

# US Patent & Trademark Office

## Patent Public Search | Text View

United States Patent Application Publication

20250263623

Kind Code

A1

Publication Date

August 21, 2025

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### Lubricant Compositions Comprising Core-Shell Colloidal Zn-Containing Particles

#### Abstract

This invention relates to the use of colloids of a core of zinc containing compounds and a shell of metal containing surfactants, such as salicylates and or sulfonates, metal alkanoates, and or metal carboxylates, as additives in lubricant compositions having good anti-wear properties, especially for engine crankcase applications.

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**Family ID:** 1000008487551

**Appl. No.:** 19/045811

**Filed:** February 05, 2025

#### Foreign Application Priority Data

GB

2402436

Feb. 21, 2024

#### Publication Classification

**Int. Cl.:** C10M169/04 (20060101); C10M125/10 (20060101); C10M129/40 (20060101); C10M135/10 (20060101); C10M137/10 (20060101); C10M141/10 (20060101); C10M177/00 (20060101); C10N20/00 (20060101); C10N20/06 (20060101); C10N30/00 (20060101); C10N30/02 (20060101); C10N30/04 (20060101); C10N30/06 (20060101); C10N30/10 (20060101); C10N30/12 (20060101); C10N30/18 (20060101); C10N40/00

(20060101); **C10N40/04** (20060101); **C10N40/25** (20060101); **C10N50/00** (20060101); **C10N70/00** (20060101)

## U.S. Cl.:

CPC **C10M169/04** (20130101); **C10M125/10** (20130101); **C10M129/40** (20130101); **C10M135/10** (20130101); **C10M137/10** (20130101); **C10M141/10** (20130101); **C10M177/00** (20130101); C10M2201/14 (20130101); C10M2203/003 (20130101); C10M2223/045 (20130101); C10N2020/06 (20130101); C10N2020/061 (20200501); C10N2030/02 (20130101); C10N2030/04 (20130101); C10N2030/06 (20130101); C10N2030/10 (20130101); C10N2030/12 (20130101); C10N2030/18 (20130101); C10N2030/42 (20200501); C10N2040/04 (20130101); C10N2040/135 (20200501); C10N2040/252 (20200501); C10N2040/255 (20200501); C10N2050/01 (20200501); C10N2070/02 (20200501)

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## Background/Summary

### PRIORITY

[0001] This invention claims priority to and the benefit of Great Britain patent application number GB2402436.6, filed Feb. 21, 2024.

### FIELD OF THE INVENTION

[0002] This invention relates to the use of colloids of a core of zinc containing compounds and a shell of metal containing surfactants, such as salicylates and or sulfonates, alkanolates, and/or carboxylates, as additives in lubricant compositions having good anti-wear properties, especially for engine crankcase applications.

### BACKGROUND

[0003] The present invention relates to lubricating oil compositions such as those for combustion engines such as automotive lubricating oil compositions, or in marine oils, or transmission fluids, or gear oils, which exhibit improved wear characteristics. More specifically, the present invention relates to automotive crankcase lubricating oil compositions for use in gasoline (spark-ignited) and diesel (compression-ignited, spark assisted compression ignited) internal combustion engines, such compositions being referred to as crankcase lubricants; and to the use of additives in such lubricating oil compositions for reducing friction and/or wear between moving parts in use of such engines and/or improving the fuel economy performance of an engine lubricated with the lubricating oil composition.

[0004] Engine durability is an important consideration in the choice of a lubricant, especially for heavy duty diesel engine applications. Original equipment manufacturers are continuing to increase their oil drain intervals and the average lifetime of vehicles has steadily increased over the last few decades. Likewise, there is a trend towards use of ashless anti-wear agents which have a lower impact on after treatment systems such as diesel particulate filters in heavy duty diesel vehicles.

[0005] Environmental and regulatory requirements are driving a desire to improve the efficiency of the internal combustion engine. Lower viscosity lubricants require less energy to pump around an engine and thus can improve its fuel economy. However, lower viscosity lubricants result in thinner oil films between contacting engine parts (e.g., in the valve train, piston zone and in bearings), which can lead to higher rates of wear, reduced friction modification, etc. Conventionally, zinc dialkyl dithiophosphates (ZDDPs) are often used as lubricant additives to prevent engine wear and or reduce friction in the boundary lubrication regimes.

[0006] Alongside the drive for improved fuel economy, there is also a desire to reduce the emissions from vehicles. Control of exhaust emissions is typically achieved by after-treatment

devices, such as catalytic converters, which generally employ precious metal catalysts to convert combustion products into less undesirable species. However, these catalysts are negatively impacted by, inter alia, phosphorus and sulfur, which impacts their catalytic activity/effectiveness. Another after-treatment device is the particulate filter, which can be blocked by sulfated ash or sludge generated from combustion of heavy duty diesel oils. Hence, the levels of sulfated ash, phosphorus, and sulfur (SAPS) derived from heavy duty diesel oils are desirably reduced. ZDDP and zinc dithiocarbamate additives contribute significant quantities of SAPS to a lubricating oil, thus the use of ZDDP and the like is also desirably reduced. However, the addition of SAPS containing antiwear components is often required to ensure good antiwear performance. This makes the discovery of methods to improve the antiwear performance of lubricating oils without the further addition of phosphorus advantageous. It is also desirable to improve the antiwear performance of lubricating oils without further increasing the ash (SASH) content. Similarly, it is advantageous to improve the antiwear performance of a lubricating oil by the substitution of components such as detergents for components that offer both anti-wear and detergency properties. [0007] A common feature of inorganic materials generally is that they contribute to ash. As there are ash limits imposed by original equipment manufacturers and the like, it typically means that other ash forming components must be reduced to accommodate new inorganic materials. A main source of ash producing materials in lubricants are inorganic detergents, which are often added to, inter alia, increase the total base number of the lubricating oil. Raising the total base number (TBN) can often mean that acidic byproducts of combustion are neutralized for a longer period or under more harsh conditions. Whilst TBN can also be offered by ashless components, for example amines, basic metal salts often referred to as detergents are commonly utilized, despite their contribution to SASH.

[0008] Therefore, it would be desirable to identify anti-wear agents that are preferably phosphorus-free and/or sulfur-free, that demonstrate have excellent anti-wear and anti-scuff properties as well as providing TBN to a formulation.

[0009] U.S. Pat. No. 10,000,721 (EP3240879A1) and its US continuation-in-part U.S. Pat. No. 10,781,397 disclose stoichiometric metal salts of carboxylic acids, such as zinc stearate, zinc undecylenate, zinc oleate, and zinc naphthenate, as anti-wear components in lubricant compositions with optional detergent.

[0010] US 2008/0274041 A1 discloses methods to make dispersions of nano-sized zinc oxide particles in hydrocarbon and discusses their use as catalysts in rubber vulcanization, paints and as an antioxidant additive in galvanized steel.

[0011] Similarly, U.S. Pat. No. 4,193,769 relates to stable, fluid zinc-containing dispersions and the preparations thereof by the high temperature decomposition of  $\text{ZnCO}_3$  to ZnO in a dispersant-containing fluid.

[0012] U.S. Pat. No. 4,410,446 relates to stable, fluid zinc-containing dispersions and the preparations thereof by the high temperature decomposition of zinc acetate to ZnO in a dispersant-containing fluid, said dispersant being stable at the temperature of decomposition.

[0013] U.S. Pat. No. 8,557,751 relates to a lubricating oil composition (containing a base oil, a phosphate ester derivative and a zinc compound) having an element ratio (Zn/P) between zinc (Zn) and phosphorus (P) in the lubricating oil composition of 0.55 or more, and also having certain NO<sub>x</sub> resistance.

[0014] GB 1,195,041 (DE1644915A1) relates to an automatic transmission fluid comprising a zinc carboxylate complex of a zinc oxide complex of a zinc dialkylphosphordithioate in which each carboxylate group contains from 1 to 20 carbon atoms, and in which the alkyl groups of the zinc dialkylphosphorodithioate are normal or isoalkyl groups and each contains 6 carbons atoms.

[0015] Other references of interest include: US2016/0186088A1 and CN102827668.

## SUMMARY OF INVENTION

[0016] It has now surprisingly been found by the present inventors that colloids having a core of

zinc containing compounds, and a shell of metal bound surfactants, such as metal sulfonates, salicylates and/or metal carboxylates can be used in lubricant compositions, such as automotive lubricating oil compositions, in marine oils, transmission fluids, or gear oils, or for combustion engines, e.g. diesel engines, or to provide excellent antiwear performance along with favorable contribution to TBN. The lubricating composition of the present invention may also reduce friction, thus helping to provide improved fuel economy properties.

[0017] This invention relates to concentrates and/or lubricating oil compositions comprising or resulting from the admixing of: [0018] (A) from 1 to 99.99 wt. %, based upon the weight of the lubricating composition, of one or more base oils; [0019] (B) at least one phosphorus-containing compound selected from detergents, friction modifiers or antiwear additives other than the colloidal particles described in (C); [0020] (C) from 0.01 to 10 wt. %, based upon the weight of the composition, of colloidal particles comprising: [0021] a) a core of one or more hydrocarbon insoluble zinc containing compounds, and [0022] b) a shell of one or more of: [0023] 1) one or more metal containing surfactants, where the metal, M, comprises a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; and the surfactant comprises a hydrocarbyl-substituted sulfonate of Formula (I), or an hydrocarbyl-substituted salicylate group of Formula (II),

##STR00001##

[0024] wherein each of R.sup.A and R.sup.B is, independently of each other, a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 1 to 70 carbon atoms, wherein, for  $n > 1$ , the sum of the number of carbon atoms in the total of R.sup.A groups in Formula (I) and the sum of the number of carbon atoms in the total of R.sup.B groups in Formula (II) is 100 or less carbon atoms, and Ar is a mono- or polycyclic aromatic group; n is an integer from 1 to the maximum possible number of substitutions on Ar, with  $n = 1$  if  $m = 0$ ; m is an integer of 1 to 3, x is an integer from 1 to 5; y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; [0025] 2) one or more metal alkanoates represented by the formula (III):

##STR00002## [0026] wherein M is a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; R.sup.C is selected from a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 70 carbon atoms, or an aromatic or alkyl aromatic group with the aromatic group having from 6 to 20 carbon atoms and the alkyl group having 1 to 20 carbon atoms; x is an integer from 1 to 5, wherein for  $x > 1$  the R.sup.C groups may be the same or different, y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8, [0027] wherein the lubricating oil composition has a ratio of Zn to P (elemental mass basis as measured by ASTM D5185) of 1.1 to 5.0.

[0028] In some embodiments, the hydrocarbon insoluble zinc containing compound is selected from at least one of zinc, zinc oxide, zinc hydroxide, zinc carbonate, and zinc halides, or mixtures thereof. In some embodiments, the colloidal particles have a mean particle diameter as determined by dynamic light scattering in the range of 5 nm to 1  $\mu$ m, such as 20 nm to 500 nm, or 20 nm to 200 nm. In some embodiments, the metal M in Formula (I), (II), or (III) is selected from at least one of sodium, potassium, lithium, magnesium, calcium, barium, or mixtures thereof, or wherein the metal M is selected from at least one of gold, silver, palladium, platinum, zirconium, vanadium, molybdenum, nickel, copper, zinc, aluminum, or mixtures thereof. In some embodiments, Ar in Formula (I) or Formula (II) is benzene or naphthalene.

[0029] In certain embodiments, the surfactant of Formula (I) is a metal containing hydrocarbyl-substituted phenyl sulfonate surfactant of Formula (Ia),

##STR00003##

wherein M is selected from calcium, magnesium, barium, or zinc, or combinations thereof, such as calcium, magnesium, or zinc, or calcium, or zinc; R.sup.A is independently of each other a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 50 carbon atoms, such as 10 to 40, or 12 to 37 carbon atoms; n is an integer from 1 to 5, such as 1 to 4,

such as 1, 2, or 3, such as 1, with  $n=1$  if  $m=0$ ;  $m$  is 0 to 3, such as 0, or 1; the sum of the number of carbon atoms in the total of R.sup.A groups is 60 or less carbon atoms;  $x$  is 2;  $y$  is 2; and, optionally,  $p$  is 0.

[0030] In certain embodiments, the surfactant of Formula (II) is a metal containing hydrocarbyl-substituted phenyl salicylate surfactant of Formula (IIa),

##STR00004##

wherein  $M$  is selected from calcium, magnesium, barium, or zinc, or combinations thereof; such as calcium, magnesium, or zinc, or combinations thereof; or calcium, or zinc, or combinations thereof, R.sup.B is independently of each other a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 50 carbon atoms, such as 10 to 48, or 12 to 37 carbon atoms;  $n$  is an integer from 1 to 4, such as 1 to 3, such as 1, or 2, such as 1; the sum of the number of carbon atoms in the total of R.sup.B groups is 60 or less carbon atoms;  $x$  is 2,  $y$  is 2; and, optionally,  $p$  is 0.

[0031] In some embodiments,  $M$  in Formula (I), (Ia), (II), (IIa), or (III) is selected from calcium, magnesium, or zinc, or combinations thereof, such as calcium, or zinc, or combinations thereof. In some embodiments,  $R$  in Formula (III) is a linear, cyclic, or branched, alkyl or alkenyl group having from 6 to 48 carbon atoms, such as 8 to 40, or 10 to 20 carbon atoms. In some embodiments, the metal alkanoate of Formula (III) is one or more of zinc neodecanoate, zinc neoundecanoate, zinc neododecanoate, zinc neotridecanoate, zinc neotetradecanoate, zinc neopentadecanoate, zinc neoheptadecanoate, zinc stearate, zinc neooctadecanoate, zinc oleate, zinc neononadecanoate, and zinc neoeicosanoate. In some embodiments, the metal alkanoates have a quaternary carbon atom at the 2 position, i.e., attached to the carboxylate group.

[0032] In some embodiments, the lubricating composition further comprises one or more components selected from the group consisting of one or more friction modifiers; one or more antioxidants; one or more pour point depressants; one or more anti-foaming agents; one or more viscosity modifiers; one or more dispersants; one or more inhibitors and/or anti-rust agents; and/or one or more anti-wear agents, other than those of component (C).

[0033] In certain embodiments, the lubricating composition comprises the following components:

[0034] (A) the base oil is present at 50 to 99 wt. % based upon the weight of the lubricating composition; [0035] (B) the at least one phosphorus-containing compound selected from detergents, friction modifiers, or antiwear additives other than the colloidal particles described in (C) is present in an amount of 0.001 to 5 wt.-%; [0036] C) the colloidal particles are present at from 0.01 to 10 wt. %, such as 0.01 to 6 wt. % based on total weight of the lubricating composition; [0037] D) optionally, one or more friction modifiers other than those of component (B) are present at from 0.01 to 5 wt. %, based on total weight of the lubricating composition; E) optionally, one or more antioxidants are present at from 0.01 to 10 wt. %, based on total weight of the lubricating composition; [0038] F) optionally, one or more pour point depressants are present at from 0.01 to 5 wt. %, based on total weight of the lubricating composition; [0039] G) optionally, one or more anti-foaming agents are present at from 0.001 to 5 wt. %, based on total weight of the lubricating composition; [0040] H) optionally, one or more viscosity modifiers are present at from 0.001 to 6 wt. %, based on total weight of the lubricating composition; [0041] I) optionally, one or more dispersants are present at from 0.01 to 20 wt. %, based on total weight of the lubricating composition; [0042] J) optionally, one or more inhibitors and/or anti-rust agents are present at from 0.01 to 5 wt. %, based on total weight of the lubricating composition; and [0043] K) optionally, one or more anti-wear agents, other than those of components (B) and (C), are present at from 0.001 to 5 wt. %, based on total weight of the lubricating composition; [0044] L) optionally, one or more detergents, other than those of components (B) and in the colloidal particles described in (C) are present at from 0.1 to 20 wt. % based on total weight of the lubricating composition.

[0045] Preferably, the lubricating composition has an adhesive wear of 100 hours or more, such as

120 hours or more, 130 hours or more, or 140 hours or more, as measured by ASTM D8074-16. Preferably, the lubricating composition has a ratio of Zn to P (elemental mass basis) is 1.1 to 4.7, such as 1.2 to 4.7, or 1.3 to 4.5, 1.4 to 4.5, 1.5 to 4.5, or 2.5 to 4.0, in the lubricating composition. Preferably, the ligand L in formula (I) to (III) is selected from the group consisting of water, hydroxide, halide, ammonia, amino, amido, alcoholate, and mixtures thereof. Preferably, the colloidal particles have a molar ratio of metal to surfactant, MR, of at least 5, such as 5 to 50, or 6 to 40, or 7 to 30. In some embodiments, the lubricating composition preferably has a total base number (TBN) of the composition from 1 to 30 mgKOH/g, such as 5 to 25 mgKOH/g, 5 to 20 mgKOH/g, such as 7 to 17 mgKOH/g, such as 13 to 15 mgKOH/g, as measured by ASTM D2896. Further, the lubricating composition is having a zinc content of 500 ppm or more, such as 800 ppm or more, or 1000 ppm or more, such as 1500 ppm or more, or 2000 ppm or more, as determined by ASTM D5185.

[0046] In some embodiments, the lubricating composition has a phosphorus content of not more than 2000 ppm, such as not more than 1600 ppm, not more than 1200 ppm, such as not more than 800 ppm, such as 1 to 1600 ppm, such as 10 to 1200 ppm, such as 100 to 800 parts per million (ppm), based on the total mass of the lubricating compositions, as measured by ASTM D5185.

[0047] In some embodiments, the lubricating composition is a combustion engine oil, such as a petrol or gasoline or heavy-duty diesel engine oil, or a marine engine oil, or a gas turbine oil. In some embodiments, the lubricating composition is transmission fluid or gear oil.

[0048] In some embodiments, the lubricating composition comprises more than 500 ppm of Zn and less than 500 ppm of P, preferably more than 1000 ppm of Zn and less than 1000 ppm of P, wherein the lubricating composition has an adhesive wear of 100 hours or more, and optionally a total base number of 7 mgKOH/g or more. In some embodiments, the lubricating composition includes zinc dialkyl dithiophosphates in an amount of 2 wt. % or less, such as 1 wt. % or less. In some embodiments, the lubricating composition has a wear scar volume of less than 150  $\mu\text{m}^3$ , such as less than 140  $\mu\text{m}^3$ , or less than 135  $\mu\text{m}^3$ , determined by HFRR method as described herein.

[0049] In certain embodiments, the present invention provides a method to obtain an adhesive wear of 100 hours or more (ASTM D 8074-16) for a lubricating composition having 500 ppm or more, preferably 1000 ppm zinc or more comprising: [0050] (i) providing to a crankcase of the internal combustion engine an automotive crankcase the lubricating composition of any of claims 1 to 24; [0051] (ii) providing a hydrocarbon fuel in the internal combustion engine; and [0052] (iii) combusting the fuel in the internal combustion engine.

[0053] In certain embodiments, the present invention provides a method of lubricating an automotive internal combustion engine during operation of the engine comprising: [0054] (i) providing to a crankcase of the internal combustion engine an automotive crankcase the lubricating composition of any of claims 1 to 24; [0055] (ii) providing a hydrocarbon fuel in the internal combustion engine; and [0056] (iii) combusting the fuel in the internal combustion engine.

[0057] Preferably, the engine is a diesel engine or gas engine, or a marine engine, or an automotive engine.

[0058] In certain embodiments, the present invention provides a concentrate composition comprising or resulting from the admixing of: [0059] (A) from 1 to less than 50 wt. % of one or more base oils, based upon the weight of the concentrate composition; [0060] (B) at least one phosphorus-containing compound selected from detergents, friction modifiers or antiwear additives other than the colloidal particles described in (C); [0061] (C) from 0.1 to 50 wt. %, based upon the weight of the composition, of colloidal particles comprising: [0062] a) a core of one or more hydrocarbon insoluble zinc containing compounds, and [0063] b) a shell of one or more of: [0064] 1) one or more metal containing surfactants, where the metal, M, comprises a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; and the surfactant comprises an hydrocarbyl-substituted sulfonate of Formula (I), or an hydrocarbyl-substituted salicylate group of Formula (II),

##STR00005##

[0065] wherein each R.sup.A, and R.sup.B is, independently of each other, a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 1 to 70 carbon atoms, wherein, for  $n > 1$ , the sum of the number of carbon atoms in the total of R.sup.A groups in Formula (I) and the sum of the number of carbon atoms in the total of R.sup.B groups in Formula (II) is 100 or less carbon atoms, and Ar is a mono- or polycyclic aromatic group; n is an integer from 1 to the maximum possible number of substitutions on Ar, with  $n=1$  if  $m=0$ ; m is an integer of 0 to 3, x is an integer from 1 to 5; y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; [0066] 2) one or more metal alkanoates represented by the formula (III):

##STR00006##

[0067] wherein M is a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; R.sup.C is selected from a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 70 carbon atoms, or an aromatic or alkyl aromatic group with the aromatic group having from 6 to 20 carbon atoms and the alkyl group having 1 to 20 carbon atoms; x is an integer from 1 to 5, wherein for  $x > 1$  the R.sup.C groups may be the same or different, y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8;

[0068] wherein the concentrate composition has a ratio of Zn to P (elemental mass basis as measured by ASTM D5185) of 1.1 to 5.0.

[0069] In certain embodiments, the present invention provides a use of a composition as an antiwear additive in a combustion engine, transmission, or gear oil, the composition comprising or resulting from the admixing of: [0070] (A) from 1 to less than 50 wt. % of one or more base oils, based upon the weight of the composition; [0071] (B) at least one phosphorus-containing compound selected from detergents, friction modifiers or antiwear additives other than the colloidal particles described in (C); [0072] (C) from 0.1 to 50 wt. %, based upon the weight of the composition, of colloidal particles comprising: [0073] a) a core of one or more hydrocarbon insoluble zinc containing compounds, and [0074] b) a shell of one or more of: [0075] 1) one or more metal containing surfactants, where the metal, M, comprises a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; and the surfactant comprises an hydrocarbyl-substituted aromatic sulfonate of Formula (I), or an hydrocarbyl-substituted salicylate group of Formula (II),

##STR00007##

[0076] wherein each R.sup.A, and R.sup.B is, independently of each other, a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 1 to 70 carbon atoms, wherein, for  $n > 1$ , the sum of the number of carbon atoms in the total of R.sup.A groups in Formula (I) and the sum of the number of carbon atoms in the total of R.sup.B groups in Formula (II) is 100 or less carbon atoms, and Ar is a mono- or polycyclic aromatic group; n is an integer from 1 to the maximum possible number of substitutions on Ar, with  $n=1$  if  $m=0$ ; m is an integer of 0 to 3, x is an integer from 1 to 5; y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; [0077] 2) one or more metal alkanoates represented by the formula (III):

##STR00008##

[0078] wherein M is a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; R.sup.C is selected from a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 70 carbon atoms, or an aromatic or alkyl aromatic group with the aromatic group having from 6 to 20 carbon atoms and the alkyl group having 1 to 20 carbon atoms; x is an integer from 1 to 5, wherein for  $x > 1$  the R.sup.C groups may be the same or different, y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 4;

[0079] wherein the composition has a ratio of Zn to P (elemental mass basis as measured by ASTM D5185) of 1.1 to 5.0.

## Description

### BRIEF DESCRIPTION OF THE DRAWINGS

[0080] FIG. 1 is a graph illustrating HFRR Data of lubricating oil compositions comprising colloidal particles of the invention in comparison to a lubricating composition without the colloidal particles of the present invention.

[0081] FIG. 2 illustrates compositions having a ZnO core with Ca-surfactant shell (where the surfactant is an R-phenyl sulfonate or R-salicylate, where R is an alkyl group).

[0082] FIG. 3 illustrates compositions having a ZnO core with Zn-surfactant shell (where the surfactant is an R-phenyl sulfonate or R-salicylate, where R is an alkyl group).

[0083] FIG. 4 illustrates compositions having a ZnO core with Zn-surfactant shell (where the surfactant is a zinc alkanoate/carboxylate, where R is an alkyl group).

### DEFINITIONS

[0084] For purposes of this specification and all claims to this invention, the following words and expressions, if and when used, have the meanings ascribed below.

[0085] For purposes herein, the new numbering scheme for the Periodic Table of the Elements is used as set out in CHEMICAL AND ENGINEERING NEWS, 63(5), 27 (1985). Alkali metals are Group 1 metals (e.g., Li, Na, K, etc.). Alkaline earth metals are Group 2 metals (e.g., Mg, Ca, Ba, etc.).

[0086] The expressions “consists of” or “consists essentially of” or cognates may be embraced within “comprises” or cognates, where “consists essentially of” permits inclusion of substances not materially affecting the characteristics of the composition to which it applies.

[0087] The term “major amount” means more than 50 wt. % of a composition, such as more than 60 wt. % of a composition, such as more than 70 wt. % of a composition, such as from 80 to 99.009 wt. % of a composition, such as from 80 to 99.9 from 80 to 99.009 wt. % of a composition, of a composition based upon the mass of the composition.

[0088] The term “minor amount” means 50 wt. % or less of a composition; such as 40 wt. % or less of a composition; such as 30 wt. % or less of a composition, such as from 20 to 0.001 wt. %, such as from 20 to 0.1 wt. %, based upon the mass of the composition.

[0089] The term “wt. %” means mass percent of a component, based upon the mass of the composition as measured in grams, unless otherwise indicated, and is alternately referred to as weight percent (“weight %”, “wt. %” or “% w/w”).

[0090] The term “active ingredient” (also referred to as “a.i.” or “A.I.”) refers to additive material that is neither diluent nor solvent.

[0091] The terms “group” and “radical” are used interchangeably herein.

[0092] The term “hydrocarbon” means a compound of hydrogen and carbon atoms. A “heteroatom” is an atom other than carbon or hydrogen. When referred to as “hydrocarbons,” particularly as “refined hydrocarbons,” the hydrocarbons may also contain one or more heteroatoms or heteroatom containing groups (such as halo, especially chloro and fluoro, amino, alkoxyl, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.) in minor amounts (e.g., where the heteroatom(s) do not substantially alter the hydrocarbon properties of the hydrocarbon compound).

[0093] The term “hydrocarbyl” means a radical that contains hydrogen and carbon atoms.

Preferably, the group consists essentially of, more preferably consists only of, hydrogen and carbon atoms, unless specified otherwise. Preferably, the hydrocarbyl group comprises an aliphatic hydrocarbyl group. The term “hydrocarbyl” includes “alkyl,” “alkenyl,” “alkynyl,” and “aryl” as defined herein. Hydrocarbyl groups may contain one or more atoms/groups other than carbon and hydrogen provided they do not affect the essentially hydrocarbyl nature of the hydrocarbyl group. Those skilled in the art will be aware of such atoms/groups (e.g., halo, especially chloro and fluoro, amino, alkoxyl, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.).



[0094] The term “alkyl” means a radical of carbon and hydrogen (such as a C.sub.1 to C.sub.70, or such as a C.sub.1 to C.sub.12 group, as further detailed herein). Alkyl groups in a compound are typically bonded to the compound directly via a carbon atom. Unless otherwise specified, alkyl groups may be linear (i.e., unbranched) or branched, be cyclic, acyclic, or part cyclic/acyclic. Preferably, the alkyl group comprises a linear or branched acyclic alkyl group. Representative examples of alkyl groups include, but are not limited to, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl, hexyl, heptyl, octyl, dimethyl hexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl and triacontyl.

[0095] The term “alkene” means a compound of carbon and hydrogen (such as a C.sub.2 to C.sub.70 radical, such as a C.sub.2 to C.sub.12 radical, as further detailed herein) having at least one double bond.

[0096] The term “alkenyl” means a radical of carbon and hydrogen (such as a C.sub.2 to C.sub.70 radical, such as a C.sub.2 to C.sub.12 radical, as further detailed herein) having at least one double bond. Alkenyl groups in a compound are typically bonded to the compound directly via a carbon atom. Unless otherwise specified, alkenyl groups may be linear (i.e. unbranched) or branched, be cyclic, acyclic, or part cyclic/acyclic.

[0097] The term “alkylene” means a C.sub.1 to C.sub.20, preferably a C.sub.1 to C.sub.10, bivalent saturated aliphatic radical which may be linear or branched. Representative examples of alkylene include methylene, ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, 1-methyl ethylene, 1-ethyl ethylene, 1-ethyl-2-methyl ethylene, 1,1-dimethyl ethylene, and 1-ethyl propylene.

[0098] The term “alkynyl” means a C.sub.2 to C.sub.70 (such as a C.sub.2 to C.sub.12) radical which includes at least one carbon to carbon triple bond.

[0099] The term “aryl” means a group containing at least one aromatic ring (i.e., being monocyclic or polycyclic), such a cyclopentadiene, phenyl, naphthyl, anthracenyl, and the like. Aryl groups are typically C.sub.5 to C.sub.40 (such as C.sub.5 to C.sub.6 to C.sub.20) aryl groups, optionally substituted by one or more hydrocarbyl groups, heteroatoms, or heteroatom containing groups (such as halo, hydroxyl, alkoxy and amino groups). Preferred aryl groups include phenyl and naphthyl groups and substituted derivatives thereof, especially phenyl, and alkyl substituted derivatives of phenyl.

