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(54) LUBRICANT COMPOSITIONS FOR HIGH EFFICIENCY ENGINES

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(57) ABSTRACT

The instant disclosure is directed to a method of lubricating a sump-lubricated, high efficiency, gasoline-fueled internal combustion engine. Said method involves supplying to the engine a lubricating composition comprising an oil of lubricating viscosity, an anti-wear agent, an ashless antioxidant, a metal-containing detergent, an ashless polyolefin dispersant, and (f) a polymeric viscosity modifier. The disclosure further provides a method of operating a high efficiency sump-lubricated gasoline-fueled internal combustion engine while maintaining or improving at least one of durability, deposit control, oxidation control, fuel economy, and resistance to knock and stochastic pre-ignition.

LUBRICANT COMPOSITIONS FOR HIGH EFFICIENCY ENGINES

BACKGROUND

[0001] The disclosed technology relates to lubricants for internal combustion engines, particularly those for gasoline-fueled engines.

[0002] Modern engine designs are being developed to improve thermal efficiency without sacrificing performance or durability and without increasing the emission of potentially harmful exhaust gases, such as nitrogen oxides (NO_x), non-combusted hydrocarbons (HC), and carbon monoxide (CO).

[0003] The challenge of increasing thermal efficiency, and hence fuel efficiency, of an engine involves extracting more torque from said engine at a given displacement volume. Achieving this goal requires a combination of hardware design changes, optimization of engine operation parameters, such as fuel-air ratio, and lubricant design.

[0004] Brake mean effective pressure (BMEP) is a measure of engine output normalized for engine displacement. Improving the efficiency of gasoline-fueled engines will require operating the engine at higher BMEP and result in more demands on the lubricant to prevent damage to the engine. Chief among these threats will be increased wear resulting from higher loads, oxidation and corrosion from higher operational temperatures, and stochastic pre-ignition as the engine begins to operate in more knock-sensitive regimes.

[0005] Another indicator of engine efficiency is effective compression ratio. As engines are operated at higher BMEP, they may also achieve higher effective compression ratio. A means to increase BMEP and improve efficiency is to increase effective compression ratio.

[0006] Hardware and operational changes for gasoline-fueled engines include turbochargers, super chargers, variable valve timing, gasoline direct injection (GDI), lean burn combustion strategies, homogeneous charge compression ignition (HCCI) and various combinations of these features.

[0007] The disclosed technology provides a method for operating and lubricating a high efficiency gasoline-fueled internal combustion engine.

SUMMARY

[0008] The instant disclosure provides a method of lubricating a sump-lubricated, high efficiency, gasoline-fueled internal combustion engine, comprising supplying to the engine a lubricating composition comprising (a) an oil of lubricating viscosity, (b) an anti-wear agent in an amount 0.15 weight percent to 6 weight percent of the composition, (c) an ashless antioxidant in an amount 1.2 weight to 7 weight percent of the composition, and (d) a metal-containing detergent in an amount to deliver 0.2 weight percent sulfated ash up to 1.5 weight percent sulfated ash to the composition, (e) an ashless polyolefin dispersant in an amount 0.8 weight percent to 8 weight percent of the composition, and (f) a polymeric viscosity modifier, dispersant viscosity modifier, or mixtures thereof in an amount 0.1 weight percent to 4.5 weight percent of the composition.

[0009] In one embodiment, the instant disclosure provides a method of operating a sump-lubricated, high efficiency, gasoline-fueled internal combustion engine, comprising supplying to the engine a lubricating composition comprising (a) an oil of lubricating viscosity, (b) an anti-wear agent in an amount 0.15 weight percent to 6 weight percent of the composition, (c) an ashless antioxidant in an amount 1.2 weight to 7 weight percent of the composition, and (d) a metal-containing detergent in an amount to deliver 0.2 weight percent sulfated ash up to 1.5 weight percent sulfated ash to the composition, (e) an ashless polyolefin dispersant in an amount 0.8 weight percent to 8 weight percent of the composition, and (f) a polymeric viscosity modifier, dispersant viscosity modifier, or mixtures thereof in an amount 0.1 weight percent to 4.5 weight percent of the composition.

[0010] In some embodiments, the methods described herein relate to a spark ignited engine.

[0011] In some embodiments, the engine is operated at an effective compression ratio of at least 15:1.

[0012] In other embodiments, the engine is operated under a load with a brake mean effective pressure (BMEP) of greater than or equal to 18 bars.

[0013] In some embodiments, the engine is fueled with a liquid hydrocarbon fuel, a liquid nonhydrocarbon fuel, or mixtures thereof having an octane rating of at least 95 by the (R+M)/2 method.

[0014] In some embodiments, the internal combustion engine is a gasoline direct injection (GDI) engine.

[0015] In some embodiments, the internal combustion engine is equipped with a turbocharger, a super charger, an air booster, or combinations thereof.

[0016] In some embodiments, the internal combustion engine is operated with variable valve timing

[0017] In some embodiments, the internal combustion engine is operated with an air-fuel equivalence ratio (λ) of less than 1.2

[0018] In some embodiments, the internal combustion engine is operated at speeds less than or equal to 3000 rpm.

[0019] In one embodiment, the antiwear agent comprises a phosphorus-containing additive, a phosphorus-free additive, or combinations thereof.

[0020] In some embodiments, the lubricating composition includes at least 50 weight % of a Group II base oil, a Group III base oil, or mixtures thereof

[0021] One embodiment describes a method of operating a high efficiency sump-lubricated gasoline-fueled internal combustion engine while maintaining or improving at least one of wear reduction, durability, deposit control, oxidation control, fuel economy, and resistance to knock and stochastic pre-ignition.

[0022] In one embodiment, the additive systems reduce tribocouple stress, particularly during the power-stroke of high compression engines.

[0023] In one embodiment, the lubricant compositions decrease friction power losses in high efficiency internal combustion engines.

DETAILED DESCRIPTION

[0024] Various features and embodiments will be described below by way of non-limiting illustration. The instant disclosure relates to methods for lubricating an internal combustion engine.

The Internal Combustion Engine

[0025] The high efficiency internal combustion engine is one that may be operated under a brake mean effective pressure (BMEP) of at least 20 bars. In such circumstances the engine may be subject to more severe operating conditions. As load conditions on the engine increase, in-cylinder pressure dynamics (compression and firing pressures) can influence ring motion dynamics and impact engine durability. In addition, at the foregoing loads, stochastic pre-ignition, which may be accompanied by subsequent detonation and/or severe engine knock, can cause severe damage to the engine very quickly (often within 1 to 5 engine cycles). Engine knock may occur with stochastic pre-ignition given that, after the normal spark from the igniter is provided, multiple flames may be present.

[0026] In one embodiment, the high efficiency gasoline-fueled engine is operated at a BMEP of at least 20 bars, or at least 22 bars, or at least 24 bars, or at least 26 bars. In one embodiment, high BMEP is achieved through operating the engine with one or more features comprising gasoline direct injection (GDI), turbochargers, superchargers, variable valve timing, homogeneous charge compression ignition (HCCI), lean burn, or combinations thereof.

[0027] In one embodiment, the high efficiency engine is a gasoline direct injection engine (GDI). Direct injection engines are characterized by injection of the fuel, e.g., gasoline, directly into the cylinder. This is distinct from port fuel injection (PFI) and can result in higher efficiency, higher compression, and/or higher brake mean effective pressure than analogous PFI engines.

[0028] In one embodiment, the high efficiency engine is equipped with a turbocharger, a supercharger, or combinations thereof. Turbochargers and superchargers both work to increase the volumetric efficiency of engines, i.e. the volume of air that fills a cylinder relative to the volume of the cylinder. Turbochargers and superchargers work by forcing more air into the cylinder, resulting in higher torque for a given displacement, and hence higher BMEP. In addition to improving the efficiency of an engine, turbochargers and superchargers can increase the likelihood of stochastic pre-ignition, especially at lower speeds.

[0029] In one embodiment, the high efficiency engine is a homogeneous charge compression ignition (HCCI) engine. HCCI, also referred to as the spatial ignition or controlled auto-ignition (CAI), is based on a controlled auto-ignition of the fuel supplied to a cylinder. The fuel, usually gasoline, is generally burned with an excess of air (e.g., superstoichiometrically). Owing to the low combustion temperatures, an internal combustion engine operated in the HCCI mode exhibits relatively low nitrogen oxide emissions and likewise low, or virtually absent, soot emissions. Additionally, owing to the relatively low combustion temperatures and the associated relatively low temperature differences in the internal combustion engine, heat losses are lower than in the case of conventionally operated internal combustion engines. This leads to a higher thermal efficiency.

[0030] In one embodiment, the high efficiency engine is a spark plug controlled compression ignition engine (SPCCI). This type of engine is intermediate between a typical spark ignition engine and an HCCI engine (as described above). An SPCCI engine utilizes a pre-spark assist to provide the compression of the lean fuel mixture in order to ignite the fuel. This leads to higher efficiency with improved emissions and cleanliness.

[0031] In one embodiment, the high efficiency engine utilizes a lean burn fueling strategy. As used hereinafter, a stoichiometric ratio will be referred to using lambda, which is calculated using the following formula: 1 lambda=air/fuel ratio stoichiometric air/fuel ratio. When lambda is 1, the system is stoichiometric. When lambda greater than 1 the system is a lean system. When lambda less than 1, the system is a rich system. The lean burn combustion systems are combustion systems that operate lean by design for a majority of the operating time. Lean combustion systems are those systems operating at a lambda of greater than 1.2, greater than 1.4 or greater than 1.5.

[0032] In one embodiment, the high efficiency engine is operated at a high effective compression ratio. Geometric compression ratio is typically calculated as volume of the cylinder at bottom dead center (BDC) divided by volume of the cylinder at top dead center (TDC). Effective compression ratio takes into account the increase in the maximum pressure within the cylinder upon compression when the air in the air induction system is pre-compressed. Desirably, the effective compression ratio is at least about 17, 18, 19, 20, 22, or 24.

[0033] Effective compression ratio may be variable during operation of a high efficiency engine. In one embodiment, the effective compression ratio varies from 8:1 to 30:1 during operation of the engine, with the proviso that the compression ratio exceeds 17:1 for at least 10% of engine operation time, or at least 25% of the time, or at least 50% of the time. In one embodiment, a variable compression high efficiency engine is operated such that the compression ratio is at least 17, or at least 20, or at least 24 for at least 75% of the operational time period.

[0034] Variable valve timing (VVT) is a means of varying timing and opening of the exhaust and intake valves of the engine to improve performance, fuel economy, and/or emissions. The timing of the intake and exhaust valves can be adjusted relative to rpm to improve air motion into and out of an engine. The timing and opening can be changed by different mechanical, hydraulic and electrical methods. In one embodiment, the high efficiency engine utilizes variable valve timing in combination with one or more of the above means to achieve a BMEP of at least 20 bar.

Fuel

[0035] Embodiments of the instant disclosure provide for operating a gasoline-fueled internal combustion engine. In addition to the engine operating conditions and the lubricant composition, the composition of the fuel may impact engine performance, including but not limited to knock events and stochastic pre-ignition events. In one embodiment, the fuel may comprise a fuel which is liquid at ambient temperature and is useful in fueling a spark ignited engine, a fuel which is gaseous at ambient temperatures, or combinations thereof.

[0036] The liquid fuel is normally a liquid at ambient conditions e.g., room temperature (20 to 30° C.). The fuel can be a hydrocarbon fuel, a nonhydrocarbon fuel, or a mixture thereof. The hydrocarbon fuel may be a gasoline as defined by ASTM specification D4814. In an embodiment, the fuel is a gasoline, and in other embodiments the fuel is a leaded gasoline, or a nonleaded gasoline.

[0037] The nonhydrocarbon fuel can be an oxygen containing composition, often referred to as an oxygenate, to include an alcohol, an ether, a ketone, an ester of a carboxylic acid, a nitroalkane, or a mixture thereof. The nonhydrocarbon fuel can include for example methanol, ethanol, methyl t-butyl ether, methyl ethyl ketone, transesterified oils and/or fats from plants and animals such as rapeseed methyl ester and soybean methyl ester, and nitromethane. Mixtures of hydrocarbon and nonhydrocarbon fuels can include, for example, gasoline and methanol and/or ethanol. In an embodiment, the liquid fuel is a mixture of gasoline and ethanol, wherein the ethanol content is at least 5 volume percent of the fuel composition, or at least 10 volume percent of the composition, or at least 15 volume percent, or 15 to 85 volume percent of the composition. In one embodiment, the liquid fuel contains less than 15% by volume ethanol content, less than 10% by volume ethanol content, less than 5% ethanol content by volume, or is substantially free of (i.e. less than 0.5% by volume) of ethanol.

[0038] In several embodiments, the fuel can have a sulfur content on a weight basis that is 5000 ppm or less, 1000 ppm or less, 300 ppm or less, 200 ppm or less, 30 ppm or less, or 10 ppm or less. In another embodiment, the fuel can have a sulfur content on a weight basis of 1 to 100 ppm. In one embodiment, the fuel contains about 0 ppm to about 1000 ppm, about 0 to about 500 ppm, about 0 to about 100 ppm, about 0 to about 50 ppm, about 0 to about 25 ppm, about 0 to about 10 ppm, or about 0 to 5 ppm of alkali metals, alkaline earth metals, transition metals or mixtures thereof. In another embodiment the fuel contains 1 to 10 ppm by weight of alkali metals, alkaline earth metals, transition metals or mixtures thereof.

[0039] High efficiency engines can require higher quality fuel for operation. Octane rating, or octane number, is a measure of the propensity for a fuel to withstand compression before ignition (also referred to as detonation). Engines that experience high compression ratio or high BMEP may require fuels with higher octane ratings. The use of fuels of insufficient octane rating can result in engine knocking. Engine knock is well understood and is different than random (or stochastic) pre-ignition.

[0040] Octane rating is measured in a test engine and is defined as the comparison with a specific mixture of iso-octane and heptane. Iso-octane (i.e., 2,2,4-trimethylpentane) has an octane rating of 100; n-heptane has an octane rating of 0. Gasoline with knock characteristics similar to a 90:10 mixture of iso-octane and n-heptane is said to have an octane rating of 90. Research octane number (RON), measured according to ASTM D2699, is determined by running the fuel in a standardized, CFR single-cylinder, 4-stroke, variable compression ratio, carbureted engine with a variable compression ratio under controlled conditions at 600 rpm, and comparing the results with those for mixtures of iso-octane and n-heptane. Motor octane number (MON), measured according to ASTM D2700, uses a similar test engine to that used in RON testing, but with a preheated fuel mixture, higher engine speed (900 rpm), and variable ignition timing to further stress the fuel's knock resistance.

[0041] In some countries, octane rating is reported as the anti-knock index (AKI). Anti-knock index is the average of RON and MON, calculated as AKI=(R+M)/2. In one embodiment, the high efficiency engine is fueled with a hydrocarbon fuel having an AKI of at least 95, or at least 98, or at least 100, or at least 102. In certain embodiments, the high efficiency engine is fueled with a hydrocarbon fuel having an AKI of no more than 87, or no more than 85, or no more than 82, or no more than 78, or no more than 75

[0042] In some engine configurations requiring compression ignition, lower octane fuels may be desired. In one embodiment, compression ignition engines may be fueled with a hydrocarbon fuel having an AKI of no more than 87, or no more than 85, or no more than 82, or no more than 78, or no more than 75.

[0043] The fuel compositions described herein can further comprise one or more performance additives. Performance additives can be added to a fuel composition depending on several factors, including the type of internal combustion engine and the type of fuel being used in that engine, the quality of the fuel, and the service conditions under which the engine is being operated. In some embodiments, the performance additives added are free of nitrogen. In other embodiments, the additional performance additives may contain nitrogen.

[0044] The performance additives can include an antioxidant such as a hindered phenol or derivative thereof and/or a diarylamine or derivative thereof; a corrosion inhibitor such as an alkenylsuccinic acid; and/or a detergent/dispersant additive, such as a polyetheramine or nitrogen containing detergent, including but not limited to polyisobutylene (PIB) amine dispersants, Mannich detergents, succinimide dispersants, and their respective quaternary ammonium salts.

[0045] The performance additives may also include a cold flow improver, such as an esterified copolymer of maleic anhydride and styrene and/or a copolymer of ethylene and vinyl acetate; a foam inhibitor, such as a silicone fluid; a demulsifier such as a polyoxyalkylene and/or an alkyl polyether alcohol; a lubricity agent such as a fatty carboxylic acid, ester and/or amide derivatives of fatty carboxylic acids, or ester and/or amide derivatives of hydrocarbyl substituted succinic anhydrides; a metal deactivator, such as an aromatic triazole or derivative thereof, including but not limited to a benzotriazole such as tolytriazole; and/or a valve seat recession additive, such as an alkali metal sulfosuccinate salt. The additives may also include a biocide, an antistatic agent, a deicer, a fluidizer, such as a mineral oil and/or a poly(alpha-olefin) and/or a polyether, and a combustion improver, such as an octane or cetane improver.

[0046] The fluidizer may be a polyetheramine or a polyether compound. The polyetheramine can be represented by the formula $R[—OCH_2CH(R^1)]_nA$, where R is a hydrocarbyl group, R^1 is selected from the group consisting of hydrogen, hydrocarbyl groups of 1 to 16 carbon atoms, and mixtures thereof, n is a number from 2 to about 50, and A is selected from the group consisting of $—OCH_2CH_2CH_2NR^2R^2$ and $—NR^3R^3$, where each R^2 is independently hydrogen or hydrocarbyl, and each R^3 is independently hydrogen, hydrocarbyl or $—[R^4N(R^5)]_pR^6$, where R^4 is C_2-C_{10} alkylene, R^5 and R^6 are independently hydrogen or hydrocarbyl, and p is a number from 1-7.

[0047] The fluidizer can be a polyether, which can be represented by the formula $R^7O[CH_2CH(R^8)O]_qH$, where R^7 is a hydrocarbyl group, R^8 is selected from the group consisting of hydrogen, hydrocarbyl groups of 1 to 16 carbon atoms, and mixtures thereof, and q is a number from 2 to about 50. The fluidizer can be a hydrocarbyl-terminated poly-(oxyalklene) aminocarbamate as described U.S. Pat. No. 5,503,644. The fluidizer can be an alkoxylate, wherein the alkoxylate can comprise: (i) a polyether containing two or more ester terminal groups; (ii) a polyether containing one or more ester groups and one or more terminal ether groups; or (iii) a polyether containing one or more ester groups and one or more terminal amino groups, wherein a terminal group is defined as a group located within five connecting carbon or oxygen atoms from the end of the polymer. Connecting is defined as the sum of the connecting carbon and oxygen atoms in the polymer or end group.

[0048] The performance additives which may be present in the fuel additive compositions and fuel compositions may also include di-ester, di-amide, ester-amide, and ester-imide friction modifiers prepared by reacting a dicarboxylic acid (such as tartaric acid) and/or a tricarboxylic acid (such as citric acid), with an amine and/or alcohol, optionally in the presence of a known esterification catalyst. These friction modifiers often derived from tartaric acid, citric acid, or derivatives thereof, may be derived from amines and/or alcohols that are branched so that the friction modifier itself has significant amounts of branched hydrocarbyl groups present within it structure. Examples of suitable branched alcohols used to prepare these friction modifiers include 2-ethylhexanol, isotridecanol, Guerbet alcohols, or mixtures thereof.

[0049] In different embodiments the fuel composition may have a composition as described in the following table:

	Embodiments (ppm)		
Additive	A	C	D
Detergent/dispersant	0 to 2500	25 to 150	500 to 2500
Fluidizer	0 to 5000	1 to 250	3000 to 5000
Demulsifier	0 to 50	0.5 to 5	1 to 25
Corrosion Inhibitor	0 to 200	.5 to 10	20 to 200
Antioxidant	0 to 1000	5 to 125	500 to 1000
Friction Modifier	0 to 600	50 to 175	100 to 750
Fuel	Balance to 100%	Balance to 100%	Balance to 100%

The Lubricating Composition

[0050] A high efficiency engine as disclosed herein may be lubricated with a lubricating composition comprising (a) an oil of lubricating viscosity, (b) an anti-wear agent in an amount 0.15 weight percent to 6 weight percent of the composition, (c) an ashless antioxidant in an amount 1.2 weight to 7 weight percent of the composition, and (d) a metal-containing detergent in an amount to deliver 0.2 weight percent sulfated ash up to 1.5 weight percent sulfated ash to the composition, (e) an ashless polyolefin dispersant in an amount 0.8 weight percent to 8 weight percent of the composition, and (f) a polymeric viscosity modifier, dispersant viscosity modifier, or mixtures thereof in an amount 0.1 weight percent to 4.5 weight percent of the composition

Oil of Lubricating Viscosity

[0051] The lubricating composition comprises an oil of lubricating viscosity. Such oils include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined, re-refined oils or mixtures thereof. A more detailed description of unrefined, refined and re-refined oils is provided in International Publication WO2008/147704, paragraphs [0054] to [0056] (a similar disclosure is provided in U.S. Patent Publication 2010/0197536, see [0072] to [0073]). A more detailed description of natural and synthetic lubricating oils is described in paragraphs [0058] to [0059] respectively of WO2008/147704 (a similar disclosure is provided in U.S. Patent Publication 2010/0197536, see [0075] to [0076]). Synthetic oils may also be produced by Fischer-Tropsch reactions and typically may be hydroisomerised Fischer-Tropsch hydrocarbons or waxes. In one embodiment, oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0052] Oils of lubricating viscosity may also be defined as specified in the April 2008 version of "Appendix E—API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils", section 1.3 Sub-heading 1.3. "Base Stock Categories". The API Guidelines are also summarized in U.S. Pat. No. 7,285,516 (see column 11, line 64 to column 12, line 10). In one embodiment, the oil of lubricating viscosity may be an API Group II, Group III, or Group IV oil, or mixtures thereof. The five base oil groups are as follows:

Base Oil Category	Sulfur (%)	Saturates (%)	Viscosity Index
Group I	>0.03 and/or	<90	80 to 120
Group II	≤0.03 and	≥90	80 to 120
Group III	≤0.03 and	≥90	≥120
Group IV	All polyalphaolefins (PAO)		
Group V	All others not included in Groups I, II, III, or IV		

[0053] The amount of the oil of lubricating viscosity present is typically the balance remaining after subtracting from 100 weight % (wt %) the sum of the amount of instantly disclosed and the other performance additives.

[0054] The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the lubricating composition (comprising the additives disclosed herein) is in the form of a concentrate which may be combined with additional oil to form, in whole or in part, a finished lubricant), the ratio of the of these additives to the oil of lubricating viscosity and/or to diluent oil include the ranges of 1:99 to 99:1 by weight, or 80:20 to 10:90 by weight.

[0055] In one embodiment, the base oil has a kinematic viscosity at 100° C. from 2 mm^2/s (centiStokes—cSt) to 16 mm^2/s, from 3 mm^2/s to 10 mm^2/s, or even from 4 mm^2/s to 8 mm^2/s.

[0056] The ability of a base oil to act as a solvent (i.e. solvency) may be a contributing factor in increasing the frequency of LSPI events during operation of a direct fuel-injected engine. Base oil solvency may be measured as the ability of an un-additized base oil to act as a solvent for polar constituents. In general, base oil solvency decreases as the base oil group moves from Group Ito Group IV (PAO). That is, solvency of base oil may be ranked as follows for oil of a given kinematic viscosity: Group I>Group II>Group III>Group IV. Base oil solvency also decreases as the viscosity increases within a base oil group; base oil of low viscosity tends to have better solvency than similar base oil of higher viscosity. Base oil solvency may be measured by aniline point (ASTM D611).

[0057] In one embodiment, the base oil comprises at least 30 wt % of Group II or Group III base oil. In another embodiment, the base oil comprises at least 60 weight % of Group II or Group III base oil, or at least 80 wt % of Group II or Group III base oil. In one embodiment, the lubricant composition comprises less than 20 wt % of Group IV (i.e. polyalphaolefin) base oil. In another embodiment, the base oil comprises less than 10 wt % of Group IV base oil. In one embodiment, the lubricating composition is substantially free of (i.e. contains less than 0.5 wt %) of Group IV base oil.

[0058] Ester base fluids, which are characterized as Group V oils, have high levels of solvency as a result of their polar nature. Addition of low levels (typically less than 10 wt %) of ester to a lubricating composition may significantly increase the resulting solvency of the base oil mixture. Esters may be broadly grouped into two categories: synthetic and natural. An ester base fluid would have a kinematic viscosity at 100° C. suitable for use in an engine oil lubricant, such as between 2 cSt and 30 cSt, or from 3 cSt to 20 cSt, or even from 4 cSt to 12 cSt.

[0059] Synthetic esters may comprise 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, alkyl malonic acids, and alkenyl malonic acids) with any of variety of monohydric alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, and 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. Other synthetic esters include those made from C5 to C12 monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, and tripentaerythritol. Esters can also be monoesters of monocarboxylic acids and monohydric alcohols.

[0060] Natural (or bio-derived) esters refer to materials derived from a renewable biological resource, organism, or entity, distinct from materials derived from petroleum or equivalent raw materials. Natural esters include fatty acid triglycerides, hydrolyzed or partially hydrolyzed triglycerides, or transesterified triglyceride esters, such as fatty acid methyl ester (or FAME). Suitable triglycerides include, but are not limited to, palm oil, soybean oil, sunflower oil, rapeseed oil, olive oil, linseed oil, and related materials. Other sources of triglycerides include, but are not limited to, algae, animal tallow, and zooplankton. Methods for producing biolubricants from natural triglycerides are described in, e.g., United States Patent Publication 2011/0009300A1.

[0061] In one embodiment, the lubricating composition comprises at least 2 weight % of an ester base fluid. In one embodiment the lubricating composition comprises at least 4 weight % of an ester base fluid, or at least 7 weight % of an ester base fluid, or even at least 10 weight % of an ester base fluid.

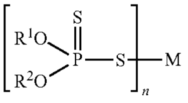
Anti-Wear Agent

[0062] Anti-wear agents include phosphorus-containing compounds as well as phosphorus free compounds. In one embodiment, the anti-wear additive comprises a phosphorus-containing compound, a phosphorus-free compound, or combinations thereof

[0063] Phosphorus-containing anti-wear agents are well known to one skilled in the art and include metal dialkyl (dithio)phosphate salts, hydrocarbyl phosphites, hydrocarbyl phosphines, hydrocarbyl phosphonates, alkylphosphate esters, amine or ammonium (alkyl)phosphate salts, and combinations thereof.

[0064] In one embodiment, the phosphorus-containing ant-wear agent may be a metal dialkyldithiophosphate, which may include a zinc dialkyldithiophosphate. Such zinc salts are often referred to as zinc dialkyldithiophosphates (ZDDP) or simply zinc dithiophosphates (ZDP). They are well known and readily available to those skilled in the art of lubricant formulation. Further zinc dialkyldithiophosphates may be described as primary zinc dialkyldithiophosphates or as secondary zinc dialkyldithiophosphates, depending on the structure of the alcohol used in its preparation. In some embodiments the instant compositions may include primary zinc dialkyldithiophosphates. In some embodiments, the compositions include secondary zinc dialkyldithiophosphates. In some embodiments, the compositions include a mixture of primary and secondary zinc dialkyldithiophosphates. In some embodiments component (b) is a mixture of primary and secondary zinc dialkyldithiophosphates where the ratio of primary zinc dialkyldithiophosphates to secondary zinc dialkyldithiophosphates (one a weight basis) is at least 1:1, or even at least 1:1.2, or even at least 1:1.5 or 1:2, or 1:10.

[0065] Examples of suitable metal dialkyldithiophosphate include metal salts of the formula:



where R^1 and R^2 are independently hydrocarbyl groups containing 3 to 24 carbon atoms, or 3 to 12 carbon atoms, or 3 to 8 carbon atoms; M is a metal having a valence n and generally incudes zinc, copper, iron, cobalt, antimony, manganese, and combinations thereof In one embodiment R^1 and R^2 are secondary aliphatic hydrocarbyl groups containing 3 to 8 carbon atoms, and M is zinc.

[0066] ZDDP may be present in the composition in an amount to deliver 0.01 weight percent to 0.12 weight percent phosphorus to the lubricating composition. ZDDP may be present in an amount to deliver at least 100 ppm, or at least 300 ppm, or at least 500 ppm of phosphorus to the composition up to no more than 1200 ppm, or no more than 1000 ppm, or no more than 800 ppm phosphorus to the composition.

[0067] In one embodiment, the phosphorus-containing anti-wear agent may be a zinc free phosphorus compound. The zinc-free phosphorus anti-wear agent may contain sulfur or may be sulfur-free. Sulfur-free phosphorus-containing antiwear agents include hydrocarbyl phosphites, hydrocarbyl phosphines, hydrocarbyl phosphonates, alkylphosphate esters, amine or ammonium phosphate salts, or mixtures thereof.

[0068] Phosphorus esters include compounds such as the dihydrocarbon and trihydrocarbon phosphites, e.g., dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite; amine salts of alkyl and dialkylphosphoric acids or derivatives including, for example, the amine salt of a reaction product of a dialkyldithiophosphoric acid with propylene oxide and subsequently followed by a further reaction with P_2O_5; and mixtures thereof (as described in U.S. Pat. No. 3,197,405).

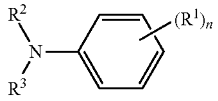
[0069] Amine phosphates may be amine salts of (i) monohydrocarbylphosphoric acid, (ii) dihydrocarbylphosphoric acid, (iii) hydroxy-substituted di-ester of phosphoric acid, or (iv) phosphorylated hydroxy-substituted di- or tri-ester of phosphoric acid. The amine salt of a sulfur-free phosphorus-containing compound may be salts of primary amines, secondary amines, tertiary amines, or mixtures thereof.

[0070] Amine phosphate salts may be derived from mono- or di-hydrocarbyl phosphoric acid (typically alkyl phosphoric acid), or mixtures thereof. The alkyl of the mono-or di- hydrocarbyl phosphoric acid may comprise linear or branched alkyl groups of 3 to 36 carbon atoms. The hydrocarbyl group of the linear or branched hydrocarbylphosphoric acid may contain 4 to 30, or 8 to 20 carbon atoms. Examples of a suitable hydrocarbyl group of the hydrocarbyl phosphoric acid may include isopropyl, n-butyl, sec-butyl, amyl, 4-methyl-2-pentyl (i.e. methylamyl), n-hexyl, n-heptyl, n-octyl, iso-octyl, 2-ethylhexyl, nonyl, 2-propylheptyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, oleyl, or combinations thereof. In one embodiment, the phosphate is a mixture of mono- and di- (2-ethylhexyl)phosphate.

[0071] Examples of suitable primary amines include ethylamine, propylamine, butylamine, 2-ethylhexylamine, octylamine, and dodecylamine, as well as such fatty amines as n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine and oleyamine. Other useful fatty amines include commercially available fatty amines such as "Armeen®" amines (products available from Akzo Chemicals, Chicago, Ill.), such as Armeen C, Armeen O, Armeen O L, Armeen T, Armeen H T, Armeen S and Armeen S D, wherein the letter designation relates to the fatty group, such as coco, oleyl, tallow, or stearyl groups.

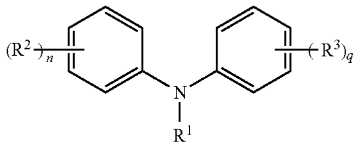
[0072] In one embodiment, the amine phosphate may be derived from aromatic amines, i.e. amines substituted with one or more aryl groups. The aryl groups may be substituted, unsubstituted, or combinations thereof. The aryl groups may be substituted with hydrocarbyl groups, acyl groups, hydroxy groups, alkoxy groups, and combinations thereof. Examples of suitable aromatic amines include anilines, diphenylamines, phenylene diamines, and derivatives thereof

[0073] In one embodiment, the aromatic amine phosphate is a phosphate salt of an aniline compound represented by the formula



where n=0, 1, or 2; each le is independently selected from a hydrocarbyl group of 1 to 20 carbon atoms, $—C(=O)XR^4$, $—OR^5$, or combinations thereof; R^2 and R^3 are independently hydrogen or an aliphatic hydrocarbyl group of 1 to 12 carbon atoms; X is oxygen or $—NR^6$-; R^4 is selected from a hydrocarbyl group of 1 to 24 carbon atoms, a (poly)ether group according to the formula $—(CH_2CHR^7O)_m—R^8$, or combinations thereof; R^5 is hydrogen, a hydrocarbyl group of 1 to 24 carbon atoms, a (poly)ether group according to the formula $—(CH_2CHR^7O)_m$-R^8; R^6 is hydrogen or a hydrocarbyl group of 1 to 12 carbon atoms; m is an integer from 1 to 20; each R^7 is independently hydrogen, a hydrocarbyl group of 1 to 20 carbon atoms, or combinations thereof; and R8 is hydrogen or a hydrocarbyl group of 1 to 24 carbon atoms. Suitable aniline compounds include N,N-dihydrocarbylanilines, such as N,N-di(hexyl)aniline; hydrocarbyl esters of anthranilic acid, such as methyl-, ethyl-, propyl-, butyl-,hexyl-, octyl, iso-octyl, 2-ethylhexyl, decyl-, isodecyl-, dodecyl-, tridecyl-, isotridecyl, hexadecyl-, oleyl, stearyl- esters and combinations thereof; and alkoxy-substituted anilines, such as p-anisidine, p-ethoxyaniline, and N,N-di(2-ethylhexyl)-p-ethoxyaniline.

[0074] In one embodiment, the aromatic amine phosphate is a phosphate salt of a diaryl amine compound represented by the formula



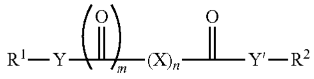
where R^1 is selected from hydrogen, a hydrocarbyl group of 1 to 24 carbon atoms, an acyl-containing group according to the formula $—CH_2CH_2(C=O)OR^4$, an alkoxylate according to the formula $—(CH_2CHR^5O)$m-R_6, or combinations thereof; R^2 and R^3 are each independently hydrocarbyl groups of 4 to 18 carbon atoms; each n and q is independently 0, 1, or 2; R^4 is a hydrocarbyl group of 1 to 18 carbon atoms; each R^5 is independently hydrogen or a hydrocarbyl group of 1 to 18 carbon atoms; R^6 is hydrogen or a hydrocarbyl group of 1 to 18 carbon atoms; and m is an integer from 1 to 20. When either n or q is 2 and the two hydrocarbyl groups (R^2 or R^3 as applicable) are on adjacent carbons of the ring, they may be taken together to form 5- or 6-membered rings that may be saturated, unsaturated, or aromatic. Suitable diaryl amine compounds include diphenylamine, phenyl-α-naphthylamine, alkylated diphenylamine, alkylated phenyl-α-naphthylamine, and combinations thereof. Alkylated diarylamines may have one, two, three, or even four alkyl groups; alkyl groups may be branched or linear and contain 4 to 18 carbon atoms, 6 to 12 carbon atoms, or 8 to 10 carbon atoms.

[0075] In one embodiment, the zinc-free phosphorus antiwear agent may be selected from phosphites, phosphonates, alkylphosphate esters, amine or ammonium phosphate salts, or mixtures thereof and is present in the lubricant composition in amount 0.01 to 5 percent by weight of the composition, or 0.1 to 3.2 weight percent of the composition, or 0.35 to 1.8 weight percent of the composition. In one embodiment, the zinc-free phosphorus anti-wear agent may be present in an amount to provide 0.01 weight percent to 0.15 weight percent phosphorus, or 0.025 to 0.085 weight percent phosphorus, or 0.025 to 0.065 weight percent phosphorus to the composition.

[0076] In one embodiment, the anti-wear agent may be a phosphorus-free compound. Examples of suitable phosphorus-free antiwear agents include titanium compounds, hydroxy-carboxylic acid derivatives such as esters, amides, imides or amine or ammonium salt, sulfurized olefins, (thio)carbamate-containing compounds, such as (thio)carbamate esters, (thio)carbamate amides, (thio)carbamic ethers, alkylene-coupled (thio)carbamates, and bis(S-alkyl (dithio)carbamyl) disulfides. Suitable hydroxy-carboxylic acid derivatives include tartaric acid derivatives, malic acid derivatives, citric acid derivatives, glycolic acid derivatives, lactic acid derivatives, and mandelic acid derivatives.

[0077] The antiwear agent may in one embodiment include a tartrate or tartrimide as disclosed in International Publication WO 2006/044411 or Canadian Patent CA 1 183 125. The tartrate or tartrimide may contain alkyl-ester groups, where the sum of carbon atoms on the alkyl groups is at least 8. The antiwear agent may in one embodiment include a citrate as is disclosed in U.S. Patent Application 20050198894.

[0078] The anti-wear agent may be represented by the formula:



$$R^1—Y—\left(\overset{O}{\overset{\|}{C}}\right)_m—(X)_n—\overset{O}{\overset{\|}{C}}—Y'—R^2$$

wherein Y and Y' are independently —O—, >NH, >NR^3, or an imide group formed by taking together both Y and Y' groups and forming a R^1-N> group between two >C═O groups; X is independently —Z—O—Z'—, >CH$_2$, >CHR^4, >CR^{4}R^5, >C(OH)(CO$_2$R^2), >C(CO$_2$R^2)$_2$, or >CHOR^6; Z and Z' are independently >CH$_2$, >CHR^4, >CR^{4}R^5, >C(OH)(CO$_2$R^2), or >CHOR^6; n is 0 to 10, with the proviso that when n=1, X is not >CH$_2$, and when n=2, both X's are not >CH$_2$; m is 0 or 1; le is independently hydrogen or a hydrocarbyl group, typically containing 1 to 150 carbon atoms, with the proviso that when le is hydrogen, m is 0, and n is more than or equal to 1; R^2 is a hydrocarbyl group, typically containing 1 to 150 carbon atoms; R^3, R^4 and R^5 are independently hydrocarbyl groups; and R^6 is hydrogen or a hydrocarbyl group, typically containing 1 to 150 carbon atoms.

[0079] The phosphorus-free antiwear agent may be present at 0 wt % to 3 wt %, or 0.1 wt % to 1.5 wt %, or 0.5 wt % to 1.1 wt % of the lubricating composition.

[0080] The antiwear agent, be it phosphorus-containing, phosphorus free, or mixtures, may be present at 0.15 weight % to 6 weight %, or 0.2 weight % to 3.0 weight %, or 0.5 weight % to 1.5 weight % of the lubricating composition.

Ashless Antioxidant

[0081] The instant compositions may include an ashless antioxidant. Ashless antioxidants may comprise one or more of arylamines, diarylamines, alkylated arylamines, alkylated diaryl amines, phenols, hindered phenols, sulfurized olefins, or mixtures thereof. In one embodiment the lubricating composition includes an antioxidant, or mixtures thereof. The antioxidant may be present at 1.2 weight % to 7 weight %, or 1.2 weight % to 6 weight %, or 1.5 weight % to 5 weight %, of the lubricating composition.

[0082] The diarylamine or alkylated diarylamine may be a phenyl-α-naphthylamine (PANA), an alkylated diphenylamine, or an alkylated phenylnapthylamine, or mixtures thereof. The alkylated diphenylamine may include di-nonylated diphenylamine, nonyl diphenylamine, octyl diphenylamine, di-octylated diphenylamine, di-decylated diphenylamine, decyl diphenylamine and mixtures thereof. In one embodiment, the diphenylamine may include nonyl diphenylamine, dinonyl diphenylamine, octyl diphenylamine, dioctyl diphenylamine, or mixtures thereof. In one embodiment the alkylated diphenylamine may include nonyl diphenylamine, or dinonyl diphenylamine. The alkylated diarylamine may include octyl, di-octyl, nonyl, di-nonyl, decyl or di-decyl phenylnapthylamines.

[0083] The diarylamine antioxidant may be present on a weight basis of this lubrication composition at 0.1% to 10%, 0.35% to 5%, or even 0.5% to 2%.

[0084] The phenolic antioxidant may be a simple alkyl phenol, a hindered phenol, or coupled phenolic compounds.

[0085] The hindered phenol antioxidant often contains a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group may be further substituted with a hydrocarbyl group (typically linear or branched alkyl) and/or a bridging group linking to a second aromatic group. Examples of suitable hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol or 4-butyl-2,6-di-tert-butylphenol, 4-dodecyl-2,6-di-tert-butylphenol, or butyl 3-(3,5-ditert-butyl-4-hydroxyphenyl)propanoate. In one embodiment, the hindered phenol antioxidant may be an ester and may include, e.g., Irganox™ L-135 from Ciba.

[0086] Coupled phenols often contain two alkylphenols coupled with alkylene groups to form bisphenol compounds. Examples of suitable coupled phenol compounds include 4,4'-methylene bis-(2,6-di-tert-butyl phenol), 4-methyl-2,6-di-tert-butylphenol, 2,2'-bis-(6-t-butyl-4-heptylphenol); 4,4'-bis(2,6-di-t-butyl phenol), 2,2'-methylenebis(4-methyl-6-t-butylphenol), and 2,2'-methylene bis(4-ethyl-6-t-butylphenol).

[0087] Phenols may include polyhydric aromatic compounds and their derivatives. Examples of suitable polyhydric aromatic compounds include esters and amides of gallic acid, 2,5-dihydroxybenzoic acid, 2,6-dihydroxybenzoic acid, 1,4-dihydroxy-2-naphthoic acid, 3,5-dihydroxynaphthoic acid, 3,7-dihydroxy naphthoic acid, and mixtures thereof.

[0088] In one embodiment, the phenolic antioxidant comprises a hindered phenol. In another embodiment the hindered phenol is derived from 2,6-ditertbutyl phenol.

[0089] In one embodiment the lubricating composition comprises a phenolic antioxidant in a range of 0.01 wt % to 5 wt %, or 0.1 wt % to 4 wt %, or 0.2 wt % to 3 wt %, or 0.5 wt % to 2 wt % of the lubricating composition.

[0090] Sulfurized olefins are well known commercial materials, and those which are substantially nitrogen-free, that is, not containing nitrogen functionality, are readily available. The olefinic compounds which may be sulfurized are diverse in nature. They contain at least one olefinic double bond, which is defined as a non-aromatic double bond; that is, one connecting two aliphatic carbon atoms. These materials generally have sulfide linkages having 1 to 10 sulfur atoms, for instance, 1 to 4, or 1 or 2.

[0091] Ashless antioxidants may be used separately or in combination. In one embodiment, two or more different antioxidants are used in combination, such that there is at least 0.1 weight percent of each of the at least two antioxidants and wherein the combined amount of the ashless antioxidants is 1.2 to 7 weight percent. In one embodiment, there may be at least 0.25 to 3 weight percent of each ashless antioxidant.

Metal-Containing Detergent

[0092] Metal-containing detergents are well known in the art. They are generally made up of metal salts, especially alkali metals and alkaline earth metals, of acidic organic substrates. Metal-containing detergents may be neutral, i.e. a stoichiometric salt of the metal and substrate also referred to as neutral soap or soap, or overbased.

[0093] Metal overbased detergents, otherwise referred to as overbased detergents, metal-containing overbased detergents or superbased salts, are characterized by a metal content in excess of that which would be necessary for neutralization according to the stoichiometry of the metal and the particular acidic organic compound, i.e. the substrate, reacted with the metal. The overbased detergent may comprise one or more of non-sulfur containing phenates, sulfur containing phenates, sulfonates, salicylates, and mixtures thereof.

[0094] The amount of excess metal is commonly expressed in terms of substrate to metal ratio. The terminology "metal ratio" is used in the prior art and herein to define the ratio of the total chemical equivalents of the metal in the overbased salt to the chemical equivalents of the metal in the salt which would be expected to result from the reaction between the hydrocarbyl substituted organic acid; the hydrocarbyl-substituted phenol or mixtures thereof to be overbased, and the basic metal compound according to the known chemical reactivity and the stoichiometry of the two reactants. Thus, in a normal or neutral salt (i.e. soap) the metal ratio is one and, in an overbased salt, the metal ratio is greater than one, especially greater than 1.3. The overbased metal detergent may have a metal ratio of 5 to 30, or a metal ratio of 7 to 22, or a metal ratio of at least 11.

[0095] 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. Overbased phenates and salicylates typically have a total base number of 180 to 450 TBN. Overbased sulfonates typically have a total base number of 250 to 600, or 300 to 500. Overbased detergents are known in the art.

[0096] Alkylphenols are often used as constituents in and/or building blocks for overbased detergents. Alkylphenols may be used to prepare phenate, salicylate, salixarate, or saligenin detergents or mixtures thereof. Suitable alkylphenols may include para-substitued hydrocarbyl phenols. The hydrocarbyl group may be linear or branched aliphatic groups of 1 to 60 carbon atoms, 8 to 40 carbon atoms, 10 to 24 carbon atoms, 12 to 20 carbon atoms, or 16 to 24 carbon atoms. In one embodiment, the alkylphenol overbased detergent is prepared from an alkylphenol or mixture thereof that is free of or substantially free of (i.e. contains less than 0.1 weight percent) p-dodecylphenol. In one embodiment, the lubricating composition contains less than 0.3 weight percent of alkylphenol, less than 0.1 weight percent of alkylphenol, or less than 0.05 weight percent of alkylphenol.

[0097] The overbased metal-containing detergent may be alkali metal or alkaline earth metal salts. In one embodiment, the overbased detergent may be sodium salts, calcium salts, magnesium salts, or mixtures thereof of the phenates, sulfur-containing phenates, sulfonates, salixarates and salicylates. In one embodiment, the overbased detergent is a calcium detergent, a magnesium detergent or mixtures thereof. In one embodiment, the overbased calcium detergent may be present in an amount to deliver at least 500 ppm calcium by weight and no more than 3000 ppm calcium by weight, or at least 1000 ppm calcium by weight, or at least 2000 ppm calcium by weight, or no more than 2500 ppm calcium by weight to the lubricating composition. In one embodiment, the overbased detergent may be present in an amount to deliver no more than 500 ppm by weight of magnesium to the lubricating composition, or no more than 330 ppm by weight, or no more than 125 ppm by weight, or no more than 45 ppm by weight. In one embodiment, the lubricating composition is essentially free of (i.e. contains less than 10 ppm) magnesium resulting from the overbased detergent. In one embodiment, the overbased detergent may be present in an amount to deliver at least 200 ppm by weight of magnesium, or at least 450 ppm by weight magnesium, or at least 700 ppm by weight magnesium to the lubricating composition. In one embodiment, both calcium and magnesium containing detergents may be present in the lubricating composition. Calcium and magnesium detergents may be present such that the weight ratio of calcium to magnesium is 10:1 to 1:10, or 8:3 to 4:5, or 1:1 to 1:3. In one embodiment, the overbased detergent is free of or substantially free of sodium.

[0098] In one embodiment, 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 U.S. Patent Publication 2005/065045 (and granted as U.S. Pat. No. 7,407,919). The linear alkylbenzene sulfonate detergent may be particularly useful for assisting in improving fuel economy. The linear alkyl group may be attached to the benzene ring anywhere along the linear chain of the alkyl group, but often in the 2, 3 or 4 position of the linear chain, and in some instances, predominantly in the 2 position, resulting in the linear alkylbenzene sulfonate detergent.

[0099] Salicylate detergents and overbased salicylate detergents may be prepared in at least two different manners. Carbonylation (also referred to as carboxylation) of a p-alkylphenol is described in many references including U.S. Pat. No. 8,399,388. Carbonylation may be followed by overbasing to form overbased salicylate detergent. Suitable p-alkylphenols include those with linear and/or branched hydrocarbyl groups of 1 to 60 carbon atoms. Salicylate detergents may also be prepared by alkylation of salicylic acid, followed by overbasing, as described in U.S. Pat. No. 7,009,072. Salicylate detergents prepared in this manner, may be prepared from linear and/or branched alkylating agents (usually 1-olefins) containing 6 to 50 carbon atoms, 10 to 30 carbon atoms, or 14 to 24 carbon atoms. In one embodiment, the overbased detergent is a salicylate detergent. In one embodiment, the salicylate detergent is free of unreacted p-alkylphenol (i.e. contains less than 0.1 weight percent). In one embodiment, the salicylate detergent is prepared by alkylation of salicylic acid.

[0100] The metal-containing overbased detergents may be present at 0.2 wt % to 15 wt %, or 0.3 wt % to 10 wt %, or 0.3 wt % to 8 wt %, or 0.4 wt % to 3 wt %. 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.

[0101] Metal-containing detergents contribute sulfated ash to a lubricating composition. Sulfated ash may be determined by ASTM D874. In one embodiment, the lubricating composition comprises a metal-containing detergent in an amount to deliver at least 0.4 weight percent sulfated ash to the total composition. In another embodiment, the metal-containing detergent is present in an amount to deliver at least 0.6 weight percent sulfated ash, or at least 0.75 weight percent sulfated ash, or even at least 0.9 weight percent sulfated ash to the lubricating composition. In one embodiment, the metal-containing overbased detergent is present in an amount to deliver 0.1 weight percent to 0.8 weight percent sulfated ash to the lubricating composition.

[0102] In addition to ash and TBN, overbased detergents contribute detergent soap, also referred to as neutral detergent salt, to the lubricating composition. Soap, being a metal salt of the substrate, may act as a surfactant in the lubricating composition. In one embodiment, the lubricating composition comprises 0.05 weight percent to 1.5 weight percent detergent soap, or 0.1 weight percent to 0.9 weight percent detergent soap. In one embodiment, the lubricating composition contains no more than 0.5 weight percent detergent soap. The overbased detergent may have a weight ratio of ash: soap of 5:1 to 1:2.3, or 3.5:1 to 1:2, or 2.9:1 to 1:1:7.

Ashless Polyolefin Dispersant

[0103] The lubricating compositions may comprise an ashless polyolefin dispersant. The dispersant may be a succinimide dispersant, a Mannich dispersant, a polyolefin succinic acid ester, amide, or ester-amide, or mixtures thereof. In one embodiment, the dispersant may be a borated succinimide dispersant. In one embodiment, the dispersant may be present as a single dispersant. In one embodiment, the dispersant may be present as a mixture of two or three different dispersants, wherein at least one may be a succinimide dispersant.

[0104] The succinimide dispersant may be a derivative of an aliphatic polyamine, or mixtures thereof. The aliphatic polyamine may be aliphatic polyamine such as an ethylenepolyamine, a propylenepolyamine, a butylenepolyamine, or mixtures thereof. In one embodiment, the aliphatic polyamine may be ethylenepolyamine. In one embodiment, the aliphatic polyamine may be selected from the group consisting of ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, polyamine still bottoms, and mixtures thereof.

[0105] The succinimide dispersant may be a derivative of an aromatic amine, an aromatic polyamine, or mixtures thereof. The aromatic amine may be 4-aminodiphenylamine (ADPA) (also known as N-phenylphenylenediamine), derivatives of ADPA (as described in United States Patent Publications 2011/0306528 and 2010/0298185), a nitroaniline, an aminocarbazole, an amino-indazolinone, an aminopyrimidine, 4-(4-nitrophenylazo)aniline, or combinations thereof. In one embodiment, the dispersant is derivative of an aromatic amine wherein the aromatic amine has at least three non-continuous aromatic rings.

[0106] The succinimide dispersant may be a derivative of a polyether amine or polyether polyamine. Typical polyether amine compounds contain at least one ether unit and will be chain terminated with at least one amine moiety. The polyether polyamines can be based on polymers derived from C_2-C_6 epoxides such as ethylene oxide, propylene oxide, and butylene oxide. Examples of polyether polyamines are sold under the Jeffamine® brand and are commercially available from Hunstman Corporation located in Houston, Texas.

[0107] The dispersant may be a N-substituted long chain alkenyl succinimide. Examples of N-substituted long chain alkenyl succinimide include polyisobutylene succinimide. Typically the polyisobutylene from which polyisobutylene succinic anhydride is derived has a number average molecular weight of 350 to 5000, or 550 to 3000 or 750 to 2500. Succinimide dispersants and their preparation are disclosed, for instance in U.S. Pat. Nos. 3,172,892, 3,219,666, 3,316,177, 3,340,281, 3,351,552, 3,381,022, 3,433,744, 3,444,170, 3,467,668, 3,501,405, 3,542,680, 3,576,743, 3,632,511, 4,234,435, Re 26,433, and 6,165,235, 7,238,650 and EP Patent 0 355 895B1 .

[0108] The dispersant may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron compounds, urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds.

[0109] The dispersant may be borated using one or more of a variety of agents selected from the group consisting of the various forms of boric acid (including metaboric acid, HBO_2, orthoboric acid, H_3BO_3, and tetraboric acid, $H_2B_4O_7$), boric oxide, boron trioxide, and alkyl borates. In one embodiment the borating agent is boric acid which may be used alone or in combination with other borating agents. Methods of preparing borated dispersants are known in the art. The borated dispersant may be prepared in such a way that they contain 0.1weight % to 2.5 weight % boron, or 0.1 weight % to 2.0 weight % boron or 0.2 to 1.5 weight % boron or 0.3 to 1.0 weight % boron.

[0110] Suitable polyisobutylenes for use in the succinimide dispersant, may include those formed from polyisobutylene or highly reactive polyisobutylene having at least about 50 mol %, such as about 60 mol %, and particularly from about 70 mol % to about 90 mol % or greater than 90 mol %, terminal vinylidene content. Suitable polyisobutenes may include those prepared using BF_3 catalysts. In one embodiment, the borated dispersant is derived from a polyolefin having number average molecular weight of 350 to

3000 Daltons and a vinylidene content of at least 50 mol %, or at least 70 mol %, or at least 90 mol %.

[0111] The dispersant may be prepared/obtained/obtainable from reaction of succinic anhydride by an "ene" or "thermal" reaction, by what is referred to as a "direct alkylation process." The "ene" reaction mechanism and general reaction conditions are summarised in "Maleic Anhydride", pages, 147-149, Edited by B. C. Trivedi and B. C. Culbertson and Published by Plenum Press in 1982. The dispersant prepared by a process that includes an "ene" reaction may be a polyisobutylene succinimide having a carbocyclic ring present on less than 50 mole %, or 0 to less than 30 mole %, or 0 to less than 20 mole %, or 0 mole % of the dispersant molecules. The "ene" reaction may have a reaction temperature of 180 ° C. to less than 300 ° C., or 200 ° C. to 250 ° C., or 200 ° C. to 220 ° C.

[0112] The dispersant may also be obtained/obtainable from a chlorine-assisted process, often involving Diels-Alder chemistry, leading to formation of carbocