid-producing compound, the latter

5 encompasses the acid itself. Such materials typically include hydrocarbyl-substituted succinic acids, anhydrides, esters (including half esters) and halides.

Succinic-based dispersants have a wide variety of chemical structures. One class of succinic-based dispersants may be represented by the formula:



10 wherein each R^1 is independently a hydrocarbyl group, such as a polyolefin-derived group. Typically the hydrocarbyl group is an alkyl group, such as a polyisobutyl group. Alternatively expressed, the R^1 groups can contain about 40 to about 500 carbon atoms, and these atoms may be present in aliphatic forms. R^2 is an alkylene group, commonly an ethylene (C_2H_4) group. Examples of succinimide dispersants include those described in, for
 15 example, U.S. Patent Nos. 3,172,892, 4,234,435 and 6,165,235.

The polyalkenes from which the substituent groups are derived are typically homopolymers and interpolymers of polymerizable olefin monomers of 2 to about 16 carbon atoms, and usually 2 to 6 carbon atoms. The amines which are reacted with the succinic acylating agents to form the carboxylic dispersant composition can be monoamines or
 20 polyamines.

Succinimide dispersants are referred to as such since they normally contain nitrogen largely in the form of imide functionality, although the amide functionality may be in the form of amine salts, amides, imidazolines as well as mixtures thereof. To prepare a succinimide dispersant, one or more succinic acid-producing compounds and one or more
 25 amines are heated and typically water is removed, optionally in the presence of a substantially inert organic liquid solvent/diluent. The reaction temperature can range from about 80°C up to the decomposition temperature of the mixture or the product, which typically falls between about 100°C to about 300°C. Additional details and examples of procedures for preparing the succinimide dispersants of the present invention include those
 30 described in, for example, U.S. Patent Nos. 3,172,892, 3,219,666, 3,272,746, 4,234,435, 6,165,235 and 6,440,905.

5 Suitable ashless dispersants may also include amine dispersants, which are reaction products of relatively high molecular weight aliphatic halides and amines, preferably polyalkylene polyamines. Examples of such amine dispersants include those described in, for example, U.S. Patent Nos. 3,275,554, 3,438,757, 3,454,555 and 3,565,804.

10 Suitable ashless dispersants may further include "Mannich dispersants," which are reaction products of alkyl phenols in which the alkyl group contains at least about 30 carbon atoms with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines). Examples of such dispersants include those described in, for example, U.S. Patent Nos. 3,036,003, 3,586,629, 3,591,598 and 3,980,569.

15 Suitable ashless dispersants may also be post-treated ashless dispersants such as post-treated succinimides, e.g., post-treatment processes involving borate or ethylene carbonate as disclosed in, for example, U.S. Patent Nos. 4,612,132 and 4,746,446; and the like as well as other post-treatment processes. The carbonate-treated alkenyl succinimide is a polybutene succinimide derived from polybutenes having a molecular weight of about 450 to about 3000, preferably from about 900 to about 2500, more preferably from about 1300 to about 2400, and most preferably from about 2000 to about 2400, as well as mixtures of these molecular weights. Preferably, it is prepared by reacting, under reactive conditions, a mixture of a polybutene succinic acid derivative, an unsaturated acidic reagent copolymer of an unsaturated acidic reagent and an olefin, and a polyamine, such as disclosed in U.S. Patent No. 5,716,912, the contents of which are incorporated herein by reference.

25 An example of a suitable ashless dispersant is a borated dispersant. Borated dispersants may be formed by boronating (borating) an ashless dispersant having basic nitrogen and/or at least one hydroxyl group in the molecule, such as a succinimide dispersant, succinamide dispersant, succinic ester dispersant, succinic ester-amide dispersant, Mannich base dispersant, or hydrocarbyl amine or polyamine dispersant. Methods that can be used for boronating the various types of ashless dispersants described above are described, for example, in U.S. Pat. Nos. 4,455,243 and 4,652,387.

35 Suitable ashless dispersants may also be polymeric, which are interpolymers of oil-solubilizing monomers such as decyl methacrylate, vinyl decyl ether and high molecular weight olefins with monomers containing polar substitutes. Examples of polymeric dispersants include those described in, for example, U.S. Patent Nos. 3,329,658; 3,449,250 and 3,666,730.

5 In one preferred embodiment of the present invention, an ashless dispersant for use in the lubricating oil composition is a bis-succinimide derived from a polyisobutenyl group having a number average molecular weight of about 700 to about 2300. The dispersant(s) for use in the lubricating oil compositions of the present invention are preferably non-polymeric (e.g., are mono- or bis-succinimides).

10 Generally, the one or more ashless dispersants are present in the lubricating oil composition in an amount ranging from about 0.01 wt. % to about 20 wt. %, based on the total weight of the lubricating oil composition.

Representative examples of metal detergents include sulphonates, alkylphenates, sulfurized alkyl phenates, carboxylates, salicylates, phosphonates, and phosphinates.

15 Commercial products are generally referred to as neutral or overbased. Overbased metal detergents are generally produced by carbonating a mixture of hydrocarbons, detergent acid, for example: sulfonic acid, alkylphenol, carboxylate etc., metal oxide or hydroxides (for example calcium oxide or calcium hydroxide) and promoters such as xylene, methanol and water. For example, for preparing an overbased calcium sulfonate, in carbonation, the
20 calcium oxide or hydroxide reacts with the gaseous carbon dioxide to form calcium carbonate. The sulfonic acid is neutralized with an excess of CaO or Ca(OH)₂, to form the sulfonate.

Metal-containing or ash-forming detergents function as both detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and
25 corrosion and extending engine life. Detergents generally comprise a polar head with a long hydrophobic tail. The polar head comprises a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as can be measured by ASTM D2896) of from 0 to about 80. A large amount of a
30 metal base may be incorporated by reacting excess metal compound (e.g., an oxide or hydroxide) with an acidic gas (e.g., carbon dioxide). The resulting overbased detergent comprises neutralized detergent as the outer layer of a metal base (e.g., carbonate) micelle. Such overbased detergents may have a TBN of about 150 or greater, and typically will have a TBN of from about 250 to about 450 or more.

35 Detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals, e.g., barium,

5 sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present in detergents used in a lubricant, and mixtures of calcium and/or magnesium with sodium. Particularly convenient metal detergents are neutral and overbased calcium sulfonates having TBN of from about 20 to about 450, neutral and overbased calcium phenates and sulfurized phenates having TBN of
10 from about 50 to about 450 and neutral and overbased magnesium or calcium salicylates having a TBN of from about 20 to about 450. Combinations of detergents, whether overbased or neutral or both, may be used.

In one embodiment, the detergent can be one or more alkali or alkaline earth metal salts of an alkyl-substituted hydroxyaromatic carboxylic acid. Suitable hydroxyaromatic
15 compounds include mononuclear monohydroxy and polyhydroxy aromatic hydrocarbons having 1 to 4, and preferably 1 to 3, hydroxyl groups. Suitable hydroxyaromatic compounds include phenol, catechol, resorcinol, hydroquinone, pyrogallol, cresol, and the like. The preferred hydroxyaromatic compound is phenol.

The alkyl substituted moiety of the alkali or alkaline earth metal salt of an alkyl-
20 substituted hydroxyaromatic carboxylic acid is derived from an alpha olefin having from about 10 to about 80 carbon atoms. The olefins employed may be linear, isomerized linear, branched or partially branched linear. The olefin may be a mixture of linear olefins, a mixture of isomerized linear olefins, a mixture of branched olefins, a mixture of partially branched linear or a mixture of any of the foregoing.

25 In one embodiment, the mixture of linear olefins that may be used is a mixture of normal alpha olefins selected from olefins having from about 12 to about 30 carbon atoms per molecule. In one embodiment, the normal alpha olefins are isomerized using at least one of a solid or liquid catalyst.

In another embodiment, the olefins are a branched olefinic propylene oligomer or
30 mixture thereof having from about 20 to about 80 carbon atoms, i.e., branched chain olefins derived from the polymerization of propylene. The olefins may also be substituted with other functional groups, such as hydroxy groups, carboxylic acid groups, heteroatoms, and the like. In one embodiment, the branched olefinic propylene oligomer or mixtures thereof have from about 20 to about 60 carbon atoms. In one embodiment, the branched olefinic propylene
35 oligomer or mixtures thereof have from about 20 to about 40 carbon atoms.

In one embodiment, at least about 75 mole% (e.g., at least about 80 mole%, at least about 85 mole%, at least about 90 mole%, at least about 95 mole%, or at least about 99

5 mole%) of the alkyl groups contained within the alkali or alkaline earth metal salt of an alkyl-substituted hydroxyaromatic carboxylic acid such as the alkyl groups of an alkaline earth metal salt of an alkyl-substituted hydroxybenzoic acid detergent are a C₂₀ or higher. In another embodiment, the alkali or alkaline earth metal salt of an alkyl-substituted hydroxyaromatic carboxylic acid is an alkali or alkaline earth metal salt of an alkyl-substituted hydroxybenzoic acid that is derived from an alkyl-substituted hydroxybenzoic acid in which the alkyl groups are the residue of normal alpha-olefins containing at least 75 mole% C₂₀ or higher normal alpha-olefins.

In another embodiment, at least about 50 mole % (e.g., at least about 60 mole %, at least about 70 mole %, at least about 80 mole %, at least about 85 mole %, at least about 90 mole %, at least about 95 mole %, or at least about 99 mole %) of the alkyl groups contained within the alkali or alkaline earth metal salt of an alkyl-substituted hydroxyaromatic carboxylic acid such as the alkyl groups of an alkali or alkaline earth metal salt of an alkyl-substituted hydroxybenzoic acid are about C₁₄ to about C₁₈.

The resulting alkali or alkaline earth metal salt of an alkyl-substituted hydroxyaromatic carboxylic acid will be a mixture of ortho and para isomers. In one embodiment, the product will contain about 1 to 99% ortho isomer and 99 to 1% para isomer. In another embodiment, the product will contain about 5 to 70% ortho and 95 to 30% para isomer.

The alkali or alkaline earth metal salts of an alkyl-substituted hydroxyaromatic carboxylic acid can be neutral or overbased. Generally, an overbased alkali or alkaline earth metal salt of an alkyl-substituted hydroxyaromatic carboxylic acid is one in which the BN of the alkali or alkaline earth metal salts of an alkyl-substituted hydroxyaromatic carboxylic acid has been increased by a process such as the addition of a base source (e.g., lime) and an acidic overbasing compound (e.g., carbon dioxide).

Overbased salts may be low overbased, e.g., an overbased salt having a BN below about 100. In one embodiment, the BN of a low overbased salt may be from about 5 to about 50. In another embodiment, the BN of a low overbased salt may be from about 10 to about 30. In yet another embodiment, the BN of a low overbased salt may be from about 15 to about 20.

Overbased detergents may be medium overbased, e.g., an overbased salt having a BN from about 100 to about 250. In one embodiment, the BN of a medium overbased salt may

5 be from about 100 to about 200. In another embodiment, the BN of a medium overbased salt may be from about 125 to about 175.

Overbased detergents may be high overbased, e.g., an overbased salt having a BN above about 250. In one embodiment, the BN of a high overbased salt may be from about 250 to about 450.

10 Sulfonates may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons. Examples included those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl or their halogen derivatives. The alkylation may be carried out in the presence of a catalyst with alkylating
15 agents having from about 3 to more than 70 carbon atoms. The alkaryl sulfonates usually contain from about 9 to about 80 or more carbon atoms, preferably from about 16 to about 60 carbon atoms per alkyl substituted aromatic moiety.

The oil soluble sulfonates or alkaryl sulfonic acids may be neutralized with oxides, hydroxides, alkoxides, carbonates, carboxylate, sulfides, hydrosulfides, nitrates, borates and
20 ethers of the metal. The amount of metal compound is chosen having regard to the desired TBN of the final product but typically ranges from about 100 to about 220 wt. % (preferably at least about 125 wt. %) of that stoichiometrically required.

Metal salts of phenols and sulfurized phenols are prepared by reaction with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products
25 may be obtained by methods well known in the art. Sulfurized phenols may be prepared by reacting a phenol with sulfur or a sulfur containing compound such as hydrogen sulfide, sulfur monohalide or sulfur dihalide, to form products which are generally mixtures of compounds in which 2 or more phenols are bridged by sulfur containing bridges.

Generally, the one or more detergents are present in the lubricating oil composition in
30 an amount ranging from about 0.01 wt. % to about 10 wt. %, based on the total weight of the lubricating oil composition.

Examples of rust inhibitors include, but are not limited to, nonionic polyoxyalkylene agents, e.g., polyoxyethylene lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonylphenyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene
35 octyl stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol monooleate, and polyethylene glycol monooleate; stearic acid and other fatty acids; dicarboxylic acids; metal soaps; fatty acid amine salts; metal salts of heavy

5 sulfonic acid; partial carboxylic acid ester of polyhydric alcohol; phosphoric esters; (short-chain) alkenyl succinic acids; partial esters thereof and nitrogen-containing derivatives thereof; synthetic alkarylsulfonates, e.g., metal dinonylnaphthalene sulfonates; and the like and mixtures thereof.

10 Examples of friction modifiers include, but are not limited to, alkoxyated fatty amines; borated fatty epoxides; fatty phosphites, fatty epoxides, fatty amines, borated alkoxyated fatty amines, metal salts of fatty acids, fatty acid amides, glycerol esters, borated glycerol esters; and fatty imidazolines as disclosed in U.S. Patent No. 6,372,696, the contents of which are incorporated by reference herein; friction modifiers obtained from a reaction product of a C₄ to C₇₅, preferably a C₆ to C₂₄, and most preferably a C₆ to C₂₀, fatty acid ester
15 and a nitrogen-containing compound selected from the group consisting of ammonia, and an alkanolamine and the like and mixtures thereof.

Examples of antifoaming agents include, but are not limited to, polymers of alkyl methacrylate; polymers of dimethylsilicone and the like and mixtures thereof.

20 Examples of a pour point depressant include, but are not limited to, polymethacrylates, alkyl acrylate polymers, alkyl methacrylate polymers, di(tetra-paraffin phenol)phthalate, condensates of tetra-paraffin phenol, condensates of a chlorinated paraffin with naphthalene and combinations thereof. In one embodiment, a pour point depressant comprises an ethylene-vinyl acetate copolymer, a condensate of chlorinated paraffin and phenol, polyalkyl styrene and the like and combinations thereof. The amount of the pour
25 point depressant may vary from about 0.01 wt. % to about 10 wt. %.

Examples of a demulsifier include, but are not limited to, anionic surfactants (e.g., alkyl-naphthalene sulfonates, alkyl benzene sulfonates and the like), nonionic alkoxyated alkylphenol resins, polymers of alkylene oxides (e.g., polyethylene oxide, polypropylene oxide, block copolymers of ethylene oxide, propylene oxide and the like), esters of oil soluble
30 acids, polyoxyethylene sorbitan ester and the like and combinations thereof. The amount of the demulsifier may vary from about 0.01 wt. % to about 10 wt. %.

Examples of a corrosion inhibitor include, but are not limited to, half esters or amides of dodecylsuccinic acid, phosphate esters, thiophosphates, alkyl imidazolines, sarcosines and the like and combinations thereof. The amount of the corrosion inhibitor may vary from
35 about 0.01 wt. % to about 5 wt. %.

The corrosion inhibitor component can be a non-polycarboxylate moiety containing thiadiazole. Preferably, the thiadiazole comprises at least one of 2,5-dimercapto-1,3,4-

5 thiadiazole; 2-mercapto-5-hydrocarbylthio-1,3,4-thiadiazoles; 2-mercapto-5-hydrocarbyldithio-1,3,4-thiadiazoles; 2,5-bis(hydrocarbylthio and 2,5-bis(hydrocarbyldithio)-1,3,4-thiadiazoles. The more preferred compounds are the 1,3,4-thiadiazoles, especially the 2-hydrocarbyldithio-5-mercapto-1,3,4-dithiadiazoles and the 2,5-bis(hydrocarbyldithio)-1,3,4-thiadiazoles, a number of which are available as articles of commerce. Most preferably,
10 a non polycarboxylate containing thiadiazole containing about 4.0 wt% 2,5-dimercapto-1,3,4-thiadiazole, which may be either Ethyl Corporation's Hitec® 4313 or Lubrizol Corporation's Lubrizol® 5955A, is used. Hitec® 4313 may be obtained from Ethyl Corporation, Richmond, Virginia and Lubrizol® 5955A may be obtained from Lubrizol Corporation, Wycliffe, Ohio.

15 Examples of an extreme pressure agent include, but are not limited to, sulfurized animal or vegetable fats or oils, sulfurized animal or vegetable fatty acid esters, fully or partially esterified esters of trivalent or pentavalent acids of phosphorus, sulfurized olefins, dihydrocarbyl polysulfides, sulfurized Diels-Alder adducts, sulfurized dicyclopentadiene, sulfurized or co-sulfurized mixtures of fatty acid esters and monounsaturated olefins, co-sulfurized blends of fatty acid, fatty acid ester and alpha-olefin, functionally-substituted
20 dihydrocarbyl polysulfides, thia-aldehydes, thia-ketones, epithio compounds, sulfur-containing acetal derivatives, co-sulfurized blends of terpene and acyclic olefins, and polysulfide olefin products, amine salts of phosphoric acid esters or thiophosphoric acid esters and the like and combinations thereof. The amount of the extreme pressure agent may
25 vary from about 0.01 wt. % to about 5 wt. %.

Each of the foregoing additives, when used, is used at a functionally effective amount to impart the desired properties to the lubricant. Thus, for example, if an additive is a friction modifier, a functionally effective amount of this friction modifier would be an amount sufficient to impart the desired friction modifying characteristics to the lubricant. Generally,
30 the concentration of each of these additives, when used, may range, unless otherwise specified, from about 0.001% to about 20% by weight, and in one embodiment about 0.01% to about 10% by weight based on the total weight of the lubricating oil composition.

In another embodiment of the invention, the lubricating oil additives of the present invention may be provided as an additive package or concentrate in which the additives are
35 incorporated into a substantially inert, normally liquid organic diluent such as, for example, mineral oil, naphtha, benzene, toluene or xylene to form an additive concentrate. These concentrates usually contain from about 20% to about 80% by weight of such diluent.

5 Typically, a neutral oil having a viscosity of about 4 to about 8.5 cSt at 100°C and preferably about 4 to about 6 cSt at 100°C will be used as the diluent, though synthetic oils, as well as other organic liquids which are compatible with the additives and finished lubricating oil can also be used.

10 The following examples are presented to exemplify embodiments of the invention but are not intended to limit the invention to the specific embodiments set forth. Unless indicated to the contrary, all parts and percentages are by weight. All numerical values are approximate. When numerical ranges are given, it should be understood that embodiments outside the stated ranges may still fall within the scope of the invention. Specific details described in each example should not be construed as necessary features of
15 the invention.

EXAMPLES

The following examples are intended for illustrative purposes only and do not limit in any way the scope of the present invention.

20 Baseline performance is exemplified by a standard GF-5 oil. This oil has SAPS levels near the mandated limit: sulfur of 0.2 wt%, phosphorus of 0.075 wt% and sulfated ash of 1.1 wt%.

When all additives contributing to SAPS levels were removed (Ultra-Low SAPS oil A) the performance on the High Temperature Corrosion Bench Test (HTCBT), Ball Rust Test (BRT) and Thermo-oxidation engine oil simulation test at moderately high temperature
25 (TEOST MHT-4) dropped to unacceptable levels (Table 1).

Table 1

Oil	Baseline GF5 oil	Ultra-Low SAPS oil A
HTCBT (Cu/Pb)	10/32	13/338
BRT	124	25
TEOST MHT-4	44.7	160.3

5 Comparative examples Ultra-Low SAPS oils A to K and inventive Example 1 are shown in Table 2. In Table 2, the unit for S (Sulfur), and P (Phosphorous) is ppm, and for Ash (Sulfated Ash) is wt% in the fully formulated lubricating oil.

 The performance of each oil was evaluated using:

 (a) The High Temperature Corrosion Bench Test (HTCBT) ASTM D6594 (Version 08).

10 Passing levels for the HTCBT are: Copper are less than 20 ppm; and Lead less than 120 ppm.

 (b) Ball Rust Test (BRT) ASTM D6557 (Version 10a). Passing for the BRT is greater than 100 Average Grey Value (AVG).

 (c) Thermo-oxidation engine oil simulation test at moderately high temperature (TEOST MHT-4) ASTM D7097 (Version 09). Passing for the TEOST MHT-4 is less than 45 mg.

15

5

Table 2

Examples>>>	A	B	C	D	E	F	G	H	I	J	K	1
Borated Dispersant, wt.%				6.5	6.5	6.5	13					13
Boron in Lubricating Oil Composition, ppm				410	410	410	820					820
Dispersant A, wt.%	2	6.5	6.5									
Dispersant B, wt.%								6.5	13	6.5	13	
Aminic AO, wt.%	0.4	1.5	1	1.5	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Phenolic AO, wt.%	0.5	3		0.5	3	3	3	3	3	3	3	3
Decomposer, wt.%			1	1	0.6	0.3	0.3	0.6	0.6	0.3	0.3	0.6
Metal Deactivator, wt.%		0.2		0.2	0.0	5	0.2	0.05	0.2	0.0	5	0.2
HTCBT Cu	13	2	29	4	9	4	28	4	16	6	8	12
HTCBT PB	322	83 2	338	177. 5	88	216	189	74 3	85 4	694	999	81
BRT	25	26	71	127	103	38	111	34	11 9	22	64	117
TEOST MHT-4	160.3	26	101. 2	58.5	56	74.8	41.6	70. 9	46. 8	52. 7	38. 2	36.5
S (Group II Baseoil)	291	26 6	275	270	268	268	250	26 7	24 9	269	249	248
P (Group II Baseoil)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ash Group II Baseoil)	0.0	0.0	0.0	300	300	300	800	0.0	0.0	0.0	0.0	800
S (Group III Baseoil)	4.9	4.4	4.6	4.5	4.5	4.5	4.2	4.5	4.1	4.5	4.1	4.1
P (Group III Baseoil)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ash Group III Baseoil)	0.0	0.0	0.0	300	300	300	800	0.0	0.0	0.0	0.0	800

In Table 2, the unit for S (Sulfur), and P (Phosphorous) is ppm and for Ash (Sulfated Ash) is wt% in the lubricating oil composition.

The components in Table 2 are described below:

- 5 Borated dispersant: An oil concentrate of borated succinimide derived from 1300 MW Poly Iso-Butylene Succinic Anhydride (PIBSA) and heavy polyamine (HPA).

Dispersant A: An oil concentrate of ethylene carbonate-treated succinimide derived from 2300 MW PIBSA and heavy polyamine (HPA).

- 10 Dispersant B: A Succinimide synthesized from 2300 MW PIBSA and heavy polyamine (HPA).

Decomposer: is the Ashless Peroxide Decomposer according to Formula 1 in the present application.

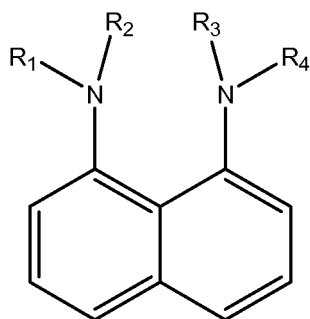
Table 3

TEST>>	Cu	Pb	BRT	TEOST
Comparative Example A	Pass	Fail	Fail	Fail
Comparative Example B	Pass	Fail	Fail	Pass
Comparative Example C	Fail	Fail	Fail	Fail
Comparative Example D	Pass	Fail	Pass	Fail
Comparative Example E	Pass	Pass	Pass	Fail
Comparative Example F	Pass	Fail	Fail	Fail
Comparative Example G	Fail	Fail	Pass	Pass
Comparative Example H	Pass	Fail	Fail	Fail
Comparative Example I	Pass	Fail	Pass	Fail
Comparative Example J	Pass	Fail	Fail	Fail
Comparative Example K	Pass	Fail	Fail	Pass
Inventive Example 1	Pass	Pass	Pass	Pass

15 Table 3 is a Pass / Fail summary of Comparative Examples A to K and Inventive Example 1 in the HT CBT (Cu, Pb), BRT and TEOST tests.

5 WHAT IS CLAIMED IS:

1. An ultra-low SAPS lubricating oil composition comprising:
an oil of lubricating viscosity;
a borated dispersant supplying at least 500 ppm boron to said lubricating oil composition;
10 an ashless peroxide decomposer present at a treat rate of from about 0.4 to 5.0 wt%;
a metal deactivator wherein the metal deactivator is present at a treat rate of greater than 0.08 wt%;
wherein said lubricating oil composition contains less than 1000 ppm sulfur, less than 300 ppm phosphorus and less than 0.25 wt% sulfated ash.
- 15 2. The composition of Claim 1, wherein the borated dispersant supplying at least 500 ppm boron is selected from a borated bis-succinimide, a borated mono-succinimide, or mixtures thereof.
3. The composition of Claim 1, wherein the borated dispersant supplies 500 to 3000 ppm boron.
- 20 4. The composition of Claim 1, wherein the ashless peroxide decomposer is a compound according to formula 1:

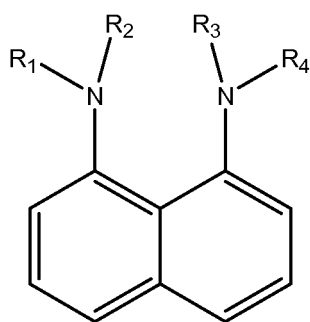


Formula I

25 wherein R₁ and R₂ and R₃ and R₄ are each independently selected from the group consisting of alkyl from 1 to 20 carbon atoms, more preferably alkyl from 1 to 10 carbon atoms and even more preferably lower alkyl from 1 to six carbon atoms.

5. The composition of Claim 1, wherein the ashless peroxide decomposer is N,N,N',N'-
30 tetramethyl-naphthalene-1,8-diamine.

- 5 6. The composition of Claim 1, wherein the metal deactivator is present at a treat rate of from about 0.08 to 3.0 wt%.
7. The composition of Claim 1, wherein the metal deactivator is selected from benzotriazole, tolyltriazole, and mixtures thereof.
- 10 8. A method of lubricating an engine with an ultra-low SAPS lubricating oil composition comprising:
an oil of lubricating viscosity;
a borated dispersant supplying at least 500 ppm boron to said lubricating oil composition;
an ashless peroxide decomposer present at a treat rate of from about 0.4 to 5.0 wt%;
- 15 a metal deactivator wherein the metal deactivator is present at a treat rate of greater than 0.08 wt%;
wherein said lubricating oil composition contains less than 1000 ppm sulfur, less than 300 ppm phosphorus and less than 0.25 wt% sulfated ash.
- 20 9. The method of Claim 8, wherein the borated dispersant supplying at least 500 ppm boron is selected from a borated bis-succinimide, a borated mono-succinimide, or mixtures thereof.
10. The method of Claim 8, wherein the borated dispersant supplies 500 to 3000 ppm boron.
- 25 11. The method of Claim 8, wherein the ashless peroxide decomposer is a compound according to formula I:



Formula I

- 5 wherein R₁ and R₂ and R₃ and R₄ are each independently selected from the group consisting of alkyl from 1 to 20 carbon atoms, more preferably alkyl from 1 to 10 carbon atoms and even more preferably lower alkyl from 1 to six carbon atoms.
12. The method of Claim 8, wherein the ashless peroxide decomposer is N,N,N',N'-tetramethyl-naphthalene-1,8-diamine.
- 10 13. The method of Claim 8, wherein the metal deactivator is present at a treat rate of from about 0.08 to 3.0 wt%.
14. The method of Claim 8, wherein the metal deactivator is selected from benzotriazole, tolyltriozole, and mixtures thereof.
- 15 15. A method of making a low SAPS lubricating oil composition, comprising mixing together:
an oil of lubricating viscosity;
a borated dispersant supplying at least 500 ppm boron to said lubricating oil composition;
an ashless peroxide decomposer present at a treat rate of from about 0.4 to 5.0 wt%;
20 a metal deactivator wherein the metal deactivator is present at a treat rate of greater than 0.08 wt%;
wherein said lubricating oil composition contains less than 1000 ppm sulfur, less than 300 ppm phosphorus and less than 0.25 wt% sulfated ash.