[0100] The term “substituted” means that a hydrogen atom has been replaced with hydrocarbon group, a heteroatom or a heteroatom containing group. An alkyl substituted derivative means a hydrogen atom has been replaced with an alkyl group. An “alkyl substituted phenyl” is a phenyl group where a hydrogen atom has been replaced by an alkyl group, such as a C.sub.1 to C.sub.20 alkyl group, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl, hexyl, heptyl, octyl, dimethyl hexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl and/or triacontyl.

[0101] The term “halogen” or “halo” means a group 17 atom or a radical of group 17 atom, such as fluoro, chloro, bromo and iodo.

[0102] The term “ashless” in relation to an additive means the additive does not include a metal.

[0103] The term “ash-containing” in relation to an additive means the additive includes a metal.

[0104] The term “effective amount” in respect of an additive means an amount of such an additive in a lubricating oil composition so that the additive provides the desired technical effect.

[0105] The term “effective minor amount” in respect of an additive means an amount of such an additive of less than 50 wt. % of the lubricating oil composition so that the additive provides the desired technical effect.

[0106] The term “ppm” means parts per million by mass, based on the total mass of the lubricating oil composition, unless otherwise indicated.

[0107] The term “metal content” of a lubricating oil composition or of an additive component, for example zinc content, magnesium content, molybdenum content or total metal content (i.e. the sum of all individual metal contents), is measured by ASTM D5185.

[0108] The term “Total Base Number” also referred to as “TBN” in relation to an additive component or of a lubricating oil composition (i.e., unused lubricating oil composition) means total base number as measured by ASTM D2896.

[0109] The term “Total Acid Number” also referred to as “TAN” means total acid number as measured by ASTM D664.

[0110] The term “adhesive wear” is determined by ASTM 8074-16, which is also referred to as the DD13 Scuffing Test.

[0111] “Phosphorus content” is measured by ASTM D5185.

[0112] “Sulfur content” is measured by ASTM D2622.

[0113] “Sulfated ash content” is measured by ASTM D874.

[0114] “Zinc content” in lubricant compositions is measured by ASTM D5185.

[0115] The term “neo acids” means carboxylic acids that exhibit highly branched structures in which the carboxylic acid functional group is attached to a quaternary carbon atom and where the other moieties bonded to the quaternary carbon are saturated linear, branched, or cyclic alkyl groups.

[0116] “Neodecanoic acid” is a mixture of C.sub.10 neo acids with the common structural formula C.sub.10H.sub.20O.sub.2. Components of the mixture are acids with the common property of three alkyl groups at carbon two, including, but not limited to: 2,2,3,5-tetramethylhexanoic acid, 2,4-dimethyl-2-isopropylpentanoic acid, 2,5-dimethyl-2-ethylhexanoic acid, 2,2-dimethyloctanoic acid, and 2,2-diethylhexanoic acid.

[0117] The term “aliphatic hydrocarbyl fatty acid” means a monocarboxylic acid having an aliphatic C.sub.7 to C.sub.29, preferably a C.sub.9 to C.sub.27, most preferably a C.sub.11 to C.sub.23 hydrocarbyl chain. Such compounds may be referred to herein as aliphatic (C.sub.7 to C.sub.29), more preferably (C.sub.9 to C.sub.27), most preferably (C.sub.11 to C.sub.23), hydrocarbyl monocarboxylic acid(s) or hydrocarbyl fatty acid(s) (wherein C.sub.x to C.sub.y designates the total number of carbon atoms in the aliphatic hydrocarbyl chain of the fatty acid, the fatty acid itself due to the presence of the carboxyl carbon atom includes a total of C.sub.x+1 to C.sub.y+1 carbon atoms). Preferably, the aliphatic hydrocarbyl fatty acid, inclusive of the carboxyl carbon atom, has an even number of carbon atoms. The aliphatic hydrocarbyl chain of the fatty acid may be saturated or unsaturated (i.e. includes at least one carbon to carbon double bond); preferably, the aliphatic hydrocarbyl chain is unsaturated and includes at least one carbon to carbon double bond—such fatty acids may be obtained from natural sources (e.g. derived from animal or vegetable oils) and/or by reduction of the corresponding saturated fatty acid. It will be appreciated that a proportion of the aliphatic hydrocarbyl chain(s) of the corresponding aliphatic hydrocarbyl fatty acid ester(s) is unsaturated (i.e., includes at least one carbon to carbon double bond) to permit reaction with other agents, such as sulfur, to form the corresponding functionalized, such as sulfurized, aliphatic hydrocarbyl fatty acid ester(s).

[0118] The term “aliphatic hydrocarbyl fatty acid ester” means an ester obtainable by converting the monocarboxylic acid functional group of the corresponding aliphatic hydrocarbyl fatty acid into an ester group. Suitably, the monocarboxylic acid functional group of the aliphatic hydrocarbyl fatty acid is converted to a hydrocarbyl ester, preferably a C.sub.1 to C.sub.30 aliphatic hydrocarbyl ester, such as an alkyl ester, preferably a C.sub.1 to C.sub.6 alkyl ester, especially a methyl ester. Alternatively, or additionally, the monocarboxylic acid functional group of the aliphatic hydrocarbyl fatty acid may be in the form of the natural glycerol ester. Accordingly, the term “aliphatic hydrocarbyl fatty acid ester” embraces aliphatic hydrocarbyl fatty acid glycerol ester(s) and aliphatic hydrocarbyl fatty acid C.sub.1 to C.sub.30 aliphatic hydrocarbyl ester(s), (e.g. aliphatic hydrocarbyl fatty acid alkyl ester(s), more preferably aliphatic hydrocarbyl fatty acid

C.sub.1 to C.sub.6 alkyl ester(s), especially aliphatic hydrocarbyl fatty acid methyl ester(s)). Suitably, the term “aliphatic hydrocarbyl fatty acid ester” embraces aliphatic (C.sub.7 to C.sub.29) hydrocarbyl, more preferably aliphatic (C.sub.9 to C.sub.27) hydrocarbyl, most preferably aliphatic (C.sub.11 to C.sub.23) hydrocarbyl fatty acid glycerol ester(s) and aliphatic (C.sub.7 to C.sub.29) hydrocarbyl, more preferably aliphatic (C.sub.9 to C.sub.27) hydrocarbyl, most preferably aliphatic (C.sub.11 to C.sub.23) hydrocarbyl fatty acid C.sub.1 to C.sub.30 aliphatic hydrocarbyl ester(s). Suitably, to permit functionalization, such as sulfurization, of the aliphatic hydrocarbyl fatty acid ester(s) a proportion of the aliphatic hydrocarbyl chain(s) of the fatty acid ester(s) is unsaturated and includes at least one carbon to carbon double bond.

[0119] The term “sulfurized aliphatic hydrocarbyl fatty acid ester” means a compound obtained by sulfurizing an aliphatic hydrocarbyl fatty acid ester as defined herein.

[0120] The term “absent” as it relates to components included within the lubricating oil compositions described herein and the claims thereto means that the particular component is present at 0 wt. %, based upon the weight of the lubricating oil composition, or if present in the lubricating oil composition the component is present at levels that do not impact the lubricating oil composition properties, such as less than 10 ppm, or less than 1 ppm or less than 0.001 ppm.

[0121] The terms “oil-soluble” and “oil-dispersible,” or cognate terms, used herein do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible, or are capable of being suspended in the oil in all proportions. These do mean, however, that they are, for example, soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Particularly, the terms “oil-soluble” and “oil-dispersible,” mean that the designated compound/material is soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed, without precipitation within a period of at least 4 weeks, such as 6 weeks, 8 weeks, 10 weeks, or 12 weeks. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

[0122] The terms “oil-insoluble” and “oil-indispersible,” or cognate terms, used herein do not necessarily indicate that the compounds or additives are insoluble, indissolvable, immiscible, or are incapable of being suspended in the oil in all proportions. These do mean, however, that they are, for example, not soluble or not stably dispersible in oil to an extent impairing or deteriorating exertion of their intended effect in the environment in which the oil is employed. Particularly, the terms “oil-insoluble” and “oil-indispersible,” mean that the designated compound/material reveals precipitation within a period of less than 4 weeks, such as 3 weeks.

[0123] Kinematic viscosity (KV.sub.100, KV.sub.40) is determined pursuant to ASTM D445-19a reported in unites of cSt, unless otherwise specified.

[0124] Unless otherwise indicated, all percentages reported are wt. % on an active ingredient basis, i.e., without regard to carrier or diluent oil.

[0125] Also, it will be understood that various components used, essential as well as optimal and customary, may react under conditions of formulation, storage or use and that the invention also provides the product obtainable or obtained as a result of any such reaction.

[0126] Further, it is understood that any upper and lower quantity, range, and ratio limits set forth herein may be independently combined.

[0127] Also, it will be understood that the preferred features of each aspect of the present invention are regarded as preferred features of every other aspect of the present invention. Accordingly, preferred and more preferred features of one aspect of the present invention may be independently combined with other preferred and/or more preferred features of the same aspect or different aspects of the present invention.

#### DETAILED DESCRIPTION

[0128] The features of the invention relating, where appropriate, to each and all aspects of the invention, will now be described in more detail as follows.

[0129] The lubricating oil compositions of the invention comprise components that may or may not remain the same chemically before and after mixing with an oleaginous carrier (such as a base oil) and/or other additives. This invention encompasses compositions which comprise the components before mixing, or after mixing, or both before and after mixing.

[0130] Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

#### Lubricating Oil Compositions

[0131] This invention relates to lubricating oil compositions (also referred to as “lubricant compositions,” “lubricating compositions,” or “lubricant oil compositions”) comprising or resulting from the admixing of: [0132] (A) from 1 to 99.99 wt. %, (alternately 30 to 95 wt. %, alternately 50 to 90 wt. %, alternately 60 to 95 wt. %, alternately 70 to 85 wt. %) based upon the weight of the lubricating composition, of one or more base oils; [0133] (B) at least one phosphorus-containing compound selected from detergents, friction modifiers or antiwear additives other than the colloidal particles described in (C); [0134] (C) from 0.01 to 10 wt. %, (in particular 0.1 to 5 wt. %, alternately 0.5 to 3 wt. %, alternately 0.75 to 2 wt. %, alternately 0.75 to 1.5 wt. %) based upon the weight of the composition, of colloidal particles, comprising: [0135] a) a core of one or more hydrocarbon insoluble zinc containing compounds, and [0136] b) a shell of one or more of: [0137] 1) one or more metal containing surfactants, where the metal, M, comprises a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal, such as sodium, potassium, lithium, magnesium, calcium, barium, gold, silver, palladium, platinum, zirconium, vanadium, molybdenum, molybdenum, nickel, copper, zinc, aluminum or mixtures of 2, 3, 4, 5, 6, 7, or 8 metals, such as a mixture of 2 or 3 of sodium, magnesium, calcium, zinc, nickel, copper, and aluminum, such as calcium, or magnesium, and/or zinc; and the surfactant comprises a hydrocarbyl-substituted aliphatic or aromatic sulfonate of Formula (I), or a hydrocarbyl-substituted salicylate of Formula (II),

##STR00009##

wherein each of R<sup>sup</sup>.A and R<sup>sup</sup>.B is, independently of each other, a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 1 to 70 carbon atoms, such as a C<sub>sub</sub>.1 to C<sub>sub</sub>.70 (alternately C<sub>sub</sub>.1 to C<sub>sub</sub>.60, alternately C<sub>sub</sub>.1 to C<sub>sub</sub>.40, alternately C<sub>sub</sub>.1 to C<sub>sub</sub>.40, alternately C<sub>sub</sub>.1 to C<sub>sub</sub>.30, alternately C<sub>sub</sub>.1 to C<sub>sub</sub>.20, alternately C<sub>sub</sub>.1 to C<sub>sub</sub>.10, alternately C<sub>sub</sub>.1 to C<sub>sub</sub>.6, alternately C<sub>sub</sub>.2 to C<sub>sub</sub>.4) linear, branched, or cyclic alkyl group, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, mono- or polycyclic versions thereof, or any isomer thereof, or a C<sub>sub</sub>.2 to C<sub>sub</sub>.70 (alternately C<sub>sub</sub>.2 to C<sub>sub</sub>.60, alternately C<sub>sub</sub>.2 to C<sub>sub</sub>.50, alternately C<sub>sub</sub>.2 to C<sub>sub</sub>.40, alternately C<sub>sub</sub>.2 to C<sub>sub</sub>.30, alternately C<sub>sub</sub>.2 to C<sub>sub</sub>.20, alternately C<sub>sub</sub>.2 to C<sub>sub</sub>.10, alternately C<sub>sub</sub>.2 to C<sub>sub</sub>.6, alternately C<sub>sub</sub>.2 to C<sub>sub</sub>.4) linear, branched, or cyclic alkenyl group, which includes one or more double bonds, such as ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, octadecenyl, nonadecenyl, eicosenyl, mono- or polycyclic versions thereof, or any isomer thereof, wherein, for n>1, the sum of the number of carbon atoms in the total of R<sup>sup</sup>.A groups in Formula (I) and the sum of the number of carbon atoms in the total of R<sup>sup</sup>.B groups in Formula (II) is 100 or less carbon atoms, and Ar is a mono- or polycyclic aromatic group, such as a C<sub>sub</sub>.5 to C<sub>sub</sub>.20 aromatic group, or C<sub>sub</sub>.6 to C<sub>sub</sub>.20, such as benzene, naphthene, fluorene, phenalene, phenanthrene, anthracene, pyrene, tetracene, chrysene, perylene, or mixtures thereof; n is an integer from 1 to the maximum possible number of substitutions on Ar, with n=1 if m=0; m is an integer of 0 to 3; x is an integer from 1 to 5; y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, such as water, hydroxide, halide, ammonia, amino, amido, alcoholate, and mixtures thereof, and p is an integer from 0 to 8; [0138] 2) one or more metal alkanoates represented by the Formula (III):

##STR00010##

[0139] wherein M is a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal, such as sodium, potassium, lithium, magnesium, calcium, barium, gold, silver, palladium, platinum, zirconium, vanadium, molybdenum, nickel, copper, zinc, aluminum or mixtures of 2, 3, 4, 5, 6, 7, or 8 metals, such as a mixture of 2 or 3 of sodium, magnesium, calcium, zinc, nickel, copper, and aluminum, such as calcium, or magnesium, and/or zinc; R<sup>sup</sup>.C is a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 70 carbon atoms, such as a C<sub>6</sub> to C<sub>70</sub> (alternately C<sub>1</sub> to C<sub>60</sub>, alternately C<sub>6</sub> to C<sub>40</sub>, alternately C<sub>6</sub> to C<sub>40</sub>, alternately C<sub>6</sub> to C<sub>30</sub>, alternately C<sub>6</sub> to C<sub>20</sub>, alternately C<sub>6</sub> to C<sub>10</sub>, alternately C<sub>6</sub> to C<sub>8</sub>, or C<sub>10</sub> to C<sub>20</sub>) linear, branched, or cyclic alkyl group, such as hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, mono- or polycyclic versions thereof, or any isomer thereof; or a C<sub>6</sub> to C<sub>70</sub> (alternately C<sub>6</sub> to C<sub>60</sub>, alternately C<sub>6</sub> to C<sub>20</sub>, alternately C<sub>6</sub> to C<sub>40</sub>, alternately C<sub>6</sub> to C<sub>30</sub>, alternately C<sub>6</sub> to C<sub>20</sub>, alternately C<sub>6</sub> to C<sub>10</sub>, alternately C<sub>6</sub> to C<sub>8</sub>) linear, branched, or cyclic alkenyl group, which includes one or more double bonds, such as hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, octadecenyl, nonadecenyl, eicosenyl, mono- or polycyclic versions thereof, or any isomer thereof; or an aromatic or alkyl aromatic group with the aromatic group having from 6 to 20 carbon atoms, such as benzene, naphthene, fluorene, phenalene, phenanthrene, anthracene, pyrene, tetracene, chrysene, perylene, such as benzene or naphthalene, or mixtures thereof, and the alkyl group having 1 to 20 carbon atoms, (alternately C<sub>1</sub> to C<sub>10</sub>, alternately C<sub>1</sub> to C<sub>6</sub>, alternately C<sub>2</sub> to C<sub>4</sub>) linear, branched, or cyclic alkyl group, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, or any isomer thereof); x is an integer from 1 to 5, wherein for x>1 the R<sup>sup</sup>.C groups may be the same or different, y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, such as water, hydroxide, halide, ammonia, amino, amido, alcoholate, and mixtures thereof; and p is an integer from 0 to 8; wherein the lubricating oil composition has a ratio of Zn to P (elemental mass basis as measured by ASTM D5185) of 1.1 to 5.0.

[0140] In an embodiment thereof, this invention relates to lubricating oil compositions comprising or resulting from the admixing of: [0141] (A) from 1 to 99.99 wt. %, (alternately 30 to 95 wt. %, alternately 50 to 90 wt. %, alternately 60 to 95 wt. %, alternately 70 to 85 wt. %) based upon the weight of the lubricating composition, of one or more base oils; [0142] (B) at least one phosphorus-containing compound selected from detergents, friction modifiers or antiwear additives other than the colloidal particles described in (C); [0143] (C) from 0.01 to 10 wt. %, (in particular 0.1 to 5 wt. %, alternately 0.5 to 3 wt. %, alternately 0.75 to 2 wt. %, alternately 0.75 to 1.5 wt. %) based upon the weight of the composition, of colloidal particles, comprising: [0144] a) a core of one or more hydrocarbon insoluble zinc containing compounds, and [0145] b) a shell of one or more of hydrocarbyl-substituted aliphatic or aromatic sulfonate surfactant of Formula (I),

##STR00011##

[0146] where the metal, M, comprises a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal, such as sodium, potassium, lithium, magnesium, calcium, barium, gold, silver, palladium, platinum, zirconium, vanadium, molybdenum, nickel, copper, zinc, aluminum or mixtures of 2, 3, 4, 5, 6, 7, or 8 metals, such as a mixture of 2 or 3 of sodium, magnesium, calcium, zinc, nickel, copper, and aluminum, such as calcium, or magnesium, and/or zinc;

[0147] wherein each R<sup>sup</sup>.A is, independently of each other, a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 1 to 70 carbon atoms, such as a C<sub>1</sub> to C<sub>70</sub> (alternately C<sub>1</sub> to C<sub>60</sub>, alternately C<sub>1</sub> to C<sub>50</sub>, alternately C<sub>1</sub> to C<sub>40</sub>, alternately C<sub>1</sub> to C<sub>30</sub>, alternately C<sub>1</sub> to C<sub>20</sub>, alternately C<sub>1</sub> to C<sub>10</sub>, alternately C<sub>1</sub> to C<sub>6</sub>, alternately C<sub>2</sub> to C<sub>4</sub>) linear, branched, or cyclic

alkyl group, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, mono- or polycyclic versions thereof, or any isomer thereof, or a C.sub.2 to C.sub.70 (alternately C.sub.2 to C.sub.60, alternately C.sub.2 to C.sub.50, alternately C.sub.2 to C.sub.40, alternately C.sub.2 to C.sub.30, alternately C.sub.2 to C.sub.20, alternately C.sub.2 to C.sub.10, alternately C.sub.2 to C.sub.6, alternately C.sub.2 to C.sub.4) linear, branched, or cyclic alkenyl group, which includes one or more double bonds, such as ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, octadecenyl, nonadecenyl, eicosenyl, mono- or polycyclic versions thereof, or any isomer thereof, wherein, for  $n > 1$ , the sum of the number of carbon atoms in the total of R.sup.A groups in Formula (I) is 100 or less carbon atoms; and Ar is a mono- or polycyclic aromatic group, such as a C.sub.5 to C.sub.20 aromatic group, such as benzene, naphthene, fluorene, phenalene, phenanthrene, anthracene, pyrene, tetracene, chrysene, perylene, such as benzene or naphthalene, or benzene, or mixtures thereof, n is an integer from 1 to the maximum possible number of substitutions on Ar, with  $n=1$  if  $m=0$ ; m is an integer of 0 to 3, x is an integer from 1 to 5; y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, such as water, hydroxide, halide, ammonia, amino, amido, alcoholate, and mixtures thereof; and p is an integer from 0 to 8; wherein the lubricating oil composition has a ratio of Zn to P (elemental mass basis as measured by ASTM D5185) of 1.1 to 5.0.

[0148] In an exemplary embodiment thereof, the surfactant of Formula (I) is a metal containing hydrocarbyl-substituted sulfonate surfactant of Formula (Ia):

##STR00012##

[0149] In embodiments including colloidal particles with a shell of sulfonate surfactants of Formula (I) or (Ia), the sulfonate may be an aliphatic sulfonate, so  $m=0$  and Ar is absent, and n is 1, so the sulfonate has a formula R.sup.A—SO<sub>3</sub><sup>-</sup>, with R.sup.A as defined herein.

[0150] In other embodiments including colloidal particles with a shell of sulfonate surfactants of Formula (I) or (Ia), the sulfonate may be an aromatic sulfonate, so m is at least 1, or 2, or 3, and Ar is present, and n is at least 1, up to the maximum possible number of substitutions on Ar, e.g., n is 1 to 5 for benzene and n is 1 to 7 for naphthalene. For Ar=benzene, n may be 1 to 3, such as 1 or 2, or 1, and the surfactant may also be a mixture of sulfonates with different numbers of R.sup.A substitutions.

[0151] In a particular embodiment of the surfactant of Formula (Ia), the metal M is selected from calcium, magnesium, barium, or zinc, or combinations thereof, such as calcium, magnesium, or zinc, or calcium, or zinc; R.sup.A is independently of each other a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 50 carbon atoms, such as 10 to 40, or 12 to 37 carbon atoms; n is an integer from 1 to 5, such as 1 to 4, such as 1, 2, or 3, such as 1; m is 0 to 3, such as 0, or 1, or 2; with  $n=1$  if  $m=0$ ; the sum of the number of carbon atoms in the total of R.sup.A groups is 60 or less carbon atoms; x is 2; and y is 2.

[0152] In exemplary embodiments,  $m=1$ , and the surfactant of Formula (Ia) is a hydrocarbyl-substituted phenyl or naphthyl sulfonate. In further exemplary embodiments, the lubricating composition comprises colloidal particles having a core of zinc, zinc oxide, of zinc salts such as zinc carbonate, zinc hydroxide, zinc halides such as zinc fluoride, zinc chloride, zinc bromide, zinc iodide, preferably zinc oxide, and a shell of surfactants of Formula (Ia) with the metal M being calcium or magnesium, or mixtures thereof, preferably calcium, and R.sup.A being a C.sub.30 to C.sub.40 alkyl group and n being 1 or 2, such as 1, or mixtures thereof.

[0153] In a further embodiment, this invention relates to lubricating oil compositions comprising or resulting from the admixing of: [0154] (A) from 1 to 99.99 wt. %, (alternately 30 to 95 wt. %, alternately 50 to 90 wt. %, alternately 60 to 95 wt. %, alternately 70 to 85 wt. %) based upon the weight of the lubricating composition, of one or more base oils; [0155] (B) at least one phosphorus-containing compound selected from detergents, friction modifiers or antiwear additives other than

the colloidal particles described in (C); a [0156] (C) from 0.01 to 10 wt. %, (in particular 0.1 to 5 wt. %, alternately 0.5 to 3 wt. %, alternately 0.75 to 2 wt. %, alternately 0.75 to 1.5 wt. %) based upon the weight of the composition, of colloidal particles, comprising: [0157] a) a core of one or more hydrocarbon insoluble zinc containing compounds, and [0158] b) a shell of one or more hydrocarbyl-substituted salicylate surfactants of Formula (II):

##STR00013##

[0159] where the metal, M, comprises a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal, such as sodium, potassium, lithium, magnesium, calcium, barium, gold, silver, palladium, platinum, zirconium, vanadium, molybdenum, nickel, copper, zinc, aluminum or mixtures of 2, 3, 4, 5, 6, 7, or 8 metals, such as a mixture of 2 or 3 of sodium, magnesium, calcium, zinc, nickel, copper, and aluminum, such as calcium, or magnesium, and/or zinc;

[0160] wherein each R<sup>sup</sup>.B is, independently of each other, a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 1 to 70 carbon atoms, such as a C<sub>sub</sub>.1 to C<sub>sub</sub>.70 (alternately C<sub>sub</sub>.1 to C<sub>sub</sub>.60, alternately C<sub>sub</sub>.1 to C<sub>sub</sub>.50, alternately C<sub>sub</sub>.1 to C<sub>sub</sub>.40, alternately C<sub>sub</sub>.1 to C<sub>sub</sub>.30, alternately C<sub>sub</sub>.1 to C<sub>sub</sub>.20, alternately C<sub>sub</sub>.1 to C<sub>sub</sub>.10, alternately C<sub>sub</sub>.1 to C<sub>sub</sub>.6, alternately C<sub>sub</sub>.2 to C<sub>sub</sub>.4) linear, branched, or cyclic alkyl group, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, mono- or polycyclic versions thereof, or any isomer thereof, or a C<sub>sub</sub>.2 to C<sub>sub</sub>.70 (alternately C<sub>sub</sub>.2 to C<sub>sub</sub>.60, alternately C<sub>sub</sub>.2 to C<sub>sub</sub>.50, alternately C<sub>sub</sub>.2 to C<sub>sub</sub>.40, alternately C<sub>sub</sub>.2 to C<sub>sub</sub>.30, alternately C<sub>sub</sub>.2 to C<sub>sub</sub>.20, alternately C<sub>sub</sub>.2 to C<sub>sub</sub>.10, alternately C<sub>sub</sub>.2 to C<sub>sub</sub>.6, alternately C<sub>sub</sub>.2 to C<sub>sub</sub>.4) linear, branched, or cyclic alkenyl group, which includes one or more double bonds, such as ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, octadecenyl, nonadecenyl, eicosenyl, mono- or polycyclic versions thereof, or any isomer thereof, wherein, for n>1, the sum of the number of carbon atoms in the total of R<sup>sup</sup>.B groups in Formula (II) is 70 or less carbon atoms, and Ar is a mono- or polycyclic aromatic group, such as a C<sub>sub</sub>.5 to C<sub>sub</sub>.20 aromatic group, such as benzene, naphthene, fluorene, phenalene, phenanthrene, anthracene, pyrene, tetracene, chrysene, perylene, or mixtures thereof; n is an integer from 1 to the maximum possible number of substitutions on Ar, m is an integer of 1 to 3, x is an integer from 1 to 5; y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, such as water, hydroxide, halide, ammonia, amino, amido, alcoholate, and mixtures thereof; and p is an integer from 0 to 8; wherein the lubricating oil composition has a ratio of Zn to P (elemental mass basis as measured by ASTM D5185) of 1.1 to 5.0.

[0161] In an exemplary embodiment thereof, the surfactant of Formula (II) is a metal containing hydrocarbyl-substituted phenyl salicylate surfactant of Formula (IIa):

##STR00014##

[0162] In a particular embodiment thereof, the metal M is selected from calcium, magnesium, barium, or zinc, or combinations thereof; such as calcium, magnesium, or zinc, or combinations thereof, or calcium, or zinc, or combinations thereof; R<sup>sup</sup>.B is independently of each other a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 50 carbon atoms, such as 10 to 48, or 12 to 37 carbon atoms; n is an integer from 1 to 4, such as 1 to 3, such as 1, or 2, such as 1; the sum of the number of carbon atoms in the total of R<sup>sup</sup>.B groups is 60 or less carbon atoms; x is 2, and y is 2.

[0163] In still a further embodiment, this invention relates to lubricating oil compositions comprising or resulting from the admixing of: [0164] (A) from 1 to 99.99 wt. %, (alternately 30 to 95 wt. %, alternately 50 to 90 wt. %, alternately 60 to 95 wt. %, alternately 70 to 85 wt. %) based upon the weight of the lubricating composition, of one or more base oils; [0165] (B) at least one phosphorus-containing compound selected from detergents, friction modifiers or antiwear additives other than the colloidal particles described in (C); [0166] (C) from 0.01 to 10 wt. %, (in particular

0.1 to 5 wt. %, alternately 0.5 to 3 wt. %, alternately 0.75 to 2 wt. %, alternately 0.75 to 1.5 wt. %) based upon the weight of the composition, of colloidal particles, comprising: [0167] a) a core of one or more hydrocarbon insoluble zinc containing compounds, and [0168] b) a shell of one or more of one or more metal alkanoates represented by the formula (III):

##STR00015##

[0169] wherein M is a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal, such as sodium, potassium, lithium, magnesium, calcium, barium, gold, silver, palladium, platinum, zirconium, vanadium, molybdenum, nickel, copper, zinc, aluminum or mixtures of 2, 3, 4, 5, 6, 7, or 8 metals, such as a mixture of 2 or 3 of sodium, magnesium, calcium, zinc, nickel, copper, and aluminum, such as calcium, or magnesium, and/or zinc; R<sup>sup</sup>.C is a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 70 carbon atoms, such as a C<sub>8</sub> to C<sub>70</sub> (alternately C<sub>6</sub> to C<sub>60</sub>, alternately C<sub>6</sub> to C<sub>50</sub>, alternately C<sub>6</sub> to C<sub>40</sub>, alternately C<sub>6</sub> to C<sub>30</sub>, alternately C<sub>6</sub> to C<sub>20</sub>, alternately C<sub>6</sub> to C<sub>10</sub>, alternately C<sub>6</sub> to C<sub>8</sub>, or C<sub>10</sub> to C<sub>20</sub>) linear, branched, or cyclic alkyl group, such as hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, mono- or polycyclic versions thereof, or any isomer thereof; or a C<sub>6</sub> to C<sub>70</sub> (alternately C<sub>6</sub> to C<sub>60</sub>, alternately C<sub>6</sub> to C<sub>50</sub>, alternately C<sub>6</sub> to C<sub>40</sub>, alternately C<sub>6</sub> to C<sub>30</sub>, alternately C<sub>6</sub> to C<sub>20</sub>, alternately C<sub>6</sub> to C<sub>10</sub>, alternately C<sub>6</sub> to C<sub>8</sub>) linear, branched, or cyclic alkenyl group, which includes one or more double bonds, such as hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, octadecenyl, nonadecenyl, eicosenyl, mono- or polycyclic versions thereof, or any isomer thereof; or an aromatic or alkylaromatic (aralkyl) group with the aromatic group having from 6 to 20 carbon atoms, such as benzene, naphthene, fluorene, phenalene, phenanthrene, anthracene, pyrene, tetracene, chrysene, perylene, such as benzene or naphthalene, or mixtures thereof, and the alkyl group of the aralkyl having 1 to 20 carbon atoms, (alternately C<sub>1</sub> to C<sub>10</sub>, alternately C<sub>1</sub> to C<sub>6</sub>, alternately C<sub>2</sub> to C<sub>4</sub>) linear, branched, or cyclic alkyl group, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, or any isomer thereof); x is an integer from 1 to 5, wherein for x>1 the R<sup>sup</sup>.C groups may be the same or different, y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, such as water, hydroxide, halide, ammonia, amino, amido, alcoholate, and mixtures thereof, and p is an integer from 0 to 8; wherein the lubricating oil composition has a ratio of Zn to P (elemental mass basis as measured by ASTM D5185) of 1.1 to 5.0.

[0170] In an exemplary embodiment thereof, the surfactant of Formula (III) is one of Formula (IIIa), as further defined below.

[0171] In an embodiment thereof, the metal alkanoate of Formula (III) is a zinc alkanoate, wherein R<sup>sup</sup>.C is derived from a fatty acid, such as mono- or di-unsaturated fatty acids, for example mono-unsaturated fatty acids such as crotonic acid, myristoleic acid, palmitoleic acid, sapienic acid, oleic acid, elaidic acid, vaccenic acid, gadoleic acid, eicosenoic acid, erucic acid, nervonic acid; or di-unsaturated fatty acid, linoleic acid, eicosadienoic acid, docosadienoic acid; any isomers or mixtures thereof.

[0172] In a particular embodiment, the metal alkanoate of Formula (III) is a zinc alkanoate, wherein R<sup>sup</sup>.C is derived from one or more neo-acids such as neodecanoic acid, neoundecanoic acid, neododecanoic acid, neotridecanoic acid, neotetradecanoic acid, neopentadecanoic acid, neohexadecanoic acid, neoheptadecanoic acid, neo-octadecanoic acid, neononadecanoic acid, neoeicosanoic acid, and isomers thereof. In particular, useful zinc alkanoates can be a zinc neodecanoate and/or n zinc ethylhexanoate. In some embodiments, the metal alkanoates have a quaternary carbon atom at the 2 position, i.e., attached to the carboxylate group.

[0173] In some embodiments, the metal alkanoate of Formula (III) is a zinc alkanoate, wherein



R.sup.C is derived from one or more linear aliphatic acids such as capric acid, lauric acid, myristic acid, stearic acid, arachidic acid, or unsaturated carboxylic acids or fatty acids such as myristoleic acid, palmitoleic acid, oleic acid, linoleic acid, aracidonic acid, and erucic acid.

[0174] Particularly, the metal alkanoate of Formula (III) can be a metal alkanoate of Formula (IIIa): ##STR00016## [0175] wherein M is a group 4, 5, 10, 11, or 12 metal, such as nickel, palladium, platinum, copper, silver, gold, zinc, tin, zirconium, hafnium, titanium, vanadium, molybdenum, niobium, tantalum, or mixtures of 2, 3, 4, 5, 6, 7, or more group 4, 5, 10, 11, and 12 metals, preferably M is zirconium, vanadium, molybdenum, or zinc, preferably M is zinc; [0176] each of R.sup.1, R.sup.2, and R.sup.3 is, independently, hydrogen or a C.sub.1 to C.sub.20 (alternately C.sub.1 to C.sub.10, alternately C.sub.1 to C.sub.6, alternately C.sub.2 to C.sub.4) linear, branched, or cyclic alkyl group, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, or any isomer thereof, where 3, 2, 1, or none of R.sup.1, R.sup.2, and R.sup.3 are hydrogen, [0177] each of R.sup.4, R.sup.5, and R.sup.6 is, independently, a C.sub.1 to C.sub.20 (alternately C.sub.1 to C.sub.10, alternately C.sub.1 to C.sub.6, alternately C.sub.2 to C.sub.4) linear, branched, or cyclic alkyl group, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, or any isomer thereof, and where R.sup.1+R.sup.2+R.sup.3=7 or more carbon atoms, i.e., the sum of the number of carbon atoms in R.sup.1, R.sup.2, and R.sup.3 is 7 or more carbon atoms (alternately from 7 to 40, alternately from 8 to 22, alternately 7, 8, 9, 10, 11, 12, 13, or 14 carbon atoms); and [0178] R.sup.4+R.sup.5+R.sup.6=7 or more carbon atoms, i.e., the sum of the number of carbon atoms in R.sup.4, R.sup.5, and R.sup.6 is 7 or more carbon atoms (alternately from 7 to 40, alternately from 8 to 22, alternately 7, 8, 9, 10, 11, 12, 13, or 14 carbon atoms); and [0179] R.sup.1+R.sup.2+R.sup.3 and R.sup.4+R.sup.5+R.sup.6 may be the same or different (i.e., a symmetric alkanoate) and are independently 7 or more carbon atoms, such as 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, or 30 carbon atoms, in particular 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 carbon atoms.

[0180] In particular, R.sup.1, R.sup.2, and R.sup.3 are derived from one or more neo acids; and R.sup.4, R.sup.5, and R.sup.6 are derived from the same or different neo acids (such as neodecanoic acid, neoundecanoic acid, neododecanoic acid, neotridecanoic acid, neotetradecanoic acid, neopentadecanoic acid, neohexadecanoic acid, neoheptadecanoic acid, neo-octadecanoic acid, neononadecanoic acid, neo-eicosanoic acid, and isomers thereof).

[0181] In particular, useful metal surfactants/soaps of formula (I), (Ia), (II), (IIa), (III), or (IIIa) for use as a shell in the colloidal particles of the present invention are liquid at 24° C. and are preferably liquid at 60° C. In particular, useful metal surfactants for use in and the colloidal particles as described herein themselves remain stably dispersed at engine start up temperatures, such as -32° C. or more, such as 0° C. or more, such as 30° C. or more, such as 40° C. or more, such as 60° C. or more, such as -30° C. to 60° C., such as 0 to less than 80° C. and liquid at engine operating temperatures, such as 80° C. or more, such as 150° C. or more, such as 200° C. or more. In embodiments, the metal surfactant is liquid at -15° C. and liquid at 80° C.

[0182] In all embodiments of Formula (I), (Ia), (II), (IIa), (III), or (IIIa), the hydrocarbon insoluble zinc containing compound may be selected from at least one of zinc, zinc oxide, zinc salts such as zinc carbonate, zinc hydroxide, zinc halides such as zinc fluoride, zinc chloride, zinc bromide, zinc iodide, preferably at least one of zinc, zinc oxide and zinc carbonate, or mixtures thereof.

[0183] The colloidal particles may have a mean particle diameter as determined by dynamic light scattering as described in the examples section below in the range of 5 nm to 1 μm, such as 20 nm to 500 nm, or 20 nm to 200 nm.

[0184] In certain embodiments, the metal M in Formula (I), (Ia), (II), (IIa), (III), or (IIIa) is selected from at least one of sodium, potassium, lithium, magnesium, calcium, barium, or mixtures thereof, preferably calcium or magnesium; or the metal M is selected from at least one of gold, silver,

palladium, platinum, zirconium, vanadium, molybdenum, nickel, copper, zinc, aluminum, or mixtures thereof, preferably zinc, or calcium, or a mixture of 2, or 3 of zinc, calcium and magnesium.

[0185] Preferably, Ar in Formula (I) or Formula (II) is benzene or naphthalene.

[0186] In embodiments, the lubricating compositions as described herein may further comprise one or more of the following components: [0187] D) one or more friction modifiers; [0188] E) one or more antioxidants; [0189] F) one or more pour point depressants; [0190] G) one or more anti-foaming agents; [0191] H) one or more viscosity modifiers; [0192] I) one or more dispersants; [0193] J) one or more inhibitors and/or anti-rust agents; and/or [0194] K) one or more anti-wear agents, not falling within Formula (I); [0195] L) one or more detergents, other than those of component (B) and in the colloidal particles described in (C).

[0196] In certain embodiments of the lubricating compositions: [0197] A) the base oil is present at 50 to 99 wt. % based upon the weight of the lubricating composition; and [0198] B) the at least one phosphorus-containing compound selected from detergents, friction modifiers, or antiwear additives other than the colloidal particles described in (C) is present in an amount of 0.001 to 5 wt.-%; and [0199] C) the colloidal particles are present at from 0.01 to 10 wt.-%, or 0.01 to 6 wt. % based on total weight of the lubricating composition.

[0200] In embodiments of the lubricating composition: [0201] D) optionally, one or more friction modifiers other than those of component (B) are present at from 0.01 to 5 wt. %, based on total weight of the lubricating composition; [0202] E) optionally, one or more antioxidants are present at from 0.01 to 5 wt. %, based on total weight of the lubricating composition; [0203] F) optionally, one or more pour point depressants are present at from 0.01 to 5 wt. %, based on total weight of the lubricating composition; [0204] G) optionally, one or more anti-foaming agents are present at from 0.001 to 5 wt. %, based on total weight of the lubricating composition; [0205] H) optionally, one or more viscosity modifiers are present at from 0.001 to 6 wt. %, based on total weight of the lubricating composition; [0206] I) optionally, one or more dispersants are present at from 0.01 to 20 wt. %, based on total weight of the lubricating composition; [0207] J) optionally, one or more inhibitors and/or anti-rust agents are present at from 0.001 to 5 wt. %, based on total weight of the lubricating composition; [0208] K) optionally, one or more anti-wear agents, other than those of components B) and C), are present at from 0.001 to 5 wt. %, based on total weight of the lubricating composition; and [0209] L) optionally, one or more detergents, other than those of components (B) and in the colloidal particles described in (C) are present at from 0.1 to 20 wt. % based on total weight of the lubricating composition

[0210] For purposes of this invention and the claims thereto, component C), the colloidal particles are not added in the elements B, D, E, F G, H, I, J, K, and/or L above for determining weight percents, even though they may show similar properties, e.g., element C) colloidal particles may impact wear positively, but are not added into element K) for determining weight percent of anti-wear agents.

[0211] In embodiments, all of elements D, E, F G, H, I, J, K, and L are present in addition to the base oil, phosphorus-containing compound, and the one or more colloidal particles described herein.

[0212] In embodiments, elements D, E, F G, H, I, and J are present in addition to the base oil, phosphorus-containing compound, and the colloidal particles described herein.

[0213] In embodiments, elements I, F, and G are present in addition to the base oil, phosphorus-containing compound, and the one or more colloidal particles described herein.

[0214] In embodiments, elements D, E, F G, H, I, and J are present in addition to the base oil, phosphorus-containing compound, and the one or more colloidal particles described herein.

[0215] In embodiments, elements I, F, and G are present in addition to the base oil, phosphorus-containing compound, and the one or more colloidal particles described herein.

[0216] Suitably, the lubricant composition may have an adhesive wear of 100 hours or more,

alternately 120 hours or more, alternately 130 hours or more, alternately 140 hours or more, such as 100 to 200 hours, as measured by ASTM D8074-16.

[0217] Suitably, the lubricant composition may have a total base number (TBN) of 1 to 30 mgKOH/g, such as 5 to 25 mgKOH/g, 6 to 20 mgKOH/g, such as 7 to 17 mgKOH/g, such as 13 to 16 mgKOH/g, as measured by ASTM D2896, or 4 to 17 mgKOH/g, preferably 5 to 16 mgKOH/g, such as 6 to 15 mgKOH/g, such as 8 to 14 mgKOH/g, as measured by ASTM D2896.

[0218] Suitably, the lubricant composition may have: [0219] i. an adhesive wear of 100 hours or more, alternately 120 hours or more, a ratio of Zn to P (elemental mass basis) of 1.1 to 5.0 (such as 1.1 to 4.7, or 1.2 to 4.7, or 1.3 to 4.5, 1.4 to 4.5, 1.5 to 4.5, or 2.5 to 4.0); and [0220] ii. a total base number (TBN) of 4 to 17 mgKOH/g, preferably 5 to 16 mgKOH/g, such as 6 to 15 mgKOH/g, such as 8 to 14 mgKOH/g, as measured by ASTM D2896.

[0221] Suitably, the lubricant composition may have a total base number (ASTM D2896) that is at least 5% more (alternately at least 10% more, alternately at least 20% more, alternately at least 50% more) than the TBN amount measured in the same formulation tested under the same conditions except that common detergents (such as calcium salicylate with a TBN of 225 mgKOH/g) are used in place of the zinc containing colloidal particles as defined in the invention at the same total detergent content.

[0222] Alternately, the lubricant composition may have a total base number (ASTM D2896) that is at least 10% more (alternately at least 20% more, alternately at least 50% more) than the TBN amount measured in the same formulation tested under the same conditions at the same total detergent content except that the zinc containing colloidal particles as defined in the invention are absent.

[0223] Furthermore, the use of colloidal particles in lubricant compositions as described herein offers a way to improve antiwear by adding on top of existing SASH in a lubricant composition formulation, however, without adding more phosphorus. Alternately, the use of colloidal particles as described herein can be used to maintain detergency (TBN) whilst improving antiwear performance after substitution of detergents with colloidal zinc-containing particles.

[0224] Suitably, the lubricant composition may have an adhesive wear, as measured by ASTM D8074, that is at least 20% more (alternately at least 30% more, alternately at least 40% more, alternately at least 50% more, alternately at least 60% more, alternately at least 70% more, alternately at least 100% more) than the adhesive wear measured in the same formulation tested under the same conditions except that calcium alkylphenylsulfonate is used in place of the zinc containing colloidal particles as defined in the invention.

[0225] Suitably, the lubricant composition may have an adhesive wear, as measured by ASTM D8074-16, that is at least 20% more (alternately at least 30% more, alternately at least 40% more, alternately at least 50% more, alternately at least 60% more, alternately at least 70% more, alternately at least 100% more) than the adhesive wear measured in the same formulation tested under the same conditions except that the zinc containing colloidal particles as defined in the invention are absent.

[0226] The zinc containing colloidal particles in the lubricating compositions of the present invention may have a molar ratio of metal to surfactant MR of at least 5, such as 5 to 50, or 6 to 40, or 7 to 30, determined as the mole of metal per mole equivalent of metal surfactant (soap), calculated from actual Zn content of the prepared colloidal particle dispersion and the amount of surfactant employed to form the soap, assuming 100% conversion rate.

[0227] The lubricating compositions of the present invention may contain a zinc content of 500 ppm or more, such as 800 ppm or more, or 1000 ppm or more, such as 1500 ppm or more, or 2000 ppm or more, or 2500 ppm or more, or 3000 ppm or more, or 3500 ppm or more, or 4000 ppm or more, as determined by ASTM D5185, such as 1500 to 4500 ppm, or 2000 to 4000 ppm.

[0228] The lubricating compositions of the present invention may contain low levels of phosphorus, namely not more than 2000 ppm, such as not more than 1600 ppm, not more than

1200 ppm, such as not more than 800 ppm, such as 1 to 1600 ppm, such as 10 to 1200 ppm, such as 100 to 800 parts per million (ppm), based on the total mass of the lubricating compositions, as measured by ASTM D5185.

[0229] The lubricating composition of the present invention may be a heavy-duty diesel engine oil, or a marine engine oil, or a petrol or gasoline engine oil, or a lubricating oil for engine fueled by liquefied petroleum gas (LPG), or an alternative fuel type comprising at least one of ammonia, hydrogen, methanol, ethanol, or biodiesel.

[0230] In an embodiment, the lubricating composition comprises more than 1000 ppm of Zn such as more than 1500 ppm, or more than 2000 ppm Zn, and less than 1000 ppm P, such as less than 900 ppm, or less than 800 ppm P, based on the total mass of the lubricating composition, as measured by ASTM D5185, wherein the lubricating composition has an adhesive wear of 100 hours or more (ASTM D 8074-16), and optionally a total base number of 7 mgKOH/g or more as measured by ASTM D2896.

[0231] In the lubricating composition, such as those for combustion engines, zinc dialkyl dithiophosphates are present at 2 wt. % or less, such as 1.5 wt. % or less, or 1 wt. % or less, based on the total mass of the lubricating composition.

[0232] The lubricating composition may have a wear scar volume of less than 150  $\mu\text{m}^3$ , such as less than 140  $\mu\text{m}^3$ , or less than 135  $\mu\text{m}^3$ , determined by High Frequency Reciprocating Rig-HFRR method as described in the experimental section herein below.

[0233] The lubricating compositions of the present invention may contain a ratio of atoms of zinc to atoms of phosphorus, based on the total mass of the lubricating compositions, as measured by ASTM D5185, of 1.2 to 5.0, alternatively 2.0 to 4.5, preferably 2.5 to 4.0.

[0234] Typically, the lubricating compositions may contain low levels of sulfur. Preferably, the lubricating composition contains up to 0.4, more preferably up to 0.3, most preferably up to 0.2, such as 0.1 to 0.4 wt. % sulfur, based on the total mass of the lubricating composition, as measured by ASTM D2622.

[0235] Typically, the lubricating compositions, such as those for combustion engines, e.g., heavy duty diesel engines, may contain low levels of sulfated ash, such as 1.0 wt. % or less, preferably 0.9 wt. % or less, preferably 0.8 wt. % or less, or 0.7 wt. % or less, preferably 0.5 or less wt. %, alternately 0.001 to 0.5 wt. % sulfated ash, based on the total mass of the lubricating composition, as measured by ASTM D874.

[0236] Generally, the kinematic viscosity at 100° C. (“KV100”) of the lubricating composition, such as those for combustion engines, ranges from 2 to 30 cSt, such as 2 to 20 cSt, such as 5 to 15 cSt (as determined according to ASTM D445-19a). For marine oils, the kinematic viscosity will typically be higher than the above values.

[0237] Generally, the total base number of the lubricating composition ranges from 1 to 30, such as 5 to 15 mgKOH/g (as determined according to ASTM D2896).

[0238] Generally, the high temperature high shear viscosity (HTHS) at 150° C. and  $1.0 \times 10^6 \text{ s}^{-1}$  shear rate, of the lubricating composition is from 0.5 to 20, such as 1 to 10 cP, such as 2 to 4 cP (as determined according to ASTM D4683-20).

[0239] Preferably, the lubricating composition of the present invention is a multigrade oil identified by the viscometric descriptor SAE 20W-X, SAE 15W-X, SAE 10W-X, SAE 5W-X or SAE 0W-X, where X represents any one of 8, 12, 16, 20, 30, 40 and 50; the characteristics of the different viscometric grades can be found in the SAE J300 classification. The lubricating composition is preferably in the form of an SAE 10W-X, SAE 5W-X, or SAE 0W-X, more preferably in the form of a SAE 5W-X or SAE 0W-X, wherein X represents any one of 8, 12, 16, 20, 30, 40, and 50. Preferably X is 8, 12, 16, or 20. (See standard SAE J300 published by SAE International, formerly known as Society of Automotive Engineers.)

#### A. Base Oil

[0240] The base oil (also referred to as “base stock,” “lubricating oil basestock,” or “oil of

lubricating viscosity”) used herein may be a single oil or a blend of oils, and is typically a large liquid constituent of a lubricating composition, also referred to as a lubricant, into which additives and optional additional oils are blended, for example to produce a lubricating composition, such as a final lubricant composition, a concentrate, or other lubricating composition.

[0241] A base oil may be selected from vegetable, animal, mineral, and synthetic lubricating oils, and mixtures thereof. It may range in viscosity from light distillate mineral oils to heavy lubricating oils such as gas engine oil, mineral lubricating oil, motor vehicle oil and heavy-duty diesel oil. Generally, the kinematic viscosity at 100° C. (“KV.sub.100”) of the base oil ranges from 2 to 30, especially 5 to 20 cSt (as determined according to ASTM D445-19a). Generally, the high temperature high shear (HTHS) viscosity at 150° C. and  $1.0 \times 10^6$  s.sup.-1 shear rate of the base oil ranges from 0.5 to 20 cP, such as 1 to 10 cP, such as 2 to 5 cP (as determined according to ASTM D4683-20).

[0242] Typically, when lubricating oil basestock(s) is used to make a concentrate, it may advantageously be present in a concentrate-forming amount to give a concentrate containing, from 1 to 99 wt. %, from 5 wt. % to 80 wt. %, from 10 wt. % to 70 wt. %, or from 5 wt. % to 50 wt. % of active ingredient, based upon the weight of the concentrate.

[0243] Common oils useful as base oils include animal and vegetable oils (e.g., castor and lard oil), liquid petroleum oils, and hydrorefined and/or solvent-treated mineral lubricating oils of the paraffinic, naphthenic, and mixed paraffinic-naphthenic types. Oils derived from coal or shale are also useful base oils. Base stocks may be manufactured using a variety of different processes including, but not limited to, distillation, solvent refining, hydrogen processing, oligomerization, esterification, and re-refining.

[0244] Synthetic lubricating oils useful herein as base oils include hydrocarbon oils such as homopolymerized and copolymerized olefins, referred to as polyalphaolefins or PAO's or group IV base oils [according to the API EOLCS 1509 definition (American Petroleum Institute Publication 1509, see section E.1.3, 19th edition, January 2021, [www.API.org](http://www.API.org))]. Examples of PAO's useful as base oils include: poly(ethylenes), copolymers of ethylene and propylene, polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes), homo- or co-polymers of C.sub.8 to C.sub.20 alkenes, homo- or co-polymers of C.sub.8, and/or C.sub.10, and/or C.sub.12 alkenes, C.sub.8/C.sub.10 copolymers, C.sub.8/C.sub.10/C.sub.12 copolymers, and C.sub.10/C.sub.12 copolymers, and the derivatives, analogues, and homologues thereof.

[0245] In another embodiment, the base oil comprises polyalphaolefins comprising oligomers of linear olefins having 6 to 14 carbon atoms, more preferably 8 to 12 carbon atoms, more preferably 10 carbon atoms having a Kinematic viscosity at 100° C. of 10 or more (as measured by ASTM D445); and preferably having a viscosity index (“VI”), as determined by ASTM D2270, of 100 or more, preferably 110 or more, more preferably 120 or more, more preferably 130 or more, more preferably 140 or more; and/or having a pour point of -5° C. or less (as determined by ASTM D97), more preferably -10° C. or less, more preferably -20° C. or less.

[0246] In another embodiment, polyalphaolefin oligomers useful in the present invention comprise C.sub.20 to C.sub.1500 paraffins, preferably C.sub.40 to C.sub.1000 paraffins, preferably C.sub.50 to C.sub.750 paraffins, preferably C.sub.50 to C.sub.500 paraffins. The PAO oligomers are dimers, trimers, tetramers, pentamers, etc., of C.sub.5 to C.sub.14 alpha-olefins in one embodiment, and C.sub.6 to C.sub.12 alpha-olefins in another embodiment, and C.sub.8 to C.sub.12 alpha-olefins in another embodiment. Suitable olefins include 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, and 1-dodecene. In one embodiment, the olefin is 1-decene, and the PAO is a mixture of dimers, trimers, tetramers, and pentamers (and higher) of 1-decene. Useful PAO's are described more particularly in, for example, U.S. Pat. Nos. 5,171,908 and 5,783,531, and in Synthetic Lubricants and High-Performance Functional Fluids 1-52 (Leslie R. Rudnick & Ronald L. Shubkin, ed. Marcel Dekker, Inc. 1999).

[0247] PAO's useful in the present invention typically possess a number average molecular weight of from 100 to 21,000 g/mol in one embodiment, and from 200 to 10,000 g/mol in another embodiment, and from 200 to 7,000 g/mol in yet another embodiment, and from 200 to 2,000 g/mol in yet another embodiment, and from 200 to 500 g/mol in yet another embodiment. Desirable PAO's are commercially available as SpectraSyn™ Hi-Vis, SpectraSyn™ Low-Vis, SpectraSyn™ plus, SpectraSyn™ Elite PAO's (ExxonMobil Chemical Company, Houston Texas) and Durasyn PAO's from Ineos Oligomers USA LLC.

[0248] Synthetic lubricating oils useful as base oils also include hydrocarbon oils such as homopolymerized and copolymerized: alkylbenzenes [e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes]; polyphenols (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides; and the derivatives, analogues, and homologues thereof.

[0249] Another suitable class of synthetic lubricating oils useful as base oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) reacted with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0250] Esters useful as synthetic oils herein also include those made from C.sub.5 to C.sub.12 monocarboxylic acids and polyols, and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, and tripentaerythritol.

[0251] Desirable ester base oils are commercially available as Esterex™ Esters (ExxonMobil Chemical Company, Houston Texas).

[0252] Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxysilicone oils and silicate oils comprise another useful class of synthetic lubricants useful herein; such oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methyl-2-ethylhexyl)silicate, tetra-(p-tert-butyl-phenyl) silicate, hexa-(4-methyl-2-ethylhexyl)disiloxane, poly(methyl)siloxanes and poly(methylphenyl)-siloxanes.

[0253] Other synthetic lubricating oils useful herein include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

[0254] Unrefined, refined, and re-refined oils can be used in the lubricating compositions of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation, or an ester oil obtained directly from an esterification process and used without further treatment is considered an unrefined oil. 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. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration, and percolation are used by those in the art. Re-refined oils are oils obtained by processes similar to those used to obtain refined oils where the refining processes are applied to previously refined oils which have been previously used in service. Such re-refined oils are also referred to as reclaimed or reprocessed oils and often are additionally processed for removal of spent additive and oil breakdown products. A re-refined base oil is preferably substantially free from materials introduced through manufacturing, contamination, or previous use.

[0255] Other examples of useful base oils are gas-to-liquid ("GTL") base oils, i.e., the base oil is an

oil derived from hydrocarbons made from synthesis gas ("syn gas") containing H<sub>2</sub> and CO using a Fischer-Tropsch catalyst. These hydrocarbons typically require further processing in order to be useful as a base oil. For example, they may, by methods known in the art, be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed. For further information on useful GTL base oils and blends thereof, please see U.S. Pat. No. 10,913,916 (column 4, line 62 to column 5, line 60) and 10,781,397 (column 14, line 54 to column 15, line 5, and column 16, line 44 to column 17, line 55).

[0256] The various base oils are often categorized as Group I, II, III, IV, or V according to the API EOLCS 1509 definition (American Petroleum Institute Publication 1509, see section E.1.3, 19th edition, January 2021, [www.API.org](http://www.API.org)). Generally speaking, Group I base stocks have a viscosity index of between about 80 to 120 and contain greater than about 0.03% sulfur and/or less than about 90% saturates. Group II base stocks have a viscosity index of between about 80 to 120 and contain less than or equal to about 0.03% sulfur and greater than or equal to about 90% saturates. Group III base stocks have a viscosity index greater than about 120 and contain less than or equal to about 0.03% sulfur and greater than about 90% saturates. Group IV base stocks include polyalphaolefins (PAO). Group V base stocks include base stocks not included in Groups I-IV. (Viscosity index measured by ASTM D2270, saturates is measured by ASTM D2007, and sulfur is measured by ASTM D2622, ASTM D4294, ASTM D4927, and ASTM D3120).

[0257] Base oils for use in the formulated lubricating compositions useful in the present disclosure are any one, two, three, or more of the variety of oils described herein. In desirable embodiments, base oils for use in the formulated lubricating compositions useful in the present disclosure are those described as API Group I, Group II, Group III (including Group III+), Group IV, and Group V oils and mixtures thereof, preferably API Group II, Group III, Group IV, and Group V oils and mixtures thereof, more preferably the Group III, Group III+, IV and Group V base oils due to their exceptional volatility, stability, viscometric and cleanliness features. Minor quantities of Group I basestock, such as the amount used to dilute additives for blending into formulated lube oil products, can be tolerated but are typically kept to a minimum, e.g., amounts only associated with their use as diluent/carrier oil for additives used on an "as-received" basis. In regard to the Group II stocks, it is more useful that the Group II base stock be in the higher quality range associated with that stock, i.e., a Group II stock having a viscosity index in the range from 100 to 120.

[0258] The base oil useful herein may be selected from any of the synthetic, natural, or re-refined oils (such as those typically used as crankcase lubricating oils for spark-ignited and compression-ignited engines). Mixtures of synthetic and/or natural and/or re-refined base oils may be used if desired. Multi-modal mixtures (such as bi- or tri-modal mixtures) of Group I, II, III, IV, and/or V base stocks may be used if desired.

[0259] The base oil or base oil blend used herein conveniently has a kinematic viscosity at 100° C. [KV.sub.100, as measured according to ASTM D445-19a, and reported in units of centistoke (cSt) or its equivalent, mm<sup>2</sup>/s], of about 2 to about 40 cSt, alternately of 3 to 30 cSt, alternately 4 to 20 cSt at 100° C., alternately 5 to 10 cSt, alternately the base oil or base oil blend may have a kinematic viscosity at 100° C. of 2 to 20 cSt, of 2.5 to 2 cSt, and preferably of about 2.5 cSt to about 9 cSt.

[0260] The base oil or base oil blend preferably has a saturate content of at least 65 wt. %, more preferably at least 75 wt. %, such as at least 85 wt. %, such as greater than 90 wt. % as determined by ASTM D2007.

[0261] Preferably, the base oil or base oil blend will have a sulfur content of less than 1 wt. %, preferably less than 0.6 wt. %, most preferably less than 0.4 wt. %, such as less than 0.3 wt. %, based on the total mass of the lubricating composition, as measured by ASTM D2622.

[0262] In embodiments, the volatility of the base oil or base oil blend, as measured by the Noack test (ASTM D5800, procedure B), is less than or equal to 30 wt. %, such as less than or equal to 25 wt. %, such as less than or equal to 20 wt. %, such as less than or equal to 16 wt. %, such as less

than or equal to 12 wt. %, such as less than or equal to 10 wt. %, based on the total mass of the lubricating composition.

[0263] In embodiments, the viscosity index (VI) of the base oil is at least 95, preferably at least 110, more preferably at least 120, even more preferably at least 125, most preferably from about 130 to 240, in particular from about 105 to 140 (as determined by ASTM D2270).

[0264] The base oil may be provided in a major amount, in combination with a minor amount of one or more additive components as described hereinafter, constituting a lubricant. This preparation may be accomplished by adding the additives directly to the oil or by adding the one or more additives in the form of a concentrate thereof to disperse or dissolve the additive(s). Additives may be added to the oil by any method known to those skilled in the art, either before, at the same time as, or after addition of other additives.

[0265] The base oil may be provided in a minor amount, in combination with minor amounts of one or more additive components as described hereinafter, constituting an additive concentrate. This preparation may be accomplished by adding the additives directly to the oil or by adding the one or more additives in the form of a solution, slurry, or suspension thereof to disperse or dissolve the additive(s) in the oil. Additives may be added to the oil by any method known to those skilled in the art, either before, at the same time as, or after addition of other additives.

[0266] The base oil typically constitutes the major component of an engine oil lubricant composition of the present disclosure and typically is present in an amount ranging from about 50 to about 99 wt. %, preferably from about 70 to about 95 wt. %, and more preferably from about 80 to about 95 wt. %, based on the total weight of the composition.

[0267] Typically, one or more base oils are present in the lubricating composition in an amount of 32 wt. % or more, alternately 55 wt. % or more, alternately 60 wt. % or more, alternately 65 wt. % or more, based on the total weight of the lubricating composition. Typically, one or more base oils are present in the lubricating composition at an amount of 98 wt. % or less, more preferably 95 wt. % or less, even more preferably 90 wt. % or less. Alternately, one or more base oils are present in the lubricating composition at from 1 to 99 wt. %, alternately 50 to 97 wt. %, alternately 60 to 95 wt. %, alternately 70 to 95 wt. %, based upon the weight of the lubricating composition.

[0268] This invention also relates to lubricating oil compositions comprising or resulting from the admixing of the functionalized hydrogenated/saturated polymers described herein and at least 40 wt. % hydrocarbon basestock oil, such as Group I, II, and/or III oil, such as a group II or III oil.

[0269] This invention also relates to additive concentrates comprising or resulting from the admixing of the functionalized hydrogenated/saturated polymers described herein and at least 1 wt. % hydrocarbon basestock oil, such as Group I, II, and/or III oil, such as a group I or II oil.

[0270] The base oils and blends thereof described above are also useful for making concentrates, as well as for making lubricants therefrom.

[0271] Concentrates constitute a convenient means of handling additives before their use, as well as facilitating solution or dispersion of additives in lubricants. When preparing a lubricant that contains more than one type of additive (sometime referred to as “additive components”), each additive may be incorporated separately, each in the form of a concentrate. In many instances, however, it is convenient to provide a so-called additive “package” (also referred to as an “adpack”) comprising one or more co-additives, such as described hereinafter, in a single concentrate.

[0272] A concentrate, also referred to as an additive package or adpack, is a composition typically having less than 50 wt. % (such as less than 40%, such as less than 30 wt. %, such as less than 25%, such as less than 20%) base oil which is typically then further blended with further base oil and other components, such as viscosity modifiers and pour point depressants to form a lubricating oil product.

[0273] This invention relates to concentrate compositions comprising or resulting from the admixing of: [0274] (A) from 1 to less than 50 wt. % (alternately 5 to 45 wt. %, alternately 7 to 40



wt. %, alternately 10 to 35 wt. %, alternately 10 to 25 wt. %), based upon the weight of the composition, of one or more base oil(s); [0275] (B) optionally, from 0.001 to 5 wt. % (in particular 0.01 to 4 wt. %, alternately 0.02 wt. % to 3 wt. %, alternately 0.1 to 2 wt. %), based upon the weight of the composition, of at least one phosphorus-containing compound selected from detergents, friction modifiers or antiwear additives other than the colloidal particles described in (C); [0276] (C) from 0.1 to 50 wt. % (in particular 0.15 to 20 wt. %, alternately 0.20 wt. % to 10 wt. %, alternately 0.25 to 5 wt. %), based upon the weight of the composition, of one or more dispersions of colloidal particles comprising: [0277] a) a core of one or more hydrocarbon insoluble zinc containing compounds, and [0278] b) a shell of one or more of: [0279] 1) one or more metal containing surfactants, where the metal, M, comprises a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; and the surfactant comprises an hydrocarbyl-substituted sulfonate or an hydrocarbyl-substituted salicylate group of Formula (I) or (II),

##STR00017## [0280] wherein each R.sup.A, and R.sup.B is, independently of each other, a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 1 to 70 carbon atoms, wherein, for  $n > 1$ , the sum of the number of carbon atoms in the total of R.sup.A groups in Formula (I) and the sum of the number of carbon atoms in the total of R.sup.B groups in Formula (II) is 100 or less carbon atoms, and Ar is a mono- or polycyclic aromatic group; n is an integer from 1 to the maximum possible number of substitutions on Ar, m is an integer of 1 to 3, x is an integer from 1 to 5; y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; [0281] 2) one or more metal alkanoates represented by the formula (III):

##STR00018## [0282] wherein M is a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; R.sup.C is selected from a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 70 carbon atoms, or an aromatic or alkyl aromatic group with the aromatic group having from 6 to 20 carbon atoms and the alkyl group having 1 to 20 carbon atoms; x is an integer from 1 to 5, wherein for  $x > 1$  the R.sup.C groups may be the same or different, y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; [0283] (D) optional additional components, anti-oxidants, pour point depressants, anti-foam agents, viscosity modifiers, corrosion inhibitors, anti-wear agents, extreme pressure additives, demulsifiers, seal compatibility agents, additive diluent base oils, friction modifier(s) (such as organic FM, such as organic ester, such as fatty acid ester), acid scavengers, etc.

[0284] In embodiments of the concentrates, the surfactants of Formula (I), (II), or (III) may be those of formula (Ia), (IIa), or (IIIa), including all preferred embodiments thereof, as described herein above.

[0285] Concentrates may be present in the lubricating oil composition at from 0.5 wt. % to 35 wt. %, such as 5 wt. % to 30 wt. %, such as 7.5 wt. % to 25 wt. %, such as 10 to 22.5 wt. %, such as 15 to 20 wt. %, based upon the mass of the lubricating oil composition.

## B. Colloidal Particles

[0286] Useful colloidal particles of the present invention are typically prepared as dispersions in base oil, and the dispersions comprise core shell-type colloidal particles having: [0287] a) a core of one or more hydrocarbon insoluble zinc containing compounds, and [0288] b) a shell of one or more of: [0289] 1) one or more metal containing surfactants, where the metal, M, comprises a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; and the surfactant comprises an hydrocarbyl-substituted aromatic sulfonate or an hydrocarbyl-substituted salicylate group of Formula (I) or (II),

##STR00019##

[0290] wherein each R.sup.A, and R.sup.B is, independently of each other, a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 1 to 70 carbon atoms, wherein, for  $n > 1$ , the sum of the number of carbon atoms in the total of R.sup.A groups in Formula (I) and the sum of the number of carbon atoms in the total of R.sup.B groups in Formula (II) is 100 or less carbon atoms, and Ar is a mono- or polycyclic aromatic group; n is an integer from 1 to the

maximum possible number of substitutions on Ar, m is an integer of 1 to 3, x is an integer from 1 to 45; y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 4; [0291] 2) one or more metal alkanoates represented by the formula (III):

##STR00020##

[0292] wherein M is a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; R<sub>sup</sub>.C is selected from a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 70 carbon atoms, or an aromatic or alkyl aromatic group with the aromatic group having from 6 to 20 carbon atoms and the alkyl group having 1 to 20 carbon atoms; x is an integer from 1 to 5, wherein for x>1 the R<sub>sup</sub>.C groups may be the same or different, y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8.

[0293] Preferred dispersions of core shell-type colloidal particles may also have surfactants of Formula (Ia), (IIa), or (IIIa), including all preferred embodiments thereof, as described herein above.

### Synthesis

[0294] Dispersions of colloidal zinc containing particles having a core shell structure as described herein can be produced in several ways, for example, involving heating ZnCO<sub>sub.3</sub> in the presence of a high boiling base oil containing a dispersing agent soluble in said base oil to effect its decomposition into ZnO and CO<sub>sub.2</sub> at temperatures substantially lower than required when ZnCO<sub>sub.3</sub> in the dry state is decomposed into ZnO.

[0295] For zinc-only dispersions, i.e., ZnO core in a Zn-surfactant shell, a suitable metal free surfactant, such as those described herein, for example an alkylaryl sulfonic acid, or alkyl salicylic acid, or an alkanolic acid, is combined with a high boiling base oil and zinc carbonate. This mixture is heated in an inert gas steam under stirring to a temperature of about 200 to 400° C., such as 250 to 350° C., or about 300° C. for several hours, such as 2 to 6 hours, for example 3 to 5 hours, or about 4 hours. After cooling back to room temperature, the crude product is dissolved in about 5 times its volume of an organic solvent such as xylene and centrifuged, for example at about 3000 rpm, such as 2900 rpm for about 1 hr. The supernatant is decanted away from the residues and the solvent stripped on a rotary evaporator. The resulting product is a stable dispersion of particles comprising a ZnO core in a shell of Zn-detergent.

[0296] For producing mixed metal systems, such as Ca—or Mg-sulfonate or salicylate stabilised colloids (or metal containing surfactants of other group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metals as disclosed herein elsewhere), this same method can be used by employing pre-made metal containing surfactant species, i.e., Ca or Mg sulfonates, salicylates, alkanoates, and the like, instead of the metal free acids.

[0297] In another embodiment of the process for preparing dispersions of zinc containing particles having a core shell structure as described herein, a detergent or surfactant (free acid form) is combined with an organic solvent such as xylene, and a high boiling base oil. Calcium hydroxide and methanol is added, and the mixture is heated to about 40° C. for 20 min, and then cooled back to room temperature, i.e. 25° C. Methanolic solutions of zinc chloride and sodium hydroxide are simultaneously but separately from each other added to the reaction mixture. After addition the mixture is heated to about 70° C. over about 45 min, until the onset of methanol reflux. Then, the methanol was completely drawn off, and the temperature is raised further to about 140° C. and held for a certain time before being allowed to cool back to room temperature. Once cool, further xylene is charged to the reactor and the mixture stirred and then allowed to settle. The mixture is centrifuged, the supernatant is decanted away from the residues and volatile solvent removed on the rotary evaporator. The resulting product is a stable dispersion of particles comprising a ZnO core in a shell of Zn-surfactant.

[0298] In another embodiment of the process for preparing dispersions of zinc containing particles having a core shell structure as described herein, detergent or surfactant is charged to a reactor along with a high boiling base oil and metal hydroxide. Under a nitrogen stream and stirring, the

mixture is heated to about 150° C. and soaked for 10 min to remove water from the reaction. Zinc carbonate is then added, maintaining the internal temperature between about 140 to 155° C. The reaction was then heated to a temperature of about 200 to 400° C., such as 250 to 350° C., or about 300° C. for several hours, such as 2 to 6 hours, for example 3 to 5 hours, or about 4 hours, before being allowed to cool back to room temperature. The crude product was dissolved in about 5 times its volume of xylene and centrifuged. The supernatant was decanted away from the residues and the solvent stripped on the rotary evaporator. The resulting product is a stable dispersion of particles comprising a ZnO core in a shell of metal-surfactant.

[0299] Particle sizes of the colloidal particles in the dispersions may range from about 5 nm to 1 µm, such as 5 nm to 500 nm, or 10 nm to 300 nm, or 10 nm to 200 nm, or 20 nm to 150 nm, as determined by dynamic light scattering, volume average, as described in the examples section.

[0300] The colloidal dispersions may have a Zn content as determined by ASTM D4891 of about 5 to 35 wt. %, based on the total weight of the colloidal dispersion, such as 5 to 30 wt. %, or 5 to 35 wt. %. such as 5 to 30 wt. %. In certain embodiments, the Zn content is the maximum content possible whilst still providing a stable dispersion, i.e., showing no precipitates over a period of at least 4 weeks.

[0301] The colloidal dispersions produced by the methods described above are neutral, or overbased, typically overbased detergent systems, i.e., having a higher/above stoichiometric ratio of metal to ligand than would be expected for a neutral metal species. The colloidal dispersions may have a TBN as measured by ASTM D2896 of 100 mgKOH/g or more, such as 200 mgKOH/g or more, 250 mgKOH/g or more, 300 mgKOH/g or more, such as from 200 to 800 mgKOH/g, 225 to 700 mgKOH/g, 250 to 650 mgKOH/g, or 300 to 600 mgKOH/g, such as 150 to 650 mgKOH/g.

[0302] In certain embodiments, the colloidal dispersions used in lubricating oil compositions or concentrates of the present invention are free of sulfur and/or phosphorus.

[0303] In certain embodiments, the colloidal particles have a (non-stoichiometric) molar ratio of metal (zinc) to surfactant, MR, of greater than 1, such as equal to or greater than 2, 3, 5, 10, 15, 20, 30, or 40, and less than 40, 30, 35, 20, 15, such as a molar ratio of metal compound to surfactant of greater than 1 to 40, 2 to 30, 5 to 30, 10 to 30, or 10 to 20.

[0304] The dispersions of colloidal particles as prepared are stable and preferably remain stable in oil formulations for at least 4 weeks at 25° C.

[0305] In certain embodiments, the colloidal dispersions used in lubricating oil compositions or concentrates of the present invention are mixed metal systems, i.e., wherein the colloidal particles comprise a core of Zn containing compound, such as Zn, ZnO, ZnCO.sub.3, or mixtures thereof, preferably ZnO, and a shell of a metal containing surfactant of group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metals other than Zn. In a certain embodiments thereof, the colloidal particles comprise a core of Zn containing compound, such as Zn, ZnO, ZnCO.sub.3, or mixtures thereof, preferably ZnO, and a shell of a metal containing surfactant of group 1, or 2 metals, such as alkaline earth metals, such as calcium, magnesium, or barium, preferably Ca or Mg, such as Ca. In particular embodiments, the colloidal particles comprise a core of ZnO or a mixture of ZnO and ZnCO.sub.3, and a Ca—or Mg-surfactant, such as ZnO core and Ca-surfactant shell.

[0306] In other embodiments, the colloidal dispersions used in lubricating oil compositions or concentrates of the present invention are Zinc-only systems, i.e., wherein the colloidal particles comprise a core of Zn containing compound, such as Zn, ZnO, ZnCO.sub.3, or mixtures thereof, preferably ZnO, and a shell of a zinc containing detergent. In a certain embodiments thereof, the colloidal particles comprise a core of Zn containing compound, such as Zn, ZnO, ZnCO.sub.3, or mixtures thereof, preferably ZnO, and a shell of a zinc alkyl aromatic sulfonate of formula (I), or (Ia), a zinc alkyl salicylate of formula (II), or (IIa), or a zinc alkanoate of formula (III). In particular embodiments, the colloidal particles comprise a core of ZnO, or a mixture of ZnO and ZnCO.sub.3, and a shell of zinc alkanoate of formula (III). In certain embodiments, the colloidal particles comprise a core of ZnO, or a mixture of ZnO and ZnCO.sub.3, and a shell of zinc alkyl salicylate

of formula (II), such as (IIa). In other embodiments, the colloidal particles comprise a core of ZnO, or a mixture of ZnO and ZnCO.sub.3, and a shell of zinc alkyl aromatic sulfonate of formula (I), such as (Ia).

[0307] In embodiments of the present invention, the lubricating composition may comprise combinations of colloidal particles (C) where the shell may include surfactants of Formula (I), (II) and/or (III), such as mixtures of colloidal particles based on Formula (I) and (II), (I) and (III), (II) and (III), or (I), (II) and (III). Therein, the colloidal particles of Formula (I) may be aliphatic sulfonates, or aromatic sulfonates, or mixtures of aliphatic and aromatic sulfonates. As described above, the surfactants of Formula (I) and/or (II) may also be mixed metal systems, with M being different from Zn, such as calcium, or magnesium. It is believed that mixed metal systems may offer difference in particle size and stability in some compositions, so the colloidal particles are adjustable to the properties of the other additives in the lubricant composition.

[0308] The lubricating compositions herein may generally comprise from 0.01 to 10 wt. %, alternately, 0.1 to 10 wt. %, alternately, 0.2 to 5 wt. %, alternately 0.3 to 2.5 wt. %, alternately 0.4 to 1.2 wt. %, preferably 0.5 to 1 wt. % of one or more zinc containing colloidal dispersions as described herein, based on total weight of the lubricating composition.

[0309] The zinc containing colloidal dispersions can be included in the lubricating composition of the present invention as an individual component or as part of concentrate, such as an additive package, together with other additive components. The concentrate (such as additive package) compositions herein may generally comprise from 0.01 to 10 wt. %, alternately, 0.1 to 10 wt. %, alternately, 0.2 to 5 wt. %, alternately 0.3 to 2.5 wt. %, alternately 0.4 to 1.2 wt. %, in some embodiments 0.5 to 1 wt. % of one or more zinc containing colloidal compositions as described herein, based on total weight of the concentrate composition.

[0310] The lubricating composition according to the present invention may further comprise one or more additives such as detergents, friction modifiers, anti-oxidants, pour point depressants, anti-foam agents, viscosity modifiers, dispersants, corrosion inhibitors, anti-wear agents, extreme pressure additives, demulsifiers, seal compatibility agents, additive diluent base oils, etc. Specific examples of such additives are described in for example Kirk-Othmer Encyclopedia of Chemical Technology, third edition, volume 14, pages 477-526, and several are discussed in further detail below.

### C. Detergents

[0311] The lubricating composition may comprise one or more metal detergents (such as blends of metal detergents) also referred to as a “detergent additive.” Metal detergents typically function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with a long hydrophobic tail, with the polar head comprising 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 (“TBN” as measured by ASTM D2896) of up to 150 mg KOH/g, such as from 0 to 80 (or 5-30) mg KOH/g. A large, greater than stoichiometric amount of a metal base may be incorporated. Such detergents, sometimes referred to as overbased, may have a TBN of 100 mg KOH/g or more (such as 200 mgKOH/g or more), and typically will have a TBN of 250 mg KOH/g or more, such as 300 mg KOH/g or more, such as from 200 to 800 mg KOH/g, 225 to 700 mg KOH/g, 250 to 650 mg KOH/g, or 300 to 600 mg KOH/g, such as 150 to 650 mg KOH/g. Overbased metal detergent salts may be obtained, for example, by reacting excess metal compound (e.g., an oxide or hydroxide) with an acidic gas (e.g., carbon dioxide), or other methods generally known to the skilled person in the field.

[0312] Suitable detergents include, oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali metals (Group 1 metals, e.g., Li, Na, K, Rb) or alkaline earth

metals (Group 2 metals, e.g., Be, Mg, Ca, Sr, Ba), particularly, sodium, potassium, lithium, calcium, and magnesium, such as Ca and or Mg. Furthermore, the detergent may comprise hybrid detergent comprising any combination of sodium, potassium, lithium, calcium, or magnesium salts of sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates or other oil-soluble carboxylates of a Group 1 and/or 2 metal.

[0313] Preferably, the detergent additive(s) useful in the present invention comprises calcium and/or magnesium metal salts. The detergent may a calcium and or magnesium carboxylate (including salicylates), sulfonate, or phenate detergent. More preferably, the detergents additives are selected from magnesium salicylate, calcium salicylate, magnesium sulfonate, calcium sulfonate, magnesium phenate, calcium phenate, and hybrid detergents comprising two, three, four or more of more of these detergents and/or combinations thereof.

[0314] The metal-containing detergent may also include “hybrid” detergents formed with mixed surfactant systems including phenate and/or sulfonate components, e.g., phenate/salicylates, sulfonate/phenates, sulfonate/salicylates, sulfonates/phenates/salicylates, as described, for example, in U.S. Pat. Nos. 6,429,178; 6,429,179; 6,153,565; and 6,281,179. Where, for example, a hybrid sulfonate/phenate detergent is employed, the hybrid detergent would be considered equivalent to amounts of distinct phenate and sulfonate detergents introducing like amounts of phenate and sulfonate soaps, respectively.

[0315] The overbased metal-containing detergent may be sodium salts, calcium salts, magnesium salts, or mixtures thereof of the phenates, sulfur-containing phenates, sulfonates, salixarates, and salicylates. Overbased phenates and salicylates typically have a total base number of 180 to 650 mg KOH/g, such as 200 to 450 TBN mg KOH/g. Overbased sulfonates typically have a total base number of 250 to 600 mg KOH/g, or 300 to 500 mg KOH/g. In embodiments, the sulfonate detergent may be predominantly a linear alkylbenzene sulfonate detergent having a metal ratio of at least 8 as is described in paragraphs [0026] to [0037] of US Patent Publication 2005/065045 (and granted as U.S. Pat. No. 7,407,919). The overbased detergent may be present at 0 wt. % to 15 wt. %, or 0.1 wt. % to 10 wt. %, or 0.2 wt. % to 8 wt. %, or 0.2 wt. % to 3 wt. %, based upon of the lubricating composition. For example, in a heavy duty diesel engine, the detergent may be present at 2 wt. % to 3 wt. % of the lubricating composition. For a passenger car engine, the detergent may be present at 0.2 wt. % to 1 wt. % of the lubricating composition.

[0316] The detergent additive(s) may comprise one or more magnesium sulfonate detergents. The magnesium detergent may be a neutral salt or an overbased salt. Suitably the magnesium detergent is an overbased magnesium sulfonate having TBN of from 80 to 650 mg KOH/g (ASTM D2896), such as 200 to 500 mg KOH/g, such as 240 to 450 mg KOH/g.

[0317] Alternately, the detergent additive(s) is a magnesium salicylate. Suitably the magnesium detergent is a magnesium salicylate having TBN of from 30 to 650 mg KOH/g (ASTM D2896), such as 50 to 500 mg KOH/g, such as 200 to 500 mg KOH/g, such as 240 to 450 mg KOH/g or alternately of 150 mg KOH/g or less, such as 100 mg KOH/g or less.

[0318] Alternately, the detergent additive(s) is a combination of magnesium salicylate and magnesium sulfonate.

[0319] The magnesium detergent provides the lubricating composition thereof with from 200-4000 ppm of magnesium atoms, suitably from 200-2000 ppm, from 300 to 1500 or from 450-1200 ppm of magnesium atoms (ASTM D5185).

[0320] The detergent composition may comprise (or consist of) a combination of one or more magnesium sulfonate detergents and one or more calcium salicylate detergents.

[0321] The combination of one or more magnesium sulfonate detergents and one or more calcium salicylate detergents provides the lubricating composition thereof with: 1) from 200-4000 ppm of magnesium atoms, suitably from 200-2000 ppm, from 300 to 1500 or from 450-1200 ppm of magnesium atoms (ASTM D5185), and 2) at least 500 ppm, preferably at least 750 more preferably at least 900 ppm of atomic calcium, such as from 500-4000 ppm, preferably from 750-3000 ppm,

more preferably from 900-2000 ppm atomic calcium (ASTM D5185).

[0322] The detergent may comprise one or more calcium detergents such as calcium carboxylate (e.g., salicylate), sulfonate, or phenate detergent.

[0323] Suitably the calcium detergent has a TBN of from 30 to 700 mg KOH/g (ASTM D2896), such as 50 to 650 mg KOH/g, such as 200 to 500 mg KOH/g, such as 240 to 450 mg KOH/g or alternately of 150 mg KOH/g or less, such as 100 mg KOH/g or less, or 200 mg KOH/g or more, or 300 mg KOH/g or more, or 350 mg KOH/g or more.

[0324] Suitably the calcium detergent is a calcium salicylate, sulfonate or phenate having TBN of from 30 to 700 mg KOH/g, 30 to 650 mg KOH/g (ASTM D2896), such as 50 to 650 mg KOH/g, such as 200 to 500 mg KOH/g, such as 240 to 450 mg KOH/g or alternately of 150 mg KOH/g or less, such as 100 mg KOH/g or less, or 200 mg KOH/g or more, or 300 mg KOH/g or more, or 350 mg KOH/g or more.

[0325] Calcium detergent is typically present in amount sufficient to provide at least 500 ppm, preferably at least 750 more preferably at least 900 ppm atomic calcium to the lubricating oil composition (ASTM D5185). If present, any calcium detergent is suitably present in amount sufficient to provide no more than 4000 ppm, preferably no more than 3000, more preferably no more than 2000 ppm atomic calcium to the lubricating oil composition (ASTM D5185). If present, any calcium detergent is suitably present in amount sufficient to provide at from 500-4000 ppm, preferably from 750-3000 ppm more preferably from 900-2000 ppm atomic calcium to the lubricating oil composition (ASTM D5185).

[0326] Suitably the total atomic amount of metal from detergent other than resulting from the colloidal particles as described herein in the lubrication composition according to all aspects of the invention is no more than 5000 ppm, preferably no more than 4000  $\mu\text{m}$  and more preferably no more than 2000 ppm (ASTM D5185). The total amount of atomic metal from detergent other than resulting from the colloidal particles as described herein in the lubrication oil composition according to all aspects of the invention is suitably at least 500 ppm, preferably at least 800 ppm and more preferably at least 1000 ppm (ASTM D5185). The total amount of atomic metal from detergent other than resulting from the colloidal particles as described herein in the lubrication oil composition according to all aspects of the invention is suitably from 500 to 5000 ppm, preferably from 500 to 3000 ppm and more preferably from 500 to 2000 ppm (ASTM D5185). In some embodiments of the invention, these detergents may be partially or completely replaced with the colloidal particles/dispersions as described herein, by maintaining overall detergency (TBN), whilst maintaining or improving antiwear performance of the lubricant composition.

[0327] Sulfonate detergents 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 such as chlorobenzene, chlorotoluene and chloronaphthalene. The alkylation may be carried out in the presence of a catalyst with alkylating 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 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 220 wt. % (preferably at least 125 wt. %) of that stoichiometrically required.

[0328] 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 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.

[0329] Carboxylate detergents, e.g., salicylates, can be prepared by reacting an aromatic carboxylic acid (such as a C.sub.5-100, C.sub.9-30, C.sub.14-24 alkyl-substituted hydroxy-benzoic acid) with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. The aromatic moiety of the aromatic carboxylic acid can contain heteroatoms, such as nitrogen and oxygen. Preferably, the moiety contains only carbon atoms; more preferably the moiety contains six or more carbon atoms; for example, benzene is a preferred moiety. The aromatic carboxylic acid may contain one or more aromatic moieties, such as one or more benzene rings, either fused or connected via alkylene bridges.

[0330] Preferred substituents in oil-soluble salicylic acids are alkyl substituents. In alkyl-substituted salicylic acids, the alkyl groups advantageously contain 5 to 100, preferably 9 to 30, especially 14 to 20, carbon atoms. Where there is more than one alkyl group, the average number of carbon atoms in all of the alkyl groups is preferably at least 9 to ensure adequate oil solubility.

[0331] In embodiments, the ratio of atomic detergent metal to atomic molybdenum in the lubricating oil composition may be less than 3:1, such as less than 2:1.

[0332] Further, as metal organic and inorganic base salts which are used as detergents can contribute to the sulfated ash content of a lubricating oil composition, in embodiments of the present invention, the amounts of such additives are minimized. In order to maintain a low sulfur level, salicylate detergents can be used, and the lubricating composition herein may comprise one or more salicylate detergents (said detergents are preferably used in amounts in the range of 0.05 to 20.0 wt. %, more preferably from 1.0 to 10.0 wt. % and most preferably in the range of from 2.0 to 5.0 wt. %, based on the total weight of the lubricating composition).

[0333] The total sulfated ash content of the lubricating composition herein is typically not greater than 2.0 wt. %, alternately at a level of not greater than 1.0 wt. % and alternately at a level of not greater than 0.8 wt. %, based on the total weight of the lubricating composition as determined by ASTM D874.

[0334] Furthermore, it is useful that each of the detergents, independently, have a TBN (total base number) value in the range of from 10 to 700 mgKOH/g, 10 to 500 mgKOH/g, alternately in the range of from 100 to 650, alternately in the range of from, 10 to 500 mgKOH/g, alternately in the range of from 30 to 350 mgKOH/g and alternately in the range of from 50 to 300 mgKOH/g, as measured by ISO 3771.

[0335] Typically, lubricating compositions formulated for use in a heavy duty diesel engines comprise detergents at from about 0.5 to about 10 wt. %, alternately from about 2.5 to about 7.5 wt. %, alternately from about 4 to about 6.5 wt. %, based on the lubricating composition.

#### D. Friction Modifiers

[0336] A friction modifier is any material or materials that can alter the coefficient of friction of a surface lubricated by any lubricant or fluid containing such material(s). Friction modifiers, also known as friction reducers, or lubricity agents or oiliness agents, and other such agents that change the ability of base oils, formulated lubricating compositions, or functional fluids, to modify the coefficient of friction of a lubricated surface may be effectively used in combination with the base oils or lubricating compositions of the present disclosure if desired. Friction modifiers that lower the coefficient of friction are particularly advantageous in combination with the base oils and lubricating compositions of this disclosure.

[0337] Illustrative friction modifiers may include, for example, organometallic compounds or materials, or mixtures thereof. Illustrative organometallic friction modifiers useful in the lubricating oil formulations of this disclosure include, for example, tungsten and or molybdenum compounds, such as molybdenum amine, molybdenum diamine, an organotungstenate, a molybdenum dithiocarbamate, molybdenum dithiophosphates, molybdenum amine complexes, molybdenum carboxylates, and the like, and mixtures thereof. Examples of useful molybdenum-

containing compounds may conveniently include molybdenum dithiocarbamates, trinuclear molybdenum compounds, for example as described in WO 98/26030, sulfides of molybdenum and molybdenum dithiophosphate.

[0338] Other known friction modifiers comprise oil-soluble organo-molybdenum compounds. Such organo-molybdenum friction modifiers may also provide antioxidant and antiwear credits to a lubricating oil composition. Examples of such oil-soluble organo-molybdenum compounds include dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and the like, and mixtures thereof. Particularly preferred are molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl xanthates and alkylthioxanthates.

[0339] Additionally, the molybdenum compound may be an acidic molybdenum compound. These compounds will react with a basic nitrogen compound as measured by ASTM test D-664 or D-2896 titration procedure and are typically hexavalent. Included are molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, and other alkali metal molybdates and other molybdenum salts, e.g., hydrogen sodium molybdate,  $\text{MoOCl}_4$ ,  $\text{MoO}_2\text{Br}_2$ ,  $\text{MoO}_3\text{Cl}_6$ , molybdenum trioxide or similar acidic molybdenum compounds.

[0340] Among the molybdenum compounds useful in the compositions of this invention are organo-molybdenum compounds of the formula

$\text{Mo}(\text{R}''\text{OCS})_2$  and

$\text{Mo}(\text{R}''\text{SCS})_2$

wherein  $\text{R}''$  is an organo group selected from the group consisting of alkyl, aryl, aralkyl and alkoxyalkyl, generally of from 1 to 30 carbon atoms, and preferably 2 to 12 carbon atoms and most preferably alkyl of 2 to 12 carbon atoms. Especially preferred are the dialkyldithiocarbamates of molybdenum.

[0341] Another group of organo-molybdenum compounds useful in the lubricating compositions of this invention are trinuclear molybdenum compounds, especially those of the formula  $\text{Mo}_3\text{S}_k\text{L}_n\text{Q}_z$  and mixtures thereof wherein the L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 to 7, Q is selected from the group of neutral electron donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. At least 21 carbon atoms should be present among all the ligand organo groups, such as at least 25, at least 30, or at least 35, carbon atoms.

[0342] Lubricating oil compositions useful in all aspects of the present invention preferably contain at least 10 ppm, at least 30 ppm, at least 40 ppm and more preferably at least 50 ppm molybdenum. Suitably, lubricating oil compositions useful in all aspects of the present invention contain no more than 1000 ppm, no more than 750 ppm or no more than 500 ppm of molybdenum. Lubricating oil compositions useful in all aspects of the present invention preferably contain from 10 to 1000, such as 30 to 750 or 40 to 500, ppm of molybdenum (measured as atoms of molybdenum).

[0343] For more information or useful friction modifiers containing Mo, please see U.S. Pat. No. 10,829,712 (column 8, line 58 to column 11, line 31).

[0344] Ashless friction modifiers may be present in the lubricating oil compositions of the present invention and are known generally and include esters formed by reacting carboxylic acids and anhydrides with alkanols and amine-based friction modifiers. Other useful friction modifiers generally include a polar terminal group (e.g., carboxyl or hydroxyl) covalently bonded to an oleophilic hydrocarbon chain. Esters of carboxylic acids and anhydrides with alkanols are described in U.S. Pat. No. 4,702,850. Examples of other conventional organic friction modifiers are described by M. Belzer in the "Journal of Tribology" (1992), Vol. 114, pp. 675-682 and M. Belzer and S. Jahanmir in "Lubrication Science" (1988), Vol. 1, pp. 3-26. Typically, the total amount of



organic ashless friction modifier in a lubricant according to the present invention does not exceed 5 wt. %, based on the total mass of the lubricating oil composition and preferably does not exceed 2 wt. % and more preferably does not exceed 0.5 wt. %.

[0345] Illustrative friction modifiers useful in the lubricating compositions described herein include, for example, alkoxyated fatty acid esters, alkanolamides, polyol fatty acid esters, borated glycerol fatty acid esters, fatty alcohol ethers, and mixtures thereof.

[0346] Illustrative alkoxyated fatty acid esters include, for example, polyoxyethylene stearate, fatty acid polyglycol ester, and the like. These can include polyoxypropylene stearate, polyoxybutylene stearate, polyoxyethylene isostearate, polyoxypropylene isostearate, polyoxyethylene palmitate, and the like.

[0347] Illustrative alkanolamides include, for example, lauric acid diethylalkanolamide, palmitic acid diethylalkanolamide, and the like. These can include oleic acid diethylalkanolamide, stearic acid diethylalkanolamide, oleic acid diethylalkanolamide, polyethoxylated hydrocarbylamides, polypropoxylated hydrocarbylamides, and the like.

[0348] Illustrative polyol fatty acid esters include, for example, glycerol mono-oleate, saturated mono-, di-, and tri-glyceride esters, glycerol mono-stearate, and the like. These can include polyol esters, hydroxyl-containing polyol esters, and the like.

[0349] Illustrative borated glycerol fatty acid esters include, for example, borated glycerol mono-oleate, borated saturated mono-, di-, and tri-glyceride esters, borated glycerol mono-stearate, and the like. In addition to glycerol polyols, these can include trimethylolpropane, pentaerythritol, sorbitan, and the like. These esters can be polyol monocarboxylate esters, polyol dicarboxylate esters, and on occasion polyoltricarboxylate esters. Preferred can be the glycerol mono-oleates, glycerol dioleates, glycerol trioleates, glycerol monostearates, glycerol distearates, and glycerol tristearates and the corresponding glycerol monopalmitates, glycerol dipalmitates, and glycerol tripalmitates, and the respective isostearates, linoleates, and the like. Ethoxylated, propoxylated, butoxylated fatty acid esters of polyols, especially using glycerol as underlying polyol are useful herein.

[0350] Illustrative fatty alcohol ethers include, for example, stearyl ether, myristyl ether, and the like. Alcohols, including those that have carbon numbers from C.sub.3 to C.sub.50, can be ethoxylated, propoxylated, or butoxylated to form the corresponding fatty alkyl ethers. The underlying alcohol portion can preferably be stearyl, myristyl, C.sub.11-C.sub.13 hydrocarbon, oleyl, isosteryl, and the like.

[0351] Useful concentrations of friction modifiers may range from 0.01 weight percent to 5 weight percent, or about 0.1 weight percent to about 2.5 weight percent, or about 0.1 weight percent to about 1.5 weight percent, or about 0.1 weight percent to about 1 weight percent. Concentrations of molybdenum-containing materials are often described in terms of Mo metal concentration.

Advantageous concentrations of Mo may range from 25 ppm to 700 ppm or more, and often with a preferred range of 50-200 ppm. Friction modifiers of all types may be used alone or in mixtures with the materials of this disclosure. Often mixtures of two or more friction modifiers, or mixtures of friction modifier(s) with alternate surface active material(s), are also desirable. For example, combinations of Mo containing compounds with polyol fatty acid esters, such as glycerol mono-oleate are useful herein.

#### E. Antioxidants

[0352] Antioxidants retard the oxidative degradation of base oils during service. Such degradation may result in deposits on metal surfaces, the presence of sludge, or a viscosity increase in a lubricant. A wide variety of oxidation inhibitors that are useful in lubricating oil compositions. See *Lubricants and Related Products*, Klamann, Wiley VCH, 1984; U.S. Pat. Nos. 4,798,684; and 5,084,197, for example.

[0353] Useful antioxidants include hindered phenols. These phenolic antioxidants may be ashless (metal-free) phenolic compounds or neutral or basic metal salts of certain phenolic compounds.

Typical phenolic antioxidant compounds are the hindered phenolics which contain a sterically hindered hydroxyl group, and these include those derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or p-position to each other. Typical phenolic antioxidants include the hindered phenols substituted with C.sub.6+ alkyl groups and the alkylene coupled derivatives of these hindered phenols. Examples of phenolic materials of this type 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-t-butyl-4-heptyl phenol; and 2-methyl-6-t-butyl-4-dodecyl phenol. Other useful hindered mono-phenolic antioxidants may include, for example, hindered 2,6-di-alkyl-phenolic propionic ester derivatives. Bis-phenolic antioxidants may also be advantageously used herein. Examples of ortho-coupled phenols include: 2,2'-bis(4-heptyl-6-t-butyl-phenol); 2,2'-bis(4-octyl-6-t-butyl-phenol); and 2,2'-bis(4-dodecyl-6-t-butyl-phenol). Para-coupled bisphenols include for example 4,4'-bis(2,6-di-t-butyl phenol) and 4,4'-methylene-bis(2,6-di-t-butyl phenol).

[0354] Effective amounts of one or more catalytic antioxidants may also be used. The catalytic antioxidants comprise an effective amount of a) one or more oil soluble polymetal organic compounds; and effective amounts of b) one or more substituted N,N'-diaryl-o-phenylenediamine compounds or c) one or more hindered phenol compounds; or a combination of both b) and c). Catalytic antioxidants useful herein are more fully described in U.S. Pat. No. 8,048,833.

[0355] Non-phenolic oxidation inhibitors which may be used include aromatic amine antioxidants and these may be used either as such or in combination with phenolics. Typical examples of non-phenolic antioxidants include: alkylated and non-alkylated aromatic amines such as aromatic monoamines of the formula R.sup.8R.sup.9R.sup.10N, where R.sup.8 is an aliphatic, aromatic or substituted aromatic group, R.sup.9 is an aromatic or a substituted aromatic group, and R.sup.10 is H, alkyl, aryl or R.sup.11S(O).sub.XR.sup.12 where R.sup.11 is an alkylene, alkenylene, or aralkylene group, R.sup.12 is an alkyl group, or an alkenyl, aryl, or alkaryl group, and x is 0, 1 or 2. The aliphatic group R.sup.8 may contain from 1 to about 20 carbon atoms, and preferably contains from about 6 to 12 carbon atoms. The aliphatic group is typically a saturated aliphatic group. Preferably, both R.sup.8 and R.sup.9 are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring aromatic group such as naphthyl. Aromatic groups R.sup.8 and R.sup.9 may be joined together with other groups such as S.

[0356] Typical aromatic amines antioxidants have alkyl substituent groups of at least about 6 carbon atoms. Examples of aliphatic groups include hexyl, heptyl, octyl, nonyl, and decyl. Generally, the aliphatic groups will not contain more than about 14 carbon atoms. The general types of amine antioxidants useful in the present compositions include diphenylamines, phenyl naphthylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more aromatic amines are also useful. Polymeric amine antioxidants can also be used. Particular examples of aromatic amine antioxidants useful in the present disclosure include: p,p'-dioctyldiphenylamine; t-octylphenyl-alpha-naphthylamine; phenyl-alphanaphthylamine; and p-octylphenyl-alpha-naphthylamine.

[0357] Sulfur containing anti-oxidants are also useful herein. In particular, one or more oil-soluble or oil-dispersible sulfur containing anti-oxidant(s) can be used as an antioxidant additive. For example, sulfurized alkyl phenols and alkali or alkaline earth metal salts thereof also are useful antioxidants herein. Suitably, the lubricating oil composition(s) of the present invention may include the one or more sulfur containing anti-oxidant(s) in an amount to provide the lubricating oil composition with from 0.02 to 0.2, preferably from 0.02 to 0.15, even more preferably 0.02 to 0.1, even more preferably 0.04 to 0.1, wt. % sulfur based on the total mass of the lubricating oil composition. Optionally the oil-soluble or oil-dispersible sulfur containing anti-oxidant(s) are selected from sulfurized C.sub.4 to C.sub.25 olefin(s), sulfurized aliphatic (C.sub.7 to C.sub.29) hydrocarbyl fatty acid ester(s), ashless sulfurized phenolic anti-oxidant(s), sulfur containing organo-molybdenum compound(s), and combinations thereof. For further information, on

sulfurized materials useful as anti-oxidants herein, please see U.S. Pat. No. 10,731,101 (column 15, line 55 to column 22, line 12).

[0358] Antioxidants useful herein include hindered phenols, arylamines. These antioxidants may be used individually by type or in combination with one another.

[0359] Typical antioxidants include: Irganox™ L67, ETHANOX™ 4702, Lanxess Additin™ R.sup.C 7110; ETHANOX™ 4782J; Irganox™ 1135, Irganox™ 5057, sulfurized lard oil and palm oil fatty acid methyl ester.

[0360] Antioxidant additives may be used in an amount of about 0.01 to 5 weight percent, preferably about 0.01 to 3 weight percent, more preferably 0.01 to 1.5 weight percent, more preferably 0.01 to less than 1 weight percent, based upon the weight of the lubricating composition.

[0361] Compositions according to the present disclosure may contain an additive having a different enumerated function that also has secondary effects as an antioxidant (for example, phosphorus-containing anti-wear agents (such as ZDDP) may also have antioxidant effects). These additives are not included as antioxidants for purposes of determining the amount of antioxidant in a lubricating oil composition or concentrate herein.

#### F. Pour Point Depressants

[0362] Conventional pour point depressants (also known as lube oil flow improvers) may be added to the compositions of the present disclosure if desired. These pour point depressant may be added to lubricating compositions of the present disclosure to lower the minimum temperature at which the fluid will flow or can be poured. Examples of suitable pour point depressants include polymethacrylates, polyacrylates, polyarylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, and terpolymers of dialkylfumarates, vinyl esters of fatty acids and allyl vinyl ethers. U.S. Pat. Nos. 1,815,022; 2,015,748; 2,191,498; 2,387,501; 2,655,479; 2,666,746; 2,721,877; 2,721,878; and 3,250,715 describe useful pour point depressants and/or the preparation thereof. Such additives may be used in an amount of about 0.01 to 5 weight percent, preferably about 0.01 to 1.5 weight percent.

#### G. Anti-Foam Agents

[0363] Anti-foam agents may advantageously be added to lubricant compositions described herein. These agents prevent or retard the formation of stable foams. Silicones and organic polymers are typical anti-foam agents. For example, polysiloxanes, such as silicon oil or polydimethyl siloxane, provide antifoam properties.

[0364] Anti-foam agents are commercially available and may be used in minor amounts such as 5 wt. % or less, 3 wt. % or less, 1 wt. % or less, 0.1 wt. % or less, such as from 5 to wt. % to 0.1 ppm such as from 3 wt. % to 0.5 ppm, such as from 1 wt. % to 10 ppm.

[0365] For example, it may be that the lubricating oil composition comprises an anti-foam agent comprising polyalkyl siloxane, such as a polydialkyl siloxane, for example wherein the alkyl is a C.sub.1-C.sub.10 alkyl group, e.g., a polydimethylsiloxane (PDMS), also known as a silicone oil. Alternately, the siloxane is a poly(R.sup.3) siloxane, wherein R.sup.3 is one or more same or different linear branched or cyclic hydrocarbyls, such as alkyls or aryls, typically having 1 to 20 carbon atoms. It may be that, for example, the lubricating oil composition comprises a polymeric siloxane compound according to Formula 1 below wherein R.sup.1 and R.sup.2 are independently methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl or decyl, phenyl, naphthyl, alkyl substituted phenyl, or isomers thereof (such as methyl, phenyl) and n is from 50 to 450.

[0366] Additionally, or alternatively, it may be that the lubricating oil composition comprises an organo modified siloxane (OMS), such as a siloxane modified with an organo group such as a polyether (e.g., ethylene-propylene oxide copolymer), long chain hydrocarbyl (e.g. C.sub.11-C.sub.100 alkyl), or aryl (e.g. C.sub.6-C.sub.14 aryl). It may be that, for example, the lubricating oil composition comprises an organo modified siloxane compound according to Formula 1, wherein n is from 50 to 450, and wherein R.sup.1 and R.sup.2 are the same or different, optionally wherein each of R.sup.1 and R.sup.2 is, independently an organo group, such as an organo group

selected from polyether (e.g. ethylene-propylene oxide copolymer), long chain hydrocarbyl (e.g. C.sub.11-C.sub.100 alkyl), or aryl (e.g. C.sub.6-C.sub.14 aryl). Preferably, one of R.sup.1 and R.sup.2 is CH.sub.3.

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[0367] Based on the total weight of the lubricant composition, the siloxane according to Formula 1 is incorporated so as to provide about 0.1 to less than about 30 ppm Si, or about 0.1 to about 25 ppm Si, or about 0.1 to about 20 ppm Si, or about 0.1 to about 15 ppm Si, or about 0.1 to about 10 ppm Si. More preferably, it is in the range of about 3-10 ppm Si.

[0368] In an embodiment, silicone antifoam agents useful herein are available from Dow Corning Corporation and Union Carbide Corporation, such as Dow Corning FS-1265 (1000 centistokes), Dow Corning DC-200, and Union Carbide UC-L45. Silicone anti-foamants useful herein are polydimethylsiloxane, phenyl-methyl polysiloxane, linear, cyclic or branched siloxanes, silicone polymers and copolymers, and organo-silicone copolymers. Also, a siloxane polyether copolymer antifoamant available from OSI Specialties, Inc. of Farmington Hills, Mich. and may be substituted or included. One such material is sold as SILWET-L-7220.

[0369] Acrylate polymer antifoam agent can also be used herein. Typical acrylate anti-foamants include polyacrylate antifoamant available from Monsanto Polymer Products Co. known as PC-1244. A preferred acrylate polymer antifoam agent useful herein is PX<sup>TM</sup>3841 (i.e., an alkyl acrylate polymer), commercially available from Dorf Ketl, also referred to as Mobilad<sup>TM</sup>C402.

[0370] In embodiments, a combination of silicone anti-foamant and acrylate anti-foamant can be used, such as at a weight ratio of the silicone anti-foamant to the acrylate anti-foamant of from about 5:1 to about 1:5, see for example US 2021/0189283A1.

#### H. Viscosity Modifiers

[0371] Viscosity modifiers (also referred to as viscosity index improvers or viscosity improvers) can be included in the lubricating compositions described herein. Viscosity modifiers provide lubricants with high and low temperature operability. These additives impart shear stability at elevated temperatures and acceptable viscosity at low temperatures. Suitable viscosity modifiers include high molecular weight hydrocarbons, polyesters, and viscosity modifier dispersants that can function as both a viscosity modifier and a dispersant. Typical molecular weights of these polymers are between about 10,000 to 1,500,000 g/mol, more typically about 20,000 to 1,200,000 g/mol, and even more typically between about 50,000 and 1,000,000 g/mol.

[0372] Examples of suitable viscosity modifiers are linear or star-shaped polymers and copolymers of methacrylate, butadiene, olefins, or alkylated styrenes. Polyisobutylene is a commonly used viscosity modifier. Another suitable viscosity modifier is polymethacrylate (copolymers of various chain length alkyl methacrylates, for example), some formulations of which also serve as pour point depressants. Other suitable viscosity modifiers include copolymers of ethylene and propylene, hydrogenated block copolymers of styrene and isoprene, and polyacrylates (copolymers of various chain length acrylates, for example). Specific examples include styrene-isoprene or styrene-butadiene based polymers of 50,000 to 200,000 g/mol molecular weight.

[0373] Copolymers useful as viscosity modifiers include those commercially available from Chevron Oronite Company LLC under the trade designation "PARATONE<sup>TM</sup>" (such as "PARATONE<sup>TM</sup> 8921," PARATONE<sup>TM</sup> 68231," and "PARATONE<sup>TM</sup> 8941"); from Afton Chemical Corporation under the trade designation "HiTEC<sup>TM</sup>" (such as HiTEC<sup>TM</sup> 5850B, and HiTEC<sup>TM</sup>5777); and from The Lubrizol Corporation under the trade designation "Lubrizol<sup>TM</sup> 7067C". Hydrogenated polyisoprene star polymers useful as viscosity modifiers herein include those commercially available from Infineum International Limited, e.g., under the trade designation "SV200" and "SV600". Hydrogenated diene-styrene block copolymers useful as viscosity modifiers herein are commercially available from Infineum International Limited, e.g., under the trade designation "SV 50".

[0374] Polymers useful as viscosity modifiers herein include polymethacrylate or polyacrylate

polymers, such as linear polymethacrylate or polyacrylate polymers, such as those available from Evonik Industries under the trade designation “Viscoplex™” (e.g., Viscoplex™ 6-954) or star polymers which are available from Lubrizol Corporation under the trade designation Asteric™ (e.g., Lubrizol™ 87708 and Lubrizol 87725).

[0375] Vinyl aromatic-containing polymers useful as viscosity modifiers herein may be derived from vinyl aromatic hydrocarbon monomers, such as styrenic monomers, such as styrene. Illustrative vinyl aromatic-containing copolymers useful herein may be represented by the following general formula: A-B wherein A is a polymeric block derived predominantly from vinyl aromatic hydrocarbon monomer (such as styrene), and B is a polymeric block derived predominantly from conjugated diene monomer (such as isoprene).

[0376] Typically, the viscosity modifiers may be used in an amount of about 0.01 to about 10 weight percent, such as about 0.1 to about 7 weight percent, such as 0.1 to about 4 weight percent, such as about 0.2 to about 2 weight percent, such as such as about 0.2 to about 1 weight percent, and such as such as about 0.2 to about 0.5 weight percent, based on the total weight of the formulated lubricant composition.

[0377] In embodiments, the viscosity modifier may be a functionalized, such as with one or more amines, imide, esters, alcohols, or the like to form a dispersant viscosity modifier (“DVM”). In embodiments, the lubricating composition of the invention comprises one or more dispersant viscosity modifiers. Suitable dispersant viscosity modifiers include functionalized polyolefins, for example, ethylene-propylene copolymers that have been functionalized with an acylating agent such as maleic anhydride and an amine; polymethacrylates functionalized with an amine, or esterified styrene-maleic anhydride copolymers reacted with an amine. More detailed description of dispersant viscosity modifiers are disclosed in International Publication WO2006/015130 or U.S. Pat. Nos. 4,863,623; 6,107,257; 6,107,258; and 6,117,825. In embodiments, the dispersant viscosity modifier may include those described in U.S. Pat. No. 4,863,623 (see column 2, line 15 to column 3, line 52) or in International Publication WO2006/015130 (see page 2, paragraph [0008] and preparative examples are described at paragraphs [0065] to [0073]).

[0378] Useful DVM's also include functionalized polymers described in U.S. Ser. No. 63/379,006, filed Oct. 11, 2022, including but not limited to amide, imide, ester and/or alcohol functionalized partially or fully saturated polymer comprising C.sub.45 olefins having an Mw/Mn of less than 2, a Functionality Distribution (Fd) value of 3.5 or less, and an Mn of 10,000 g/mol or more of the polymer prior to functionalization, provided that, if the polymer prior to functionalization is a copolymer of isoprene and butadiene, then the Mn of the copolymer is greater than 25,000 g/mol. The dispersant viscosity modifier may be present at 0 to 5 wt. %, or 0.01 to 4 wt. %, or 0.05 to 2 wt. % of the lubricating composition.

[0379] Viscosity modifiers are typically added as concentrates, in large amounts of diluent oil. The “as delivered” viscosity modifier or dispersant viscosity modifier typically contains from 20 weight percent to 75 weight percent of an active polymer for polymethacrylate or polyacrylate polymers, or from 8 weight percent to 20 weight percent of an active polymer for olefin copolymers, hydrogenated polyisoprene star polymers, or hydrogenated diene-styrene block copolymers, in the “as delivered” polymer concentrate.

#### I. Dispersants

[0380] During engine operation, oil-insoluble oxidation byproducts are produced. Dispersants help keep these byproducts in solution, thus diminishing their deposition on metal surfaces. Dispersants used in the formulation of the lubricating compositions herein may be ashless or ash-forming in nature. Preferably, the dispersant is ashless. So called ashless dispersants are organic materials that form substantially no ash upon combustion. For example, non-metal-containing or borated metal-free dispersants are considered ashless. In contrast, metal-containing detergents tend form ash upon combustion.

[0381] Dispersants useful herein typically contain a polar group attached to a relatively high

molecular weight hydrocarbon chain. The polar group typically contains at least one element of nitrogen, oxygen, or phosphorus. Typical hydrocarbon chains contain 50 to 400 carbon atoms.

Dispersants of (Poly)Alkenylsuccinic Derivatives

[0382] A particularly useful class of dispersants includes the (poly)alkenylsuccinic derivatives, typically produced by the reaction of a long chain hydrocarbyl substituted succinic compound, usually a hydrocarbyl substituted succinic anhydride, with a polyhydroxy or polyamino compound. The long chain hydrocarbyl group constituting the oleophilic portion of the molecule which confers solubility in the oil, is often a polyisobutylene group (typically the long chain hydrocarbyl group, such as a polyisobutylene group, has an Mn of 400 to 3000 g/mol, such as 450 to 2500 g/mol). Many examples of this type of dispersant are well known commercially and in the literature. Exemplary U.S. patents describing such dispersants include U.S. Pat. Nos. 3,172,892; 3,2145,707; 3,219,666; 3,316,177; 3,341,542; 3,444,170; 3,454,607; 3,541,012; 3,630,904; 3,632,511; 3,787,374 and 4,234,435. Other types of dispersant are described in U.S. Pat. Nos. 3,036,003; 3,200,107; 3,254,025; 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,413,347; 3,697,574; 3,725,277; 3,725,480; 3,726,882; 4,454,059; 3,329,658; 3,449,250; 3,519,565; 3,666,730; 3,687,849; 3,702,300; 4,100,082; 5,705,458. A further description of dispersants useful herein may be found, for example, in European Patent Application No. 0 471 071 and European Patent Application No. 0 451 380, to which reference is made for this purpose.

[0383] Hydrocarbyl-substituted succinic acid and hydrocarbyl-substituted succinic anhydride derivatives are useful dispersants. In particular, succinimide, succinate esters, or succinate ester amides prepared by the reaction of a hydrocarbon-substituted succinic acid or anhydride compound (typically having at least 25 carbon atoms, such as 28 to 400 carbon atoms, in the hydrocarbon substituent), with at least one equivalent of with a polyhydroxy or polyamino compound (such as an alkylene amine) are particularly useful herein. Hydrocarbyl-substituted succinic acid and hydrocarbyl-substituted succinic anhydride derivatives may have a number average molecular weight of at least 400 g/mol, such as at least 900 g/mol, such as at least 1500 g/mol, such as from 400 and 4000 g/mol, such as from 800 to 3000, such as from 2000 and 2800 g/mol, such from about 2100 to 2500 g/mol, and such as from about 2200 to about 2400 g/mol.

[0384] Succinimides, which are particularly useful herein, are formed by the condensation reaction between: 1) hydrocarbyl substituted succinic anhydrides, such as polyisobutylene succinic anhydride (PIBSA); and 2) polyamine (PAM). Examples of suitable polyamines include: polyalkylene polyamines, hydroxy-substituted polyamines, polyoxyalkylene polyamines, and combinations thereof. Examples of polyalkylene polyamines include tetraethylene pentamine, pentaethylene hexamine, tetraethylenepentamine (TEPA), pentaethylenhexamine (PEHA), n-phenyl-p-phenylenediamine (ADPA), and other polyamines having an average of 5, 6, 7, 8, or 9 nitrogen atoms per molecule). Mixtures where the average number of nitrogen atoms per polyamine molecule is greater than 7 are commonly called heavy polyamines or H-PAMs and may be commercially available under trade names such as HPA™ and HPA-X™ from Dow Chemical, E-100™ from Huntsman Chemical, et al. Examples of hydroxy-substituted polyamines include N-hydroxyalkyl-alkylene polyamines such as N-(2-hydroxyethyl)ethylene diamine, N-(2-hydroxyethyl)piperazine, and/or N-hydroxyalkylated alkylene diamines of the type described, for example, in U.S. Pat. No. 4,873,009. Examples of polyoxyalkylene polyamines include polyoxyethylene and/or polyoxypropylene diamines and triamines (as well as co-oligomers thereof) having an average Mn from about 200 to about 5000 g/mol. Products of this type are commercially available under the tradename Jeffamine™ Representative examples of useful succinimides are shown in U.S. Pat. Nos. 3,087,936; 3,172,892; 3,219,666; 3,272,746; 3,322,670; 3,652,616; 3,948,800; 6,821,307; and Canada Patent No. 1,094,044.

[0385] Succinate esters useful as dispersants include those formed by the condensation reaction between hydrocarbyl substituted succinic anhydrides and alcohols or polyols. For example, the condensation product of a hydrocarbyl substituted succinic anhydride and pentaerythritol is a useful

dispersant.

[0386] Succinate ester amides useful herein are formed by a condensation reaction between hydrocarbyl substituted succinic anhydrides and alkanol amines. Suitable alkanol amines include ethoxylated polyalkylpolyamines, propoxylated polyalkylpolyamines, and polyalkenylpolyamines such as polyethylene polyamines and or propoxylated hexamethylenediamine. Representative examples are shown in U.S. Pat. No. 4,426,305.

[0387] Hydrocarbyl substituted succinic anhydrides (such as PIBSA) esters of hydrocarbyl bridged aryloxy alcohols are also useful as dispersants herein. For information on such dispersants, please see U.S. Pat. No. 7,485,603, particularly, column 2, line 65 to column 6, line 22 and column 23, line 40 to column 26, line 46. In particular PIBSA esters of methylene-bridged naphthoxy ethanol (i.e., 2-hydroxyethyl-1-naphthol ether (or hydroxy-terminated ethylene oxide oligomer ether of naphthol) are useful herein.

[0388] The molecular weight of the hydrocarbyl substituted succinic anhydrides used in the preceding paragraphs will typically range from 350 to 4000 g/mol, such as 400 to 3000 g/mol, such as 450 to 2800 g/mol, such as 800 to 2500 g/mol. The above (poly)alkenylsuccinic derivatives can be post-reacted with various reagents such as sulfur, oxygen, formaldehyde, carboxylic acids such as oleic acid.

[0389] The dispersant may be present in the lubricant in an amount 0.1 wt. % to 20 wt. % of the composition, such as 0.2 to 15 wt. %, such as 0.25 to 10 wt. %, such as 0.3 to 5 wt. %, such as 1.0 wt. % to 3.0 wt. % of the lubricating oil composition.

[0390] The above (poly)alkenylsuccinic derivatives, can also be post reacted with boron compounds such as boric acid, borate esters or highly borated dispersants, to form borated dispersants generally having from about 0.1 to about 5 moles of boron per mole of dispersant reaction product.

[0391] Dispersants useful herein include borated succinimides, including those derivatives from mono-succinimides, bis-succinimides, and/or mixtures of mono- and bis-succinimides, wherein the hydrocarbyl succinimide is derived from a hydrocarbylene group such as polyisobutylene having a Mn of from about 300 to about 5000 g/mol, or from about 500 to about 3000 g/mol, or about 1000 to about 2000 g/mol, or a mixture of such hydrocarbylene groups, often with high terminal vinylic groups.

[0392] The boron-containing dispersant may be present at 0.01 wt. % to 20 wt. %, or 0.1 wt. % to 15 wt. %, or 0.1 wt. % to 10 wt. %, or 0.5 wt. % to 8 wt. %, or 1.0 wt. % to 6.5 wt. %, or 0.5 wt. % to 2.2 wt. % of the lubricating composition.

[0393] The boron-containing dispersant may be present in an amount to deliver boron to the composition at 15 ppm to 2000 ppm, or 25 ppm to 1000 ppm, or 40 ppm to 600 ppm, or 80 ppm to 350 ppm.

[0394] The borated dispersant may be used in combination with non-borated dispersant and may be the same or different compound as the non-borated dispersant. In one embodiment, the lubricating composition may include one or more boron-containing dispersants and one or more non-borated dispersants, wherein the total amount of dispersant may be 0.01 wt. % to 20 wt. %, or 0.1 wt. % to 15 wt. %, or 0.1 wt. % to 10 wt. %, or 0.5 wt. % to 8 wt. %, or 1.0 wt. % to 6.5 wt. %, or 0.5 wt. % to 2.2 wt. % of the lubricating composition and wherein the ratio of borated dispersant to non-borated dispersant may be 1:10 to 10:1 (weight:weight) or 1:5 to 3:1 or 1:3 to 2:1.

#### Dispersants of Mannich Bases

[0395] Mannich base dispersants useful herein are typically made from the reaction of an amine component, a hydroxy aromatic compound (substituted or unsubstituted, such as alkyl substituted), such as alkylphenols, and an aldehyde, such as formaldehyde. See U.S. Pat. Nos. 4,767,551 and 10,899,986. Process aids and catalysts, such as oleic acid and sulfonic acids, can also be part of the reaction mixture. Representative examples are shown in U.S. Pat. Nos. 3,697,574; 3,703,536; 3,704,308; 3,751,365; 3,756,953; 3,798,165; 3,803,039; 4,231,759 9,938,479; 7,491,248;

10,899,986, and WO 01/42399.

#### Dispersants of Polymethacrylate or Polyacrylate Derivatives

[0396] Polymethacrylate or polyacrylate derivatives are another class of dispersants useful herein. These dispersants are typically prepared by reacting a nitrogen containing monomer and a methacrylic or acrylic acid esters containing 5-25 carbon atoms in the ester group. Representative examples are shown in U.S. Pat. Nos. 2,100,993, and 6,323,164. Polymethacrylate and polyacrylate dispersants are typically lower molecular weights.

[0397] The lubricating composition of the invention typically comprises dispersant at 0.1 wt. % to 20 wt. % of the composition, such as 0.2 to 15 wt. %, such as 0.25 to 10 wt. %, such as 0.3 to 5 wt. %, such as 1.0 wt. % to 3.0 wt. % of the lubricating oil composition. Alternately the dispersant may be present at 0.1 wt. % to 5 wt. %, or 0.01 wt. % to 4 wt. %, or 0.05 wt. % to 2 wt. % of the lubricating composition.

[0398] For further information on dispersants useful herein, please see U.S. Pat. No. 10,829,712 column 13, line 36 to column 16, line 67; and U.S. Pat. No. 7,485,603, column 2, line 65 to column 6, line 22, column 8, line 25 to column 14, line 53, and column 23, line 40 to column 26, line 46.

#### J. Corrosion Inhibitors/Antirust Agents

[0399] Corrosion inhibitors may be used to reduce the corrosion of metals and are often alternatively referred to as metal deactivators or metal passivators. Some corrosion inhibitors may alternatively be characterized as antioxidants.

[0400] Suitable corrosion inhibitors may include nitrogen and/or sulfur containing heterocyclic compounds such as triazoles (e.g., benzotriazoles), substituted thiadiazoles, imidazoles, thiazoles, tetrazoles, hydroxyquinolines, oxazolines, imidazolines, thiophenes, indoles, indazoles, quinolines, benzoxazines, dithiols, oxazoles, oxatriazoles, pyridines, piperazines, triazines and derivatives of any one or more thereof. A particular corrosion inhibitor is a benzotriazole represented by the structure:

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wherein R<sup>sup.8</sup> is absent (hydrogen) or is a C<sub>sub.1</sub> to C<sub>sub.20</sub> hydrocarbyl or substituted hydrocarbyl group which may be linear or branched, saturated or unsaturated. It may contain ring structures that are alkyl or aromatic in nature and/or contain heteroatoms such as N, O, or S. Examples of suitable compounds may include benzotriazole, alkyl-substituted benzotriazoles (e.g., tolyltriazole, ethylbenzotriazole, hexylbenzotriazole, octylbenzotriazole, etc.), aryl substituted benzotriazole, alkylaryl- or arylalkyl-substituted benzotriazoles, and the like, as well as combinations thereof. For instance, the triazole may comprise or be a benzotriazole and/or an alkylbenzotriazole in which the alkyl group contains from 1 to about 20 carbon atoms or from 1 to about 8 carbon atoms. Non-limiting examples of such corrosion inhibitors may comprise or be benzotriazole, tolyltriazole, and/or optionally substituted benzotriazoles such as Irgamet™ 39, which is commercially available from BASF of Ludwigshafen, Germany. A preferred corrosion inhibitor may comprise or be benzotriazole and/or tolyltriazole.

[0401] Additionally, or alternatively, the corrosion inhibitor may include a substituted thiadiazoles represented by the structure:

##STR00023##

wherein R<sup>sup.15</sup> and R<sup>sup.16</sup> are independently hydrogen or a hydrocarbon group, which group may be aliphatic or aromatic, including cyclic, alicyclic, aralkyl, aryl and alkaryl, and wherein each w is independently 1, 2, 3, 4, 5, or 6 (preferably 2, 3, or 4, such as 2). These substituted thiadiazoles are derived from the 2,5-dimercapto-1,3,4-thiadiazole (DMTD) molecule. Many derivatives of DMTD have been described in the art, and any such compounds may be included in the fluid used in the present disclosure. For example, U.S. Pat. Nos. 2,719,125, 2,719,126, and 3,087,937 describe the preparation of various 2, 5-bis-(hydrocarbon dithio)-1,3,4-thiadiazoles.

[0402] Further additionally or alternatively, the corrosion inhibitor may include one or more other derivatives of DMTD, such as a carboxylic ester in which R<sup>sup.15</sup> and R<sup>sup.16</sup> may be joined to



the sulfide sulfur atom through a carbonyl group. Preparation of these thioester containing DMTD derivatives is described, for example, in U.S. Pat. No. 2,760,933. DMTD derivatives produced by condensation of DMTD with alpha-halogenated aliphatic carboxylic acids having at least 10 carbon atoms are described, for example, in U.S. Pat. No. 2,836,564. This process produces DMTD derivatives wherein R<sup>sup.15</sup> and R<sup>sup.16</sup> are HOOC—CH(R<sup>sup.19</sup>)—(R<sup>sup.19</sup> being a hydrocarbyl group). DMTD derivatives further produced by amidation, or esterification of these terminal carboxylic acid groups may also be useful.

[0403] The preparation of 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazoles is described, for example, in U.S. Pat. No. 3,663,561.

[0404] A class of DMTD derivatives may include mixtures of a 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazole and a 2,5-bis-hydrocarbyldithio-1,3,4-thiadiazole. Such mixtures may be sold under the tradename HiTEC® 4313 and are commercially available from Afton Chemical Company.

[0405] The preparation of 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazoles is described, for example, in U.S. Pat. No. 3,663,561.

[0406] A class of DMTD derivatives may include mixtures of a 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazole and a 2,5-bis-hydrocarbyldithio-1,3,4-thiadiazole. Such mixtures may be sold under the tradename HiTEC™ 4313 and are commercially available from Afton Chemical Company.

[0407] Still further additionally or alternatively, the corrosion inhibitor may include a trifunctional borate having the structure, B(OR<sup>sup.46</sup>)<sub>3</sub>, in which each R<sup>sup.46</sup> may be the same or different. As the borate may typically be desirably compatible with the non-aqueous medium of the composition, each R<sup>sup.46</sup> may in particular comprise or be a hydrocarbyl C<sub>sub.1</sub>-C<sub>sub.8</sub> moiety. For compositions in which the non-aqueous medium comprises or is a lubricating oil basestock, for example, better compatibility can typically be achieved when the hydrocarbyl moieties are each at least C<sub>sub.4</sub>. Non-limiting examples of such corrosion inhibitors thus include, but are not limited to, triethylborate, tripropylborates such as triisopropylborate, tributylborates such as tri-tert-butylborate, tripentylborates, trihexylborates, trioctylborates such as tri-(2-ethylhexyl)borate, monohexyl dibutylborate, and the like, as well as combinations thereof.

[0408] When used, a corrosion inhibitor may comprise a substituted thiadiazole, a substituted benzotriazole, a substituted triazole, a trisubstituted borate, or a combination thereof.

[0409] When desired, corrosion inhibitors can be used in any effective amount, but, when used, may typically be used in amounts from about 0.001 wt. % to 5.0 wt. %, based on the weight of the composition, e.g., from 0.005 wt. % to 3.0 wt. % or from 0.01 wt. % to 1.0 wt. %. Alternately, Such additives may be used in an amount of about 0.01 to 5 weight percent, preferably about 0.01 to 1.5 weight percent, based upon the weight of the lubricating composition.

[0410] In some embodiments, 3,4-oxypyridinone-containing compositions may contain substantially no (e.g., 0, or less than 0.001 wt. %, 0.0005 wt. % or less, not intentionally added, and/or absolutely no) triazoles, benzotriazoles, substituted thiadiazoles, imidazoles, thiazoles, tetrazoles, hydroxyquinolines, oxazolines, imidazolines, thiophenes, indoles, indazoles, quinolines, benzoxazines, dithiols, oxazoles, oxatriazoles, pyridines, piperazines, triazines, derivatives thereof, combinations thereof, or all corrosion inhibitors.

#### K. Antiwear Agents

[0411] Antiwear agents described herein exclude compounds represented by the formula (I) above. Compositions according to the present disclosure may contain an additive having a different enumerated function that also has secondary effects as an anti-wear (for example, organo-molybdenum friction modifiers (such as molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl xanthates and alkylthioxanthates) may also have anti-wear effects). These additives are not included as anti-wear additives for purposes of determining the amount of anti-wear additives in a lubricating oil composition or concentrate herein.

[0412] The lubricating oil composition of the present invention can contain one or more anti-wear agents that can reduce friction and excessive wear. Any anti-wear agent known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable anti-wear agents include zinc dithiophosphate, metal (e.g., Pb, Sb, Mo and the like) salts of dithiophosphates, metal (e.g., Zn, Pb, Sb, Mo and the like) salts of dithiocarbamates, metal (e.g., Zn, Pb, Sb and the like) salts of fatty acids, boron compounds, phosphate esters, phosphite esters, amine salts of phosphoric acid esters or thiophosphoric acid esters, reaction products of dicyclopentadiene and thiophosphoric acids and combinations thereof. The amount of the anti-wear agent may vary from about 0.01 wt. % to about 5 wt. %, from about 0.05 wt. % to about 3 wt. %, or from about 0.1 wt. % to about 1 wt. %, based on the total weight of the lubricating oil composition.

[0413] In embodiments, the anti-wear agent is or comprises a dihydrocarbyl dithiophosphate metal salt, such as zinc dialkyl dithiophosphate compounds. The metal of the dihydrocarbyl dithiophosphate metal salt may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. In some embodiments, the metal is zinc. In other embodiments, the alkyl group of the dihydrocarbyl dithiophosphate metal salt has from about 3 to about 22 carbon atoms, from about 3 to about 18 carbon atoms, from about 3 to about 12 carbon atoms, or from about 3 to about 8 carbon atoms. In further embodiments, the alkyl group is linear or branched.

[0414] Useful anti-wear agents also include substituted or unsubstituted thiophosphoric acids, and salts thereof include zinc-containing compounds such as zinc dithiophosphate compounds selected from zinc dialkyl-, diaryl- and/or alkylaryl-dithiophosphates.

[0415] A metal alkylthiophosphate and more particularly a metal dialkyl dithio phosphate in which the metal constituent is zinc, or zinc dialkyl dithio phosphate (ZDDP) can be a useful component of the lubricating compositions of this disclosure. ZDDP can be derived from primary alcohols, secondary alcohols or mixtures thereof. ZDDP compounds generally are of the formula  $Zn[SP(S)(OR_{sup.1})(OR_{sup.2})]_{sub.2}$  where  $R_{sup.1}$  and  $R_{sup.2}$  are  $C_{sub.1}-C_{sub.18}$  alkyl groups, preferably  $C_{sub.2}-C_{sub.12}$  alkyl groups. These alkyl groups may be straight chain or branched. Alcohols used in the ZDDP can be 2-propanol, butanol, secondary butanol, pentanols, hexanols such as 4-methyl-2-pentanol, n-hexanol, n-octanol, 2-ethyl hexanol, alkylated phenols, and the like. Mixtures of secondary alcohols or of primary and secondary alcohol can be used. Alkyl aryl groups may also be used. Useful zinc dithiophosphates include secondary zinc dithiophosphates such as those available from The Lubrizol Corporation under the trade designations "LZ 677A", "LZ 1095" and "LZ 1371", from Chevron Oronite under the trade designation "OLOA 262" and from Afton Chemical under the trade designation "HITEC™ 7169".

[0416] The ZDDP is typically used in amounts of from about 0.4 weight percent to about 1.2 weight percent, preferably from about 0.5 weight percent to about 1.0 weight percent, and more preferably from about 0.6 weight percent to about 0.8 weight percent, based on the total weight of the lubricating composition, although more or less can often be used advantageously. Preferably, the ZDDP is a secondary ZDDP and present in an amount of from about 0.6 to 1.0 weight percent of the total weight of the lubricating composition.

[0417] In embodiments, the zinc compound can be a zinc dithiocarbamate complex, such as the zinc dithiocarbamates represented by the formula:

##STR00024##

where each  $R_{sub.I}$  is independently a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon moiety having from 1 to about 10 carbon atoms,  $n$  is 0, 1, or 2,  $L$  is a ligand that saturates the coordination sphere of zinc, and  $x$  is 0, 1, 2, 3, or 4. In certain embodiments, the ligand,  $L$ , is selected from the group consisting of water, hydroxide, ammonia, amino, amido, alkylthiolate, halide, and combinations thereof.

[0418] The ZDDP and or the zinc carbamates are typically used in amounts of from about 0.4 weight percent to about 1.2 weight percent, preferably from about 0.5 weight percent to about 1.0

weight percent, and more preferably from about 0.6 weight percent to about 0.8 weight percent, based on the total weight of the lubricating composition, although more or less can often be used advantageously. Preferably, the ZDDP is a secondary ZDDP and present in an amount of from about 0.6 to 1.0 weight percent of the total weight of the lubricating composition.

[0419] Antiwear additives useful herein also include boron-containing compounds, such as borate esters, borated fatty amines, borated epoxides, alkali metal (or mixed alkali metal or alkaline earth metal) borates and borated overbased metal salts.

#### L. Other Additives

[0420] Other optional additives include de-emulsifiers see 10,829,712 (Col 20, ln 34-40). Typically, a small amount of a demulsifying component may be used herein. A preferred demulsifying component is described in EP 330,522. It is obtained by reacting an alkylene oxide with an adduct obtained by reacting a bis-epoxide with a polyhydric alcohol.

[0421] Other optional additives include seal compatibility agents such as organic phosphates, aromatic esters, aromatic hydrocarbons, esters (butylbenzyl phthalate, for example), and polybutenyl succinic anhydride. Such additives may be used in an amount of about 0.001 to 5 weight percent, preferably about 0.01 to 2 weight percent.

[0422] When lubricating oil compositions contain one or more of the additives discussed above, the additive(s) are typically blended into the composition in an amount sufficient for it to perform its intended function. Typical amounts of such additives useful in the present disclosure, especially for use in crankcase lubricants, are shown in Table 1 below.

[0423] It is noted that many of the additives are shipped from the additive manufacturer as a concentrate, containing one or more additives together, with a certain amount of base oil or other diluents. Accordingly, the weight amounts in the Table below, as well as other amounts mentioned herein, are directed to the amount of active ingredient (that is the non-diluent portion of the ingredient). The weight percent (wt. %) indicated below is based on the total weight of the lubricating oil composition.

#### Typical Amounts of Optional Lubricating Oil Components in LOC

TABLE-US-00001 ADDITIVE FORMULATIONS				A (wt. %)	B (wt. %)	C (wt. %)	Dispersant
(borated 0.1-40 1-20 4 to 15 and non-borated)				Detergents	0.1-20	0.2-15	2 to 10
Colloidal particles				0.01-10	0.01-5	0.11 to 5	Amine and or phenol
Antioxidant Sulfurized fatty acid ester				0.01-20	0.1 to 10	0.5- 5	Molybdenum containing
0.1 to 7				0.1 to 5	compound	Antifoaming Agent	0.001-5
0-5				0-1.5	0.1 to 5	Viscosity Modifier	0.01-25
5-15				Linear alpha olefin	0 to 10	0.1 to 5	Optional additional additives
0-20				0.1-10	0.1-5	Basestock Balance	Balance
Balance				Balance	Balance	Balance	Balance

#### Typical Amounts of Optional Lubricating Oil Components in LOC (Continued)

TABLE-US-00002 ADDITIVE FORMULATIONS				D (wt. %)	E (wt. %)	F (wt. %)	Dispersant
borated 0.1-10 0.5-8 0.5-5				Dispersant non-borated	0.1 to 30	0.5 to 20	1 to 15
Detergent				0.1-19.8	0.25-9	0.25 to 5	Colloidal Particles
0.01-9.8				0.1-8	0.5 to 5	Functionalized olefin	0.1-15
0.5-5				0.5 to 3	copolymer	Amine and or phenol (preferably	0.01-7
0.10-5				1 to 5	amine)	based antioxidant	Sulfurized fatty acid ester
0.01-20				0.1 to 10	0.5-5	Molybdenum containing	0.01-10
0.1 to 7				0.1 to 5	compound	Antifoaming Agent	0.0-5
0-1.5				0.1 to 5	Viscosity Modifier	0.01-25	1-20
5-15				Linear Alpha Olefin	0 to 10	0.1 to 5	Optional additional additives
0-20				0.1-10	0.1-10	Basestock Balance	Balance
Balance				Balance	Balance	Balance	Balance

[0424] The foregoing additives are typically commercially available materials. These additives may be added independently but are usually pre-combined in packages which can be obtained from suppliers of lubricant oil additives. Additive packages with a variety of ingredients, proportions and characteristics are available and selection of the appropriate package will take the use of the ultimate composition into account.

[0425] In another aspect the lubricating oil compositions described herein contain from 500 to 3000

ppm, alternately 500 to 2800 ppm, of group 4, 5, 10, 11, 12, or 13 metal (such as group 10, 11, 12, or 13 metal, such as zinc).

[0426] Preferably the lubricating oil composition described herein contain from 500 to 3000 ppm, alternately 500 to 2800 ppm, of metal selected from the group consisting of nickel, palladium, platinum, copper, silver, gold, zinc, tin, zirconium, hafnium, titanium, vanadium, molybdenum, niobium, and tantalum (such as zinc).

[0427] Alternately, the lubricating oil composition described herein contains from 500 to 3000 ppm, alternately 500 to 2800 ppm, alternately 500 to 2000 ppm, of zinc.

[0428] Alternately, the lubricating oil composition described herein contains from 600 to 4000 ppm, alternately 700 to 3000 ppm, alternately 800 to 2500 ppm, of zinc derived from the zinc colloidal particles and any ZDDP (zinc dialkyldithiophosphate) and or ZDDC (zinc dialkyldithiocarbamate) present.

[0429] Alternately, zinc dialkyl dithiophosphates are present in the lubricating compositions described herein at 1 wt. % or less, such as 0.5 wt. % or less, such as 0.1 wt. % or less, such as 0.01 wt. % or less, or the dialkyl dithiophosphates are absent.

[0430] Alternately, zinc dialkyldithiocarbamate are absent, or present in the lubricating compositions described herein at 1 wt. % or less, such as 0.5 wt. % or less, such as 0.1 wt. % or less, such as 0.01 wt. % or less.

[0431] Alternately, zinc dialkyl dithiophosphates and zinc dialkyldithiocarbamates are present in the lubricating compositions described herein at 1 wt. % or less, such as 0.5 wt. % or less, such as 0.1 wt. % or less, such as 0.01 wt. % or less.

[0432] Alternately the lubricating composition described herein an adhesive wear result of 100 hours or more (ASTM D 8074-16) and a ratio of Zn to P (elemental mass basis) of 1.1 to 5.0 (such as 1.1 to 4.9, or 1.1 to 4.8, or 1.1 to 4.7, or 1.2 to 4.7, or 1.3 to 4.5, or 2.5 to 4.0) by wt. %, where the lubricating composition contains a zinc containing compound other than zinc dialkyl dithiophosphate and or zinc dialkyldithiocarbamate.

[0433] Alternately the lubricating composition described herein has an adhesive wear of 100 hours or more (ASTM D 8074-16) and at least 1000 ppm zinc, where the lubricating composition contains a zinc containing compound other than zinc dialkyl dithiophosphate and or zinc dialkyldithiocarbamate.

[0434] Alternately the lubricating composition described herein has an adhesive wear of 100 hours or more (ASTM D 8074-16).

## Fuels

[0435] This invention also relates to a method of lubricating an automotive internal combustion engine during operation of the engine comprising: [0436] (i) providing to a crankcase of the automotive internal combustion engine an automotive crankcase the lubricating composition as described herein; [0437] (ii) providing a hydrocarbon fuel in the automotive internal combustion engine; and [0438] (iii) combusting the fuel in the automotive internal combustion engine, such as a spark-ignited or compression-ignited two- or four-stroke reciprocating engine, such as a diesel engine or passenger car engine (such as a spark-ignited combustion engine).

[0439] This invention also relates to a fuel composition comprising the lubricating oil compositions described herein and a hydrocarbon fuel, wherein the fuel may be derived from petroleum and or biological sources ("biofuel" or "renewable fuel"). In embodiments, the fuel comprises from 0.1 to 100 wt. % renewable fuel, alternately from 1 to 75 wt. % renewable fuel, alternately from 5 to 50 wt. % renewable fuel, based upon the total mass of the from 1 to 50 wt. % renewable fuel and the petroleum derived fuel.

[0440] The renewable fuel component is typically produced from vegetable oil (such as palm oil, rapeseed oil, soybean oil, jatropha oil), microbial oil (such as algae oil), animal fats (such as cooking oil, animal fat, and/or fish fat) and or biogas. Renewable fuel refers to biofuel produced from biological resources formed through contemporary biological processes. In an embodiment,

the renewable fuel component is produced by means of a hydrotreatment process. Hydrotreatment involves various reactions where molecular hydrogen reacts with other components, or the components undergo molecular conversions in the presence of molecular hydrogen and a solid catalyst. The reactions include, but are not limited to, hydrogenation, hydrodeoxygenation, hydrodesulfurization, hydrodenitrification, hydrodemetallization, hydrocracking, and isomerization. The renewable fuel component may have different distillation ranges which provide the desired properties to the component, depending on the intended use.

[0441] Furthermore, the lubricating compositions may be used in any type of combustion engines, for example in automotive, or in trucks, or marine engines, gas engines, large engines, or turbines. They may be used in any engine using petrol, gasoline, or diesel, or alternative fuels such as liquified natural gas (LNG), ammonia, hydrogen and the like.

#### Uses

[0442] The lubricating oils describe herein are useful in a range of internal combustion engines such as compression-ignited and spark-ignited engines. Examples include engines for passenger cars, light commercial vehicles and heavy duty on-highway trucks; engines for aviation, power-generation, locomotive and marine equipment/engines; and heavy duty off-highway engines such as may be used for agriculture, construction and mixing.

[0443] The lubricating compositions of the invention may be useful as marine lubricants, such as trunk piston engine oils (TPEOs), MDCLs (marine diesel cylinder lubricants), system oils, and such.

[0444] Furthermore, the lubricating compositions may be used as transmission fluids or oils, or gear oils.

[0445] Also, the lubricating compositions of the invention may be useful as lubricants for natural gas engines (e.g., natural gas is the fuel the engines run on, commonly called GEOs or [natural] gas engine oils).

[0446] The lubricating compositions of the invention may be used to lubricate mechanical engine components, particularly in internal combustion engines, e.g., spark-ignited or compression-ignited two- or four-stroke reciprocating engines, by adding the lubricant thereto. Typically, they are crankcase lubricants such as passenger car motor oils or heavy duty diesel engine lubricants.

[0447] In particular, the lubricating compositions of the present invention are suitably used in the lubrication of the crankcase of a compression-ignited internal combustion engine, such as a heavy duty diesel engine. The lubricating compositions of present invention are particularly suitable for internal combustion engines that are prone to piston-liner wear from long duration of operation, hence the invention might extend engine lifetime.

[0448] In particular, the lubricating compositions of the present invention are suitably used in the lubrication of the crankcase of a spark-ignited turbo charged internal combustion engine.

[0449] The lubricating oils of this disclosure are particularly useful in high compression spark ignition internal combustion engines.

[0450] The invention further relates to a use of a composition as described herein before, as an antiwear additive in a combustion engine oil, transmission or gear oil, the composition comprising or resulting from the admixing of: [0451] (A) from 1 to less than 50 mass % of one or more base oils, based upon the weight of the composition; [0452] (B) at least one phosphorus-containing compound selected from detergents, friction modifiers or antiwear additives other than the colloidal particles described in (C); [0453] (C) from 0.1 to 50 mass %, based upon the weight of the composition, of colloidal particles comprising: [0454] a) a core of one or more hydrocarbon insoluble zinc containing compounds, and [0455] b) a shell of one or more of: [0456] 1) one or more metal containing surfactants, where the metal, M, comprises a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; and the surfactant comprises an hydrocarbyl-substituted aromatic sulfonate of Formula (I), or an hydrocarbyl-substituted salicylate group of Formula (II),

##STR00025##

[0457] wherein each R.sup.A, and R.sup.B is, independently of each other, a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 1 to 70 carbon atoms, wherein, for  $n > 1$ , the sum of the number of carbon atoms in the total of R.sup.A groups in Formula (I) and the sum of the number of carbon atoms in the total of R.sup.B groups in Formula (II) is 100 or less carbon atoms, and Ar is a mono- or polycyclic aromatic group; n is an integer from 1 to the maximum possible number of substitutions on Ar, m is an integer of 1 to 3, x is an integer from 1 to 5; y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; [0458] 2) one or more metal alkanoates represented by the formula (III):

##STR00026##

[0459] wherein M is a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; R.sup.C is selected from a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 70 carbon atoms, or an aromatic or alkyl aromatic group with the aromatic group having from 6 to 20 carbon atoms and the alkyl group having 1 to 20 carbon atoms; x is an integer from 1 to 5, wherein for  $x > 1$  the R.sup.C groups may be the same or different, y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8;

[0460] wherein the composition has a ratio of Zn to P (elemental mass basis as measured by ASTM D5185) of 1.1 to 5.0; optionally with all the preferred colloidal components as described herein.

[0461] The invention further relates to:

[0462] 1. A lubricating oil composition comprising or resulting from the admixing of: [0463] (A) from 1 to 99.99 wt. %, based upon the weight of the lubricating composition, of one or more base oils; [0464] (B) at least one phosphorus-containing compound selected from detergents, friction modifiers or antiwear additives other than the colloidal particles described in (C); [0465] (C) from 0.01 to 10 wt. %, based upon the weight of the composition, of colloidal particles comprising:

[0466] a) a core of one or more hydrocarbon insoluble zinc containing compounds, and [0467] b) a shell of one or more of: [0468] 1) one or more metal containing surfactants, where the metal, M, comprises a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; and the surfactant comprises a hydrocarbyl-substituted sulfonate of Formula (I), or an hydrocarbyl-substituted salicylate group of Formula (II),

##STR00027## [0469] wherein each of R.sup.A and R.sup.B is, independently of each other, a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 1 to 70 carbon atoms, wherein, for  $n > 1$ , the sum of the number of carbon atoms in the total of R.sup.A groups in Formula (I) and the sum of the number of carbon atoms in the total of R.sup.B groups in Formula (II) is 100 or less carbon atoms, and Ar is a mono- or polycyclic aromatic group; n is an integer from 1 to the maximum possible number of substitutions on Ar, with  $n = 1$  if  $m = 0$ ; m is an integer of 1 to 3, x is an integer from 1 to 5; y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; [0470] 2) one or more metal alkanoates represented by the formula (III):

##STR00028## [0471] wherein M is a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; R.sup.C is selected from a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 70 carbon atoms, or an aromatic or alkyl aromatic group with the aromatic group having from 6 to 20 carbon atoms and the alkyl group having 1 to 20 carbon atoms; x is an integer from 1 to 5, wherein for  $x > 1$  the R.sup.C groups may be the same or different, y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8. [0472] wherein the lubricating oil composition has a ratio of Zn to P (elemental mass basis as measured by ASTM D5185) of 1.1 to 5.0.

[0473] 2. The lubricating composition of paragraph 1, wherein the hydrocarbon insoluble zinc containing compound is selected from at least one of zinc, zinc oxide, zinc hydroxide, zinc carbonate, and zinc halides, or mixtures thereof.

[0474] 3. The lubricating composition of paragraph 1 or 2, wherein the colloidal particles have a mean particle diameter as determined by dynamic light scattering in the range of 5 nm to 1  $\mu$ m, such as 20 nm to 500 nm, or 20 nm to 200 nm.

[0475] 4. The lubricating composition of any one of paragraphs 1 to 3, wherein the metal M in Formula (I), (II), or (III) is selected from at least one of sodium, potassium, lithium, magnesium, calcium, barium, or mixtures thereof; or wherein the metal M is selected from at least one of gold, silver, palladium, platinum, zirconium, vanadium, molybdenum, nickel, copper, zinc, aluminum, or mixtures thereof.

[0476] 5. The lubricating composition of any one of paragraphs 1 to 4, wherein Ar in Formula (I) or Formula (II) is benzene or naphthalene.

[0477] 6. The lubricating composition of paragraph 5, wherein the surfactant of Formula (I) is a metal containing hydrocarbyl-substituted phenyl sulfonate surfactant of Formula (Ia),  
##STR00029## [0478] wherein M is selected from calcium, magnesium, barium, or zinc, or combinations thereof, such as calcium, magnesium, or zinc, or calcium, or zinc; R<sup>sup.A</sup> is independently of each other a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 50 carbon atoms, such as 10 to 40, or 12 to 37 carbon atoms; n is an integer from 1 to 5, such as 1 to 4, such as 1, 2, or 3, such as 1, with n=1 if m=0; m is 0 to 3, such as 0, or 1; the sum of the number of carbon atoms in the total of R<sup>sup.A</sup> groups is 60 or less carbon atoms; x is 2; y is 2; and, optionally, p is 0.

[0479] 7. The lubricating composition of paragraph 5, wherein the surfactant of Formula (II) is a metal containing hydrocarbyl-substituted phenyl salicylate surfactant of Formula (IIa),  
##STR00030## [0480] wherein M is selected from calcium, magnesium, barium, or zinc, or combinations thereof; such as calcium, magnesium, or zinc, or combinations thereof; or calcium, or zinc, or combinations thereof; R<sup>sup.B</sup> is independently of each other a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 50 carbon atoms, such as 10 to 48, or 12 to 37 carbon atoms; n is an integer from 1 to 4, such as 1 to 3, such as 1, or 2, such as 1; the sum of the number of carbon atoms in the total of R<sup>sup.B</sup> groups is 60 or less carbon atoms; x is 2, y is 2; and, optionally, p is 0.

[0481] 8. The lubricating composition of any one of paragraphs 1 to 7, wherein M in Formula (I), (Ia), (II), (IIa), or (III) is selected from calcium, magnesium, or zinc, or combinations thereof; such as calcium, or zinc, or combinations thereof.

[0482] 9. The lubricating composition of any one of paragraphs 1 to 8, wherein R in Formula (III) is a linear, cyclic, or branched, alkyl or alkenyl group having from 6 to 48 carbon atoms, such as 8 to 40, or 10 to 20 carbon atoms.

[0483] 10. The lubricating composition paragraph 9, wherein the metal alkanoate of Formula (III) is one or more of zinc neodecanoate, zinc neoundecanoate, zinc neododecanoate, zinc neotridecanoate, zinc neotetradecanoate, zinc neopentadecanoate, zinc neohexadecanoate, zinc neoheptadecanoate, zinc stearate, zinc neo-octadecanoate, zinc oleate, zinc neononadecanoate, and zinc neoeicosanoate.

[0484] 11. The lubricating composition of paragraph 9 or 10, wherein the metal alkanoates have a quaternary carbon atom at the 2 position, i.e., attached to the carboxylate group.

[0485] 12. The lubricating composition of any one of paragraphs 1 to 11, further comprising one or more components selected from the group consisting of one or more friction modifiers; one or more antioxidants; one or more pour point depressants; one or more anti-foaming agents; one or more viscosity modifiers; one or more dispersants; one or more inhibitors and/or anti-rust agents; and/or one or more anti-wear agents, other than those of component (C).

[0486] 13. The lubricating composition of any one of paragraphs 1 to 12, wherein: [0487] (A) the base oil is present at 50 to 99 wt. % based upon the weight of the lubricating composition; [0488] (B) the at least one phosphorus-containing compound selected from detergents, friction modifiers, or antiwear additives other than the colloidal particles described in (C) is present in an amount of 0.001 to 5 wt.-%; [0489] C) the colloidal particles are present at from 0.01 to 10 wt. %, such as 0.01 to 6 wt. % based on total weight of the lubricating composition; [0490] D) optionally, one or more friction modifiers other than those of component (B) are present at from 0.01 to 5 wt. %, and

based on total weight of the lubricating composition; [0491] E) optionally, one or more antioxidants are present at from 0.01 to 10 wt. %, based on total weight of the lubricating composition; [0492] F) optionally, one or more pour point depressants are present at from 0.01 to 5 wt. %, based on total weight of the lubricating composition; [0493] G) optionally, one or more anti-foaming agents are present at from 0.001 to 5 wt. %, based on total weight of the lubricating composition; [0494] H) optionally, one or more viscosity modifiers are present at from 0.001 to 6 wt. %, based on total weight of the lubricating composition; [0495] I) optionally, one or more dispersants are present at from 0.01 to 20 wt. %, based on total weight of the lubricating composition; [0496] J) optionally, one or more inhibitors and/or anti-rust agents are present at from 0.01 to 5 wt. %, based on total weight of the lubricating composition; and [0497] K) optionally, one or more anti-wear agents, other than those of components (B) and (C), are present at from 0.001 to 5 wt. %, based on total weight of the lubricating composition; [0498] L) optionally, one or more detergents, other than those of components (B) and in the colloidal particles described in (C) are present at from 0.1 to 20 wt. % based on total weight of the lubricating composition.

[0499] 14. The lubricating composition of any one of paragraphs 1 to 13, wherein the lubricating composition has an adhesive wear of 100 hours or more, such as 120 hours or more, 130 hours or more, or 140 hours or more, as measured by ASTM D8074-16.

[0500] 15. The lubricating composition of any one of paragraphs 1 to 14, wherein a ratio of Zn to P (elemental mass basis) is 1.1 to 4.9, such as 1.1 to 4.8, such as 1.1 to 4.7, such as 1.2 to 4.7, or 1.3 to 4.5, 1.4 to 4.5, 1.5 to 4.5, or 2.5 to 4.0, in the lubricating composition.

[0501] 16. The lubricating composition of any one of paragraphs 1 to 15, wherein the ligand L is selected from the group consisting of water, hydroxide, halide, ammonia, amino, amido, alcoholate, and mixtures thereof.

[0502] 17. The lubricating composition of any one of paragraphs 1 to 16, wherein the colloidal particles have a molar ratio of metal to surfactant, MR, of at least 5, such as 5 to 50, or 6 to 40, or 7 to 30.

[0503] 18. The lubricating composition of any one of paragraphs 1 to 17, wherein a total base number (TBN) of the composition is from 1 to 30 mgKOH/g, such as 5 to 25 mgKOH/g, 5 to 20 mgKOH/g, such as 7 to 17 mgKOH/g, such as 13 to 15 mgKOH/g, as measured by ASTM D2896.

[0504] 19. The lubricating composition of any one of paragraphs 1 to 18, having a zinc content of 500 ppm or more, such as 800 ppm or more, or 1000 ppm or more, such as 1500 ppm or more, or 2000 ppm or more, as determined by ASTM D5185.

[0505] 20. The lubricating composition of any one of paragraphs 1 to 18, having a phosphorus content of not more than 2000 ppm, such as not more than 1600 ppm, not more than 1200 ppm, such as not more than 800 ppm, such as 1 to 1600 ppm, such as 10 to 1200 ppm, such as 100 to 800 parts per million (ppm), based on the total mass of the lubricating compositions, as measured by ASTM D5185.

[0506] 21. The lubricating composition of any one of paragraphs 1 to 20, wherein the lubricating composition is a combustion engine oil, such as a petrol or gasoline or heavy-duty diesel engine oil, or a marine engine oil, or a gas turbine oil.

[0507] 22. The lubricating composition of any one of paragraphs 1 to 20, wherein the lubricating composition is transmission fluid or gear oil.

[0508] 23. The lubricating composition of any one of paragraphs 1 to 22, comprising more than 500 ppm of Zn and less than 500 ppm of P, preferably more than 1000 ppm of Zn and less than 1000 ppm of P, wherein the lubricating composition has an adhesive wear of 100 hours or more, and optionally a total base number of 7 mgKOH/g or more.

[0509] 24. The lubricating composition of any one of paragraphs 1 to 23, wherein zinc dialkyl dithiophosphates are present at 2 wt. % or less, such as 1 wt. % or less.

[0510] 25. The lubricating composition of any one of paragraphs 1 to 24, wherein the lubricating composition has a wear scar volume of less than 150  $\mu\text{m}^3$ , such as less than 140  $\mu\text{m}^3$ , or



less than 135  $\mu\text{m}$ .sup.3, determined by HFRR method as described herein.

[0511] 26. A method to obtain an adhesive wear of 100 hours or more (ASTM D 8074-16) for a lubricating composition having 500 ppm or more, preferably 1000 ppm zinc or more comprising: [0512] (i) providing to a crankcase of the internal combustion engine an automotive crankcase the lubricating composition of any of paragraphs 1 to 24; [0513] (ii) providing a hydrocarbon fuel in the internal combustion engine; and [0514] (iii) combusting the fuel in the internal combustion engine.

[0515] 27. A method of lubricating an automotive internal combustion engine during operation of the engine comprising: [0516] (i) providing to a crankcase of the internal combustion engine an automotive crankcase the lubricating composition of any of paragraphs 1 to 24; [0517] (ii) providing a hydrocarbon fuel in the internal combustion engine; and [0518] (iii) combusting the fuel in the internal combustion engine.

[0519] 28. The method paragraph 27 wherein the engine is a diesel engine or gas engine.

[0520] 29. The method paragraph 27 wherein the engine is a marine engine.

[0521] 30. The method paragraph 27 wherein the engine is an automotive engine.

[0522] 31. A concentrate composition comprising or resulting from the admixing of: [0523] (A) from 1 to less than 50 wt. % of one or more base oils, based upon the weight of the concentrate composition; [0524] (B) at least one phosphorus-containing compound selected from detergents, friction modifiers or antiwear additives other than the colloidal particles described in (C); [0525] (C) from 0.1 to 50 wt. %, based upon the weight of the composition, of colloidal particles as described in any one of the previous claims, comprising: [0526] a) a core of one or more hydrocarbon insoluble zinc containing compounds, and [0527] b) a shell of one or more of: [0528] 1) one or more metal containing surfactants, where the metal, M, comprises a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; and the surfactant comprises an hydrocarbyl-substituted sulfonate of Formula (I), or an hydrocarbyl-substituted salicylate group of Formula (II),  
##STR00031## [0529] wherein each R.sup.A, and R.sup.B is, independently of each other, a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 1 to 70 carbon atoms, wherein, for  $n > 1$ , the sum of the number of carbon atoms in the total of R.sup.A groups in Formula (I) and the sum of the number of carbon atoms in the total of R.sup.B groups in Formula (II) is 100 or less carbon atoms, and Ar is a mono- or polycyclic aromatic group; n is an integer from 1 to the maximum possible number of substitutions on Ar, with  $n = 1$  if  $m = 0$ ; m is an integer of 0 to 3, x is an integer from 1 to 5; y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; [0530] 2) one or more metal alkanoates represented by the formula (III):

##STR00032## [0531] wherein M is a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; R.sup.C is selected from a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 70 carbon atoms, or an aromatic or alkyl aromatic group with the aromatic group having from 6 to 20 carbon atoms and the alkyl group having 1 to 20 carbon atoms; x is an integer from 1 to 5, wherein for  $x > 1$  the R.sup.C groups may be the same or different, y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; [0532] wherein the concentrate composition has a ratio of Zn to P (elemental mass basis as measured by ASTM D5185) of 1.1 to 5.0.

[0533] 29. A use of a composition as an antiwear additive in a combustion engine, transmission, or gear oil, the composition comprising or resulting from the admixing of: [0534] (A) from 1 to less than 50 wt. % of one or more base oils, based upon the weight of the composition; [0535] (B) at least one phosphorus-containing compound selected from detergents, friction modifiers or antiwear additives other than the colloidal particles described in (C); [0536] (C) from 0.1 to 50 wt. %, based upon the weight of the composition, of colloidal particles as described in any one of the previous claims, comprising: [0537] a) a core of one or more hydrocarbon insoluble zinc containing compounds, and [0538] b) a shell of one or more of: [0539] 1) one or more metal containing

surfactants, where the metal, M, comprises a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; and the surfactant comprises an hydrocarbyl-substituted aromatic sulfonate of Formula (I), or an hydrocarbyl-substituted salicylate group of Formula (II),

##STR00033## [0540] wherein each R.sup.A, and R.sup.B is, independently of each other, a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 1 to 70 carbon atoms, wherein, for  $n > 1$ , the sum of the number of carbon atoms in the total of R.sup.A groups in Formula (I) and the sum of the number of carbon atoms in the total of R.sup.B groups in Formula (II) is 100 or less carbon atoms, and Ar is a mono- or polycyclic aromatic group; n is an integer from 1 to the maximum possible number of substitutions on Ar, with  $n = 1$  if  $m = 0$ ; m is an integer of 0 to 3, x is an integer from 1 to 5; y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; [0541] 2) one or more metal alkanoates represented by the formula (III):

##STR00034## [0542] wherein M is a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; R.sup.C is selected from a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 70 carbon atoms, or an aromatic or alkyl aromatic group with the aromatic group having from 6 to 20 carbon atoms and the alkyl group having 1 to 20 carbon atoms; x is an integer from 1 to 5, wherein for  $x > 1$  the R.sup.C groups may be the same or different, y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; [0543] wherein the composition has a ratio of Zn to P (elemental mass basis as measured by ASTM D5185) of 1.1 to 5.0.

[0544] 30. A method of lubricating an internal combustion engine during operation of the engine comprising: [0545] (i) providing the lubricating composition of lubricating composition of any of paragraphs 1 to 24 to a crankcase of the internal combustion engine; [0546] (ii) providing fuel in the internal combustion engine; and [0547] (iii) combusting the fuel in the internal combustion engine, wherein the fuel comprises hydrocarbon fuel derived from petroleum and or biological sources; hydrogen fuel, optionally combined with liquified natural gas; and or ammonia fuel.

[0548] This invention also relates to:

[0549] 1A. A lubricating composition comprising or resulting from the admixing of: [0550] (A) from 1 to 99.99 wt. %, based upon the weight of the lubricating composition, of one or more base oils; [0551] (B) at least one phosphorus-containing compound selected from detergents, friction modifiers or antiwear additives other than the colloidal particles described in (C); (C) from 0.01 to 10 wt. %, based upon the weight of the composition, of colloidal particles comprising: [0552] a) a core of one or more hydrocarbon insoluble zinc containing compounds, and [0553] b) a shell of one or more of: [0554] 1) one or more metal containing surfactants, where the metal, M, comprises a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; and the surfactant comprises a hydrocarbyl-substituted sulfonate of Formula (I), or an hydrocarbyl-substituted salicylate group of Formula (II),

##STR00035## [0555] wherein each of R.sup.A and R.sup.B is, independently of each other, a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 1 to 70 carbon atoms, wherein, for  $n > 1$ , the sum of the number of carbon atoms in the total of R.sup.A groups in Formula (I) and the sum of the number of carbon atoms in the total of R.sup.B groups in Formula (II) is 100 or less carbon atoms, and Ar is a mono- or polycyclic aromatic group; n is an integer from 1 to the maximum possible number of substitutions on Ar, with  $n = 1$  if  $m = 0$ ; m is an integer of 1 to 3, x is an integer from 1 to 5; y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; [0556] 2) one or more metal alkanoates represented by the formula (III):

##STR00036## [0557] wherein M is a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; R.sup.C is selected from a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 70 carbon atoms, or an aromatic or alkyl aromatic group with the aromatic group having from 6 to 20 carbon atoms and the alkyl group having 1 to 20 carbon atoms; x is an integer from 1 to 5, [0558] wherein for  $x > 1$  the R.sup.C groups may be the same or different, y is an

integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8, wherein the lubricating oil composition has a ratio of Zn to P (elemental mass basis as measured by ASTM D5185) of 1.1 to 5.0.

[0559] 2A. The lubricating composition of paragraph 1, wherein the hydrocarbon insoluble zinc containing compound is selected from at least one of zinc, zinc oxide, zinc hydroxide, zinc carbonate, and zinc halides, or mixtures thereof.

[0560] 3A. The lubricating composition of paragraph 1 or 2, wherein the colloidal particles have a mean particle diameter as determined by dynamic light scattering in the range of 5 nm to 1  $\mu$ m, such as 20 nm to 500 nm, or 20 nm to 200 nm.

[0561] 4A. The lubricating composition of any one of paragraphs 1 to 3, wherein the metal M in Formula (I), (II), or (III) is selected from at least one of sodium, potassium, lithium, magnesium, calcium, barium, or mixtures thereof; or wherein the metal M is selected from at least one of gold, silver, palladium, platinum, zirconium, vanadium, molybdenum, nickel, copper, zinc, aluminum, or mixtures thereof.

[0562] 5A. The lubricating composition of any one of paragraphs 1 to 4, wherein Ar in Formula (I) or Formula (II) is benzene or naphthalene.

[0563] 6A. The lubricating composition of any one of paragraphs 1 to 5, further comprising one or more components selected from the group consisting of one or more friction modifiers; one or more antioxidants; one or more pour point depressants; one or more anti-foaming agents; one or more viscosity modifiers; one or more dispersants; one or more inhibitors and/or anti-rust agents; and/or one or more anti-wear agents, other than those of component (C).

[0564] 7A. The lubricating composition of any one of paragraphs 1 to 6, wherein: [0565] (A) the base oil is present at 50 to 99 wt. % based upon the weight of the lubricating composition; [0566] (B) the at least one phosphorus-containing compound selected from detergents, friction modifiers, or antiwear additives other than the colloidal particles described in (C) is present in an amount of 0.001 to 5 wt.-%; [0567] C) the colloidal particles are present at from 0.01 to 10 wt. %, such as 0.01 to 6 wt. % based on total weight of the lubricating composition; [0568] D) optionally, one or more friction modifiers other than those of component (B) are present at from 0.01 to 5 wt. %, based on total weight of the lubricating composition; [0569] E) optionally, one or more antioxidants are present at from 0.01 to 10 wt. %, based on total weight of the lubricating composition; [0570] F) optionally, one or more pour point depressants are present at from 0.01 to 5 wt. %, based on total weight of the lubricating composition; [0571] G) optionally, one or more anti-foaming agents are present at from 0.001 to 5 wt. %, based on total weight of the lubricating composition; [0572] H) optionally, one or more viscosity modifiers are present at from 0.001 to 6 wt. %, based on total weight of the lubricating composition; [0573] I) optionally, one or more dispersants are present at from 0.01 to 20 wt. %, based on total weight of the lubricating composition; [0574] J) optionally, one or more inhibitors and/or anti-rust agents are present at from 0.01 to 5 wt. %, based on total weight of the lubricating composition; and [0575] K) optionally, one or more anti-wear agents, other than those of components (B) and (C), are present at from 0.001 to 5 wt. % based on total weight of the lubricating composition; [0576] L) optionally, one or more detergents, other than those of components (B) and in the colloidal particles described in (C) are present at from 0.1 to 20 wt. % based on total weight of the lubricating composition.

[0577] 8A. The lubricating composition of any one of paragraphs 1 to 7, wherein the lubricating composition has an adhesive wear of 100 hours or more, such as 120 hours or more, 130 hours or more, or 140 hours or more, as measured by ASTM D8074-16.

[0578] 9A. The lubricating composition of any one of paragraphs 1 to 8, having a zinc content of 500 ppm or more, such as 800 ppm or more, or 1000 ppm or more, such as 1500 ppm or more, or 2000 ppm or more, as determined by ASTM D5185.

[0579] 10A. The lubricating composition of any one of paragraphs 1 to 9, having a phosphorus content of not more than 2000 ppm, such as not more than 1600 ppm, not more than 1200 ppm,

such as not more than 800 ppm, such as 1 to 1600 ppm, such as 10 to 1200 ppm, such as 100 to 800 parts per million (ppm), based on the total mass of the lubricating compositions, as measured by ASTM D5185.

[0580] 11A. A method to obtain an adhesive wear of 100 hours or more (ASTM D 8074-16) for a lubricating composition having 500 ppm or more, preferably 1000 ppm zinc or more comprising: [0581] (i) providing to a crankcase of the internal combustion engine an automotive crankcase the lubricating composition of any of paragraphs 1 to 10; [0582] (ii) providing a hydrocarbon fuel in the internal combustion engine; and [0583] (iii) combusting the fuel in the internal combustion engine.

[0584] 12A. A method of lubricating an automotive internal combustion engine during operation of the engine comprising: [0585] (i) providing to a crankcase of the internal combustion engine an automotive crankcase the lubricating composition of any of paragraphs 1 to 10; [0586] (ii) providing a hydrocarbon fuel in the internal combustion engine; and [0587] (iii) combusting the fuel in the internal combustion engine.

[0588] 13A. The method paragraph 12 wherein the engine is a diesel engine, a gas engine, or a marine engine.

[0589] 14A. A concentrate composition comprising or resulting from the admixing of: [0590] (A) from 1 to less than 50 wt. % of one or more base oils, based upon the weight of the concentrate composition; [0591] (B) at least one phosphorus-containing compound selected from detergents, friction modifiers or antiwear additives other than the colloidal particles described in (C); [0592] (C) from 0.1 to 50 wt. %, based upon the weight of the composition, of colloidal particles comprising: [0593] a) a core of one or more hydrocarbon insoluble zinc containing compounds, and [0594] b) a shell of one or more of: [0595] 1) one or more metal containing surfactants, where the metal, M, comprises a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; and the surfactant comprises an hydrocarbyl-substituted sulfonate of Formula (I), or an hydrocarbyl-substituted salicylate group of Formula (II),

##STR00037## [0596] wherein each R.sup.A, and R.sup.B is, independently of each other, a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 1 to 70 carbon atoms, wherein, for n>1, the sum of the number of carbon atoms in the total of R.sup.A groups in Formula (I) and the sum of the number of carbon atoms in the total of R.sup.B groups in Formula (II) is 100 or less carbon atoms, and Ar is a mono- or polycyclic aromatic group; n is an integer from 1 to the maximum possible number of substitutions on Ar, with n=1 if m=0; m is an integer of 0 to 3, x is an integer from 1 to 5; y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; [0597] 2) one or more metal alkanoates represented by the formula (III):

##STR00038## [0598] wherein M is a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; R.sup.C is selected from a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 70 carbon atoms, or an aromatic or alkyl aromatic group with the aromatic group having from 6 to 20 carbon atoms and the alkyl group having 1 to 20 carbon atoms; x is an integer from 1 to 5, wherein for x>1 the R.sup.C groups may be the same or different, y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; [0599] wherein the concentrate composition has a ratio of Zn to P (elemental mass basis as measured by ASTM D5185) of 1.1 to 5.0.

[0600] 15A. A use of a composition as an antiwear additive in a combustion engine, transmission, or gear oil, the composition comprising or resulting from the admixing of: [0601] (A) from 1 to less than 50 wt. % of one or more base oils, based upon the weight of the composition; [0602] (B) at least one phosphorus-containing compound selected from detergents, friction modifiers or antiwear additives other than the colloidal particles described in (C); (C) from 0.1 to 50 wt. %, based upon the weight of the composition, of colloidal particles comprising: [0603] a) a core of one or more hydrocarbon insoluble zinc containing compounds, and [0604] b) a shell of one or more of:

[0605] 1) one or more metal containing surfactants, where the metal, M, comprises a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; and the surfactant comprises an hydrocarbyl-substituted aromatic sulfonate of Formula (I), or an hydrocarbyl-substituted salicylate group of Formula (II),  
##STR00039## [0606] wherein each R.sup.A, and R.sup.B is, independently of each other, a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 1 to 70 carbon atoms, wherein, for  $n > 1$ , the sum of the number of carbon atoms in the total of R.sup.A groups in Formula (I) and the sum of the number of carbon atoms in the total of R.sup.B groups in Formula (II) is 100 or less carbon atoms, and Ar is a mono- or polycyclic aromatic group; n is an integer from 1 to the maximum possible number of substitutions on Ar, with  $n = 1$  if  $m = 0$ ; m is an integer of 0 to 3, x is an integer from 1 to 5; y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; [0607] 2) one or more metal alkanoates represented by the formula (III):

##STR00040## [0608] wherein M is a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; R.sup.C is selected from a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 70 carbon atoms, or an aromatic or alkyl aromatic group with the aromatic group having from 6 to 20 carbon atoms and the alkyl group having 1 to 20 carbon atoms; x is an integer from 1 to 5, wherein for  $x > 1$  the R.sup.C groups may be the same or different, y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; [0609] wherein the composition has a ratio of Zn to P (elemental mass basis as measured by ASTM D5185) of 1.1 to 5.0.

#### Experimental

[0610] All molecular weights are number average unless otherwise noted.

[0611] Mn (number average molecular weight), Mw (weight average molecular weight, and Mz (z average molecular weight) are determined according to the GPC procedure in the Experimental section of U.S. Ser. No. 63/379,006, filed Oct. 11, 2022, and reported in g/mol.

[0612] A.I. or a.i. is active ingredient.

#### Testing Procedures

[0613] Total Base Number is determined according to ASTM D2896 and reported in units of mgKOH/g.

[0614] HTHS150 (High Temperature High Shear 150) is determined according to ASTM D4683-20 and reported in units of centipoise (cP).

[0615] Viscosity index is measured according to ASTM D2270.

[0616] KV.sub.100 is Kinematic viscosity measured at 100° C. according to ASTM D445-19a.

[0617] Phosphorus content was determined according to ASTM D5185.

[0618] Zinc content in colloidal particle preparation samples was determined by inductively coupled plasma atomic emission spectroscopy according to ASTM D4951. Zinc content in oil formulations was determined by inductively coupled plasma atomic emission spectroscopy according to ASTM D5185.

[0619] Antiwear performance was determined via bench testing (High Frequency Reciprocating Rig-HFRR), and engine testing (DD13 Scuff—ASTM D8074-16).

[0620] HFRR Testing: The oils were tested using a High Frequency Reciprocating Rig (HFRR) available from PCS Instruments, London. In this test, a steel ball is loaded and reciprocated against the face of a steel disc. The load between the ball and the disc was set at 4N giving a contact pressure of 1.046 Gpa. The ball was driven with a frequency of 40 Hz over a stroke length of 1 mm for a duration of 300 minutes, with an increase of 20° C. every 60 minutes from 40° C. to 120° C. Tests were conducted in duplicate to provide wear scar volumes for each example. Wear scars were measured using optical profilometry (ZeScope Surface Mapping System, ZEMETRICS).

[0621] Adhesive Wear testing was performed according to ASTM D8074-16. The DD13 Scuffing Test (ASTM D8074-16) evaluates the liner scuffing and ring distress performance of engine oils in turbocharged and intercooled four-cycle diesel engines equipped with exhaust gas recycling (EGR),

uncoated top rings, and running on ultra-low sulfur diesel fuel. The test engine is a four stroke Detroit Diesel DD13 12.8 L, six-cylinder diesel engine with EGR. The engine is disassembled prior to each test, the parts solvent-cleaned and measured, and rebuilt using all new pistons, uncoated rings, cylinder liners, and connecting rod bearings. The test is performed using ASTM D8074-16 Standard Test Method for Evaluation of Diesel Engine Oils in DD13 Diesel Engine, version 20170104, where the time to scuff determination is from an end of test rating liner scuffing which is to not exceed 27%, a change in iron between any 2-hour interval which is not to exceed 25 ppm, and a crankcase pressure which is not to exceed 2 kPa absolute. The pass limit to meet the specification set by Detroit Diesel is the time to scuff of 31 hours minimum.

[0622] DLS measurement for particle size determination was done as follows: A sample is prepared for DLS analysis by diluting in heptane to approximately 2 wt %, and mixed using a vortex mixer and allowing to settle for 30 minutes before filtering through a 0.45  $\mu\text{m}$  filter. The sample is then transferred to a quartz cuvette with a 10 mm path length. Using a Malvern Zetasizer Nano, the sample is analyzed at 25° C. The sample is equilibrated for two minutes before measuring three positions in the sample. The raw data is then analyzed using Origin Pro to determine the half height full width and centroid for any peaks by integration of the volume curve, giving a volume average particle size.

#### Materials

[0623] PIB is polyisobutylene.

[0624] PIBSA is polyisobutylene succinic anhydride.

[0625] PIBSA-PAM is polyisobutylene succinic anhydride—polyalkylene amine.

[0626] M.sub.n is number average molecular weight.

#### EXAMPLES

[0627] The invention will now be described in the following examples which are not intended to limit the scope of the claims hereof.

#### Preparation of Example Colloidal Systems:

##### Example 1a—ZnO-Core, Zn-Alkylphenylsulfonate Shell

[0628] Alkylphenylsulfonate (MW about 670 g/mol) (40 g) was charged to a reactor along with a high boiling base oil (40 g) and zinc carbonate (90 g). The system was fitted with a stainless steel Rushton turbine with overhead stirrer. A nitrogen stream was introduced through a port connector on the lid and a foam over pathway connected to a flask of equal volume to the reactor. The reaction was heated to 300° C. for 4 hours before being allowed to cool back to room temperature. The crude product was dissolved in ~5 vol. of xylene and centrifuged at 2900 rpm for 1 hr. The supernatant was decanted away from the residues and the solvent stripped on the rotary evaporator. Target MR: 24.04; measured Zn 32.72 wt. %; Calculated MR: 22.12; Particle size: 10-140 nm, as measured by DLS.

##### Example 1b—ZnO-Core, Zn-Alkylphenylsulfonate Shell

[0629] Alkylphenylsulfonate (MW about 670 g/mol) (300 g) was charged to a reactor along with a high boiling base oil (300 g) and zinc carbonate (600 g). The system was fitted with a stainless steel Rushton turbine with overhead stirrer. A nitrogen stream was introduced through a port connector on the lid and a foam over pathway connected to a flask of equal volume to the reactor. The reaction was heated to 300° C. for 4 hours before being allowed to cool back to room temperature. The crude product was dissolved in ~5 vol. of xylene and centrifuged at 2900 rpm for 1 hr. The supernatant was decanted away from the residues and the solvent stripped on the rotary evaporator. Zn: 34.10 wt. %; Calculated MR: 21.96

##### Example 2—ZnO-Core, Zn-Oleate Shell

[0630] Oleic acid (11 g) was charged to a glass reactor along with high viscosity polyalphaolefin base oil (75 g) and zinc carbonate (60 g). The remaining equipment was assembled—stainless steel Rushton turbine with overhead stirrer. A nitrogen stream was introduced through a port connector on the lid and a foam over pathway connected to a flask of equal volume to the reactor. The

reaction was heated to 300° C. for 4 hours before being allowed to cool back to room temperature. The crude product was dissolved in ~5 vol. of xylene and centrifuged at 2900 rpm for 1 hr. The supernatant was decanted away from the residues and the solvent stripped on the rotary evaporator. Zn: 11.72 wt. %; Calculated MR: 10.47; Particle size: 20-140 nm, as measured by DLS.

#### Example 3—ZnO-Core, Zn-Neodecanoate Shell

[0631] Decanoic acid (26.7 g) was charged to a 3 L baffled reactor along with xylene (1067 g), methanol (42 g) and base oil (94.3). The reactor was assembled with nitrogen inlet and condenser. The system was purged with nitrogen and the stirring started at 400 rpm. A solution of Sodium Hydroxide (71.8 g) in Methanol (284 g) was charged to a pressure equalizing dropping funnel, with a further solution of Zinc Chloride (122.4 g) in methanol (242 g) charged to a separate pressure equalizing dropping funnel. The two solutions were charged to the reaction simultaneously over 10 min at the same rate. Once the additions were complete, the dropping funnels were removed, and the reaction heated to 70° C. over 45 min. Once at 70° C., the methanol had started to distil from the reaction and the temperature was ramped to 80° C. over 50 min. The temperature was then increased to 140° C. over 45 min and held for 20 min, before being allowed to cool to room temperature. Xylene (600 g) was charged to the reaction vessel and the mixture stirred for 5 min. The mixture was decanted from the reactor and put on the centrifuge at 2900 rpm for 1 hr. The supernatant was decanted away from the solids and the solvent removed on the rotary evaporator to afford the product. Zn: 22.36 wt. %; Calculated MR: 7.80.

#### Example 4a—ZnO-Core, Ca-Alkylphenylsulfonate Shell

[0632] Ca-alkylphenylsulfonate (MW about 1378 g/mol) (30 g) was charged to a 1 L glass reactor along with base oil (high viscosity synthetic polyalphaolefin 60 g) and zinc carbonate (60 g). The remaining equipment was assembled—stainless steel Rushton turbine with overhead stirrer. A nitrogen stream was introduced through a port connector on the lid and a foam over pathway connected to a flask of equal volume to the reactor. The reaction was heated to 300° C. for 4 hours before being allowed to cool back to room temperature. The crude product was dissolved in ~5 vol. of xylene and centrifuged at 2900 rpm for 1 hr. The supernatant was decanted away from the residues and the solvent stripped on the rotary evaporator. Zn: 8.78 wt. %; Calculated MR: 6.95; Particle size: 15-150 nm, as measured by DLS.

#### Example 4b—ZnO-Core, Ca-Alkylphenylsulfonate Shell

[0633] Alkyl benzene sulfonic acid (72.9 g) was charged to a 1 L baffled reactor along with high boiling base oil (75 g) and calcium hydroxide (4.0 g). The system was assembled with a nitrogen inlet to ensure there was a stream of nitrogen passing through the system. The reaction was heated to 150° C. and held for 10 min before adding zinc carbonate (150 g). No foaming was observed however the temperature would dip when cold reagent was added, so the addition was limited to keep the temperature within 10° C. of the set point. Once all the zinc carbonate had been added, the reaction was heated to 300° C. The reaction was soaked at 300° C. for 10 hr. The reaction was cooled to room temperature. Xylene (600 ml) was charged to the reactor and the mixture stirred at 400 rpm until all the material had been taken up into a mobile suspension. The mixture was centrifuged at 2900 rpm for 1 hr. The solvent was removed on the rotary evaporator to afford the product. Zn: 25.70 wt. %; Calculated MR: 17.75; Ca: 0.61 wt. %; S: 1.23 wt. %;

#### Example 4c—ZnO-Core, Ca-Alkylphenylsulfonate (Made with 2 Eq. Ca(OH).SUB.2.) Shell

[0634] Alkylphenylsulfonate (MW about 670 g/mol) (73 g) was charged to a 1 L baffled reactor along with high boiling base oil (150 g) and calcium hydroxide (8.0 g). The system was assembled with an FFKM sealing ring, stainless steel clamp, overhead stirrer, 1 L catch pot and a NaOH scrubber with an inlet to allow a nitrogen stream through the vessel. The reaction was heated to 150° C. and held for 10 min, during which time the reactor lid developed some moisture. Zinc carbonate (150 g) was charged to the reactor through a port in the reactor lid. Once all the zinc carbonate had been added, the reaction was heated to 300° C. The reactor was insulated from 200° C. to aid heating. The reaction was soaked at 300° C. for 4 hours, after which the heating was

stopped, and the reaction allowed to cool to room temperature. Xylene (600 ml) was charged to the reactor and the mixture stirred at 400 rpm until all the material had been taken up into a mobile suspension. The mixture was then discharged from the vessel and centrifuged at 2900 rpm for 1 hr. The supernatant was decanted away from the residues and the solvent removed on the rotary evaporator. The initial solvent removal was carried out at 60° C. (~20 mbar) with the temperature increased to 120° C. (10 mbar) to remove the final solvent residues. Zn: 12.80 wt. %; Ca: 0.59 wt. %; Calculated MR:11.83.

#### Example 5—ZnO-Core, Mg-Alkylphenylsulfonate Shell

[0635] Alkylphenylsulfonate (MW about 670 g/mol, 78.8 g) was charged to a 1.5 L baffled glass reactor. High boiling base oil (150 g) was then charged to the reactor along with magnesium hydroxide (3.21 g). The remaining equipment was assembled: overhead stirrer, foam over pathway (1.5 L catch pot), NaOH scrubber, stainless steel temperature probe, controller coupled heating mantle and nitrogen inlet. The reaction was heated to 150° C. over 30 min. Once the temperature was stable, zinc carbonate (150 g) was charged to the reaction through an open port. The reaction was then heated to 300° C. for 4 hr. The reaction was then allowed to cool back to room temperature. Xylene (0.6 L) was charged to the reactor and the mixture stirred until all the reaction mixture had been taken up into a brown slurry. The slurry was transferred to a large beaker and an additional 2 L of xylene added. The mixture was centrifuged at 2900 rpm for 1 hr. The supernatant was decanted away from the residues and the solvent removed on the rotary evaporator. Zn: 12.80 wt. %; Mg: 0.88 wt. %; Calculated MR: 10.43.

#### Example 6—ZnO-Core, Zn-Nonylnaphthalenesulfonate Shell

[0636] 4,6-dinonylnaphthalene-2-sulfonic acid (75 g) was charged to a 1.5 L glass reactor along with high boiling base oil (150 g) and zinc carbonate (150 g). The remaining equipment was assembled—stainless steel Rushton turbine with overhead stirrer stainless, steel temperature probe and a WEST controller coupled heating mantle. A nitrogen stream was introduced through a port connector on the lid, with the exhaust directed through a foam over pathway (flask of equal volume to the reactor) and a sodium hydroxide scrubber. The reaction was heated to 300° C. for 4 hours before being allowed to cool back to room temperature. The crude product was dissolved in ~5 vol. of xylene and centrifuged at 2900 rpm for 1 hr. The supernatant was decanted away from the residues and the solvent removed on the rotary evaporator. Zn: 14.80 wt. %; Calculated MR: 7.92.

#### Example 7—Calcium Salicylate Stabilized, Double Decomposition Reaction

[0637] To a 3 L reactor flask fitted containing alkyl salicylic acid (362 g/mole, 65 g) and xylene (1053 g), were added Base oil (121 g), calcium hydroxide (8.8 g) and methanol (59 g). The mixture was heated to 40° C. for 15 minutes, to generate the calcium salicylate, before being allowed to cool back to 25° C. A sodium hydroxide (64 g) solution in methanol (253 g) was charged to a pressure equalizing dropping funnel and fitted to the reactor. A zinc chloride (109 g) in methanol (215 g) solution was charged to a separate pressure equalizing dropping funnel and this was also fitted to the reactor. Both methanolic solutions were added simultaneously over 15 min at roughly the same volume rate, with an exotherm of 5° C. was observed. Once the additions were complete the reaction was heated to 70° C., with solvent distilling from the reaction mixture. The reaction was then heated to 140° C. over 50 min, and soaked for 20 min. The reaction was then allowed to cool to room temperature. Xylene (600 g) was charged to the vessel and the mixture stirred for 10 minutes. The mobile suspension was decanted and put on the centrifuge at 2900 rpm for 1 hr. The supernate was decanted away from the residues and the solvent removed on the rotary evaporator, leaving the product. Zn: 14.35 wt. % (18.74% by B.I.); Ca: 1.55 wt. %; Particle size: 10 to 50 nm, as measured by DLS.

#### Example 8—ZnO-Core, Zn-Salicylate Shell

Solutions of ZnCl<sub>2</sub>·6H<sub>2</sub>O (63 g) and NaOH (37 g) in MeOH (124 g and 145 g respectively) were prepared. Xylene (507 g), base oil (24 g) and the alkyl salicylate (MW=362 g/mole, 52 g) were charged to a glass reactor. The mixture was stirred at 400 rpm to form a homogenous solution. The





PIBSA ester prepared in a manner similar to Example 1 of U.S. 2009/0203559 and of a Mo Friction Modifier, except for Examples H and I that had none of each. Examples A to G included each the same amount of a blend of diphenyl amine antioxidant and a fatty acid methyl ester antioxidant, Examples H and I included each another but equal amount of a blend of diphenyl amine antioxidant and a sulfurised alkyl methyl ester instead. Examples A to F included each the same amount of a 7.2% amine functionalized hydrogenated polyisoprene prepared as described in U.S. Ser. No. 63/379,006, filed Oct. 11, 2022, Examples G to I included each the same but different amount. Examples A to G included each the same amount of a PDMS anti-foamant and of polyisobutylene (Mn~1000), Examples H and I included each another but equal amount of both instead. examples included the same amount of a pour point depressant and a viscosity modifier (830cSt KV.sub.100), and Examples H and I had non-identical ones than that of Example A to G.

[0639] By adjusting the amount of zinc containing colloid particles added in lubricating oil composition to achieve zinc to phosphorus ratios between 2.86 to 3.38 (Examples B to F), a drastic improvement in HFRR wear performance was observed over comparative Example A. The DD13 scuffing test results of Example I over comparative Example H demonstrates that lubricating oil compositions including zinc containing colloid particles were able to improve the engine's scuffing performance significantly.

[0640] All documents described herein are incorporated by reference herein, including any priority documents and/or testing procedures, to the extent they are not inconsistent with this text. As is apparent from the foregoing general description and the specific embodiments, while forms of the invention have been illustrated and described, various modifications can be made without departing from the spirit and scope of the invention. Accordingly, it is not intended that the invention be limited thereby. The term “comprising” is considered synonymous with the term “including.” Likewise, whenever a composition, an element, or a group of elements is preceded with the transitional phrase “comprising,” it is understood that we also contemplate the same composition or group of elements with transitional phrases “consisting essentially of,” “consisting of,” “selected from the group of consisting of,” or “is” preceding the recitation of the composition, element, or elements and vice versa.

## Claims

1. A lubricating oil composition comprising or resulting from the admixing of: (A) from 1 to 99.99 wt. %, based upon the weight of the lubricating composition, of one or more base oils; (B) at least one phosphorus-containing compound selected from detergents, friction modifiers or antiwear additives other than the colloidal particles described in (C); (C) from 0.01 to 10 wt. %, based upon the weight of the composition, of colloidal particles comprising: a) a core of one or more hydrocarbon insoluble zinc containing compounds, and b) a shell of one or more of: 1) one or more metal containing surfactants, where the metal, M, comprises a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; and the surfactant comprises a hydrocarbyl-substituted sulfonate of Formula (I), or an hydrocarbyl-substituted salicylate group of Formula (II), ##STR00041## wherein each of R.sup.A and R.sup.B is, independently of each other, a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 1 to 70 carbon atoms, wherein, for n>1, the sum of the number of carbon atoms in the total of R.sup.A groups in Formula (I) and the sum of the number of carbon atoms in the total of R.sup.B groups in Formula (II) is 100 or less carbon atoms, and Ar is a mono- or polycyclic aromatic group; n is an integer from 1 to the maximum possible number of substitutions on Ar, with n=1 if m=0; m is an integer of 1 to 3, x is an integer from 1 to 5; y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; 2) one or more metal alkanoates represented by the formula (III): ##STR00042## wherein M is a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; R.sup.C is selected from a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 70 carbon atoms,

- or an aromatic or alkyl aromatic group with the aromatic group having from 6 to 20 carbon atoms and the alkyl group having 1 to 20 carbon atoms; x is an integer from 1 to 5, wherein for  $x > 1$  the R.sup.C groups may be the same or different, y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8, wherein the lubricating oil composition has a ratio of Zn to P (elemental mass basis as measured by ASTM D5185) of 1.1 to 5.0.
2. The lubricating composition of claim 1, wherein the hydrocarbon insoluble zinc containing compound is selected from at least one of zinc, zinc oxide, zinc hydroxide, zinc carbonate, and zinc halides, or mixtures thereof.
3. The lubricating composition of claim 1, wherein the colloidal particles have a mean particle diameter as determined by dynamic light scattering in the range of 5 nm to 1  $\mu$ m.
4. The lubricating composition of claim 1, wherein the metal M in Formula (I), (II), or (III) is selected from at least one of sodium, potassium, lithium, magnesium, calcium, barium, or mixtures thereof; or wherein the metal M is selected from at least one of gold, silver, palladium, platinum, zirconium, vanadium, molybdenum, nickel, copper, zinc, aluminum, or mixtures thereof.
5. The lubricating composition of claim 1, wherein Ar in Formula (I) or Formula (II) is benzene or naphthalene.
6. The lubricating composition of claim 5, wherein the surfactant of Formula (I) is a metal containing hydrocarbyl-substituted phenyl sulfonate surfactant of Formula (Ia), ##STR00043## wherein M is selected from calcium, magnesium, barium, or zinc, or combinations thereof, R.sup.A is independently of each other a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 50 carbon atoms; n is an integer from 1 to 5, with  $n=1$  if  $m=0$ ; m is 0 to 3; the sum of the number of carbon atoms in the total of R.sup.A groups is 60 or less carbon atoms; x is 2; y is 2; and, optionally, p is 0.
7. The lubricating composition of claim 5, wherein the surfactant of Formula (II) is a metal containing hydrocarbyl-substituted phenyl salicylate surfactant of Formula (IIa), ##STR00044## wherein M is selected from calcium, magnesium, barium, or zinc, or combinations thereof, R.sup.B is independently of each other a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 50 carbon atoms; n is an integer from 1 to 4; the sum of the number of carbon atoms in the total of R.sup.B groups is 60 or less carbon atoms; x is 2, y is 2; and, optionally, p is 0.
8. The lubricating composition of claim 1, wherein M in Formula (I), (II), or (III) is selected from calcium, magnesium, or zinc, or combinations thereof.
9. The lubricating composition of claim 1, wherein R in Formula (III) is a linear, cyclic, or branched, alkyl or alkenyl group having from 6 to 48 carbon atoms.
10. The lubricating composition claim 9, wherein the metal alkanoate of Formula (III) is one or more of zinc neodecanoate, zinc neoundecanoate, zinc neododecanoate, zinc neotridecanoate, zinc neotetradecanoate, zinc neopentadecanoate, zinc neohexadecanoate, zinc neoheptadecanoate, zinc stearate, zinc neo-octadecanoate, zinc oleate, zinc neononadecanoate, and zinc neoeicosanoate.
11. The lubricating composition of claim 9, wherein the metal alkanoates have a quaternary carbon atom at the 2 position attached to the carboxylate group.
12. The lubricating composition of claim 10, wherein the metal alkanoates have a quaternary carbon atom at the 2 position attached to the carboxylate group.
13. The lubricating composition of claim 1, further comprising one or more components selected from the group consisting of one or more friction modifiers; one or more antioxidants; one or more pour point depressants; one or more anti-foaming agents; one or more viscosity modifiers; one or more dispersants; one or more inhibitors and/or anti-rust agents; and/or one or more anti-wear agents, other than those of component (C).
14. The lubricating composition of claim 1, wherein: (A) the base oil is present at 50 to 99 wt. % based upon the weight of the lubricating composition; (B) the at least one phosphorus-containing compound selected from detergents, friction modifiers, or antiwear additives other than the

colloidal particles described in (C) is present in an amount of 0.001 to 5 wt. %; C) the colloidal particles are present at from 0.01 to 10 wt. %, such as 0.01 to 6 wt. % based on total weight of the lubricating composition; D) optionally, one or more friction modifiers other than those of component (B) are present at from 0.01 to 5 wt. %, based on total weight of the lubricating composition; E) optionally, one or more antioxidants are present at from 0.01 to 10 wt. %, based on total weight of the lubricating composition; F) optionally, one or more pour point depressants are present at from 0.01 to 5 wt. %, based on total weight of the lubricating composition; G) optionally, one or more anti-foaming agents are present at from 0.001 to 5 wt. %, based on total weight of the lubricating composition; H) optionally, one or more viscosity modifiers are present at from 0.001 to 6 wt. %, based on total weight of the lubricating composition; I) optionally, one or more dispersants are present at from 0.01 to 20 wt. %, based on total weight of the lubricating composition; J) optionally, one or more inhibitors and/or anti-rust agents are present at from 0.01 to 5 wt. %, based on total weight of the lubricating composition; and K) optionally, one or more anti-wear agents, other than those of components (B) and (C), are present at from 0.001 to 5 wt. %, based on total weight of the lubricating composition; L) optionally, one or more detergents, other than those of components (B) and in the colloidal particles described in (C) are present at from 0.1 to 20 wt. % based on total weight of the lubricating composition.

**15.** The lubricating composition of claim 1, wherein the lubricating composition has an adhesive wear of 100 hours or more, as measured by ASTM D8074-16.

**16.** The lubricating composition of claim 1, wherein a ratio of Zn to P (elemental mass basis) is 1.1 to 4.9 in the lubricating composition.

**17.** The lubricating composition of claim 1, wherein the ligand L is selected from the group consisting of water, hydroxide, halide, ammonia, amino, amido, alcoholate, and mixtures thereof.

**18.** The lubricating composition of claim 1, wherein the colloidal particles have a molar ratio of metal to surfactant, MR, of at least 5.

**19.** The lubricating composition of claim 1, wherein a total base number (TBN) of the composition is from 1 to 30 mgKOH/g, as measured by ASTM D2896.

**20.** The lubricating composition of claim 1, having a zinc content of 500 ppm or more, as determined by ASTM D5185.

**21.** The lubricating composition of claim 1, having a phosphorus content of not more than 2000 ppm, based on the total mass of the lubricating compositions, as measured by ASTM D5185.

**22.** The lubricating composition of claim 1 wherein the lubricating composition is a combustion engine oil or a gas turbine oil.

**23.** The lubricating composition of claim 1, wherein the lubricating composition is transmission fluid or gear oil.

**24.** The lubricating composition of claim 1, comprising more than 500 ppm of Zn and less than 500 ppm of P, wherein the lubricating composition has an adhesive wear of 100 hours or more, and optionally a total base number of 7 mgKOH/g or more.

**25.** The lubricating composition of claim 1, comprising more than 1000 ppm of Zn and less than 1000 ppm of P, wherein the lubricating composition has an adhesive wear of 100 hours or more, and optionally a total base number of 7 mgKOH/g or more.

**26.** The lubricating composition of claim 1, wherein zinc dialkyl dithiophosphates are present at 2 wt. % or less.

**27.** The lubricating composition of claim 1, wherein the lubricating composition has a wear scar volume of less than 150  $\mu\text{m}^3$ , determined by HFRR method as described herein.

**28.** A method to obtain an adhesive wear of 100 hours or more (ASTM D 8074-16) for a lubricating composition having 500 ppm of zinc or more, preferably 1000 ppm of zinc or more comprising: (i) providing to the lubricating composition of claim 1 to a crankcase of an internal combustion engine; (ii) providing a hydrocarbon fuel in the internal combustion engine; and (iii) combusting the fuel in the internal combustion engine.

**29.** A method of lubricating an internal combustion engine during operation of the engine comprising: (i) providing the lubricating composition of claim 1 to a crankcase of the internal combustion engine; (ii) providing fuel in the internal combustion engine; and (iii) combusting the fuel in the internal combustion engine, wherein the fuel comprises hydrocarbon fuel derived from petroleum and or biological sources; hydrogen fuel, optionally combined with liquified natural gas; and or ammonia fuel.

**30.** The method of claim 29 wherein the engine is a diesel engine, a gas engine, or a marine engine.

**31.** A concentrate composition comprising or resulting from the admixing of: (A) from 1 to less than 50 wt. % of one or more base oils, based upon the weight of the concentrate composition; (B) at least one phosphorus-containing compound selected from detergents, friction modifiers or antiwear additives other than the colloidal particles described in (C); (C) from 0.1 to 50 wt. %, based upon the weight of the composition, of colloidal particles comprising: a) a core of one or more hydrocarbon insoluble zinc containing compounds, and b) a shell of one or more of: 1) one or more metal containing surfactants, where the metal, M, comprises a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; and the surfactant comprises an hydrocarbyl-substituted sulfonate of Formula (I), or an hydrocarbyl-substituted salicylate group of Formula (II), ##STR00045## wherein each R.sup.A, and R.sup.B is, independently of each other, a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 1 to 70 carbon atoms, wherein, for  $n > 1$ , the sum of the number of carbon atoms in the total of R.sup.A groups in Formula (I) and the sum of the number of carbon atoms in the total of R.sup.B groups in Formula (II) is 100 or less carbon atoms, and Ar is a mono- or polycyclic aromatic group; n is an integer from 1 to the maximum possible number of substitutions on Ar, with  $n=1$  if  $m=0$ ; m is an integer of 0 to 3, x is an integer from 1 to 5; y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; 2) one or more metal alkanoates represented by the formula (III): ##STR00046## wherein M is a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; R.sup.C is selected from a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 70 carbon atoms, or an aromatic or alkyl aromatic group with the aromatic group having from 6 to 20 carbon atoms and the alkyl group having 1 to 20 carbon atoms; x is an integer from 1 to 5, wherein for  $x > 1$  the R.sup.C groups may be the same or different, y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; wherein the concentrate composition has a ratio of Zn to P (elemental mass basis as measured by ASTM D5185) of 1.1 to 5.0.

**32.** An antiwear additive comprising or resulting from the admixing of: (A) from 1 to less than 50 wt. % of one or more base oils, based upon the weight of the composition; (B) at least one phosphorus-containing compound selected from detergents, friction modifiers or antiwear additives other than the colloidal particles described in (C); (C) from 0.1 to 50 wt. %, based upon the weight of the composition, of colloidal particles comprising: a) a core of one or more hydrocarbon insoluble zinc containing compounds, and b) a shell of one or more of: 1) one or more metal containing surfactants, where the metal, M, comprises a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; and the surfactant comprises an hydrocarbyl-substituted aromatic sulfonate of Formula (I), or an hydrocarbyl-substituted salicylate group of Formula (II), ##STR00047## wherein each R.sup.A, and R.sup.B is, independently of each other, a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 1 to 70 carbon atoms, wherein, for  $n > 1$ , the sum of the number of carbon atoms in the total of R.sup.A groups in Formula (I) and the sum of the number of carbon atoms in the total of R.sup.B groups in Formula (II) is 100 or less carbon atoms, and Ar is a mono- or polycyclic aromatic group; n is an integer from 1 to the maximum possible number of substitutions on Ar, with  $n=1$  if  $m=0$ ; m is an integer of 0 to 3, x is an integer from 1 to 5; y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; 2) one or more metal alkanoates represented by the formula (III): ##STR00048## wherein M is a group 1, 2, 4, 5, 6, 10, 11, 12, or 13 metal; R.sup.C is selected from a linear, cyclic, or branched, saturated or unsaturated, aliphatic hydrocarbon group having from 6 to 70 carbon atoms,

or an aromatic or alkyl aromatic group with the aromatic group having from 6 to 20 carbon atoms and the alkyl group having 1 to 20 carbon atoms; x is an integer from 1 to 5, wherein for  $x > 1$  the R.sup.C groups may be the same or different, y is an integer from 1 to 5, L is a ligand saturating the coordination sphere of M, and p is an integer from 0 to 8; wherein the composition has a ratio of Zn to P (elemental mass basis as measured by ASTM D5185) of 1.1 to 5.0.

**33.** The composition of claim 1, wherein the colloidal particles have a mean particle diameter as determined by dynamic light scattering in the range of 20 to 200 nm; wherein M in Formula (I) or (II) is selected from calcium, magnesium, or combinations thereof, wherein the metal alkanoate of Formula (III) is one or more of zinc neodecanoate, zinc neoundecanoate, zinc neododecanoate, zinc neotridecanoate, zinc neotetradecanoate, zinc neopentadecanoate, zinc neoheptadecanoate, zinc stearate, zinc neo-octadecanoate, zinc oleate, zinc neononadecanoate, and zinc neoeicosanoate, wherein the metal alkanoates have a quaternary carbon atom at the 2 position attached to the carboxylate group; wherein the ratio of Zn to P (elemental mass basis) is 1.5 to 4.5, in the lubricating composition; and wherein the colloidal particles have a molar ratio of metal to surfactant, MR, of 6 to 40.

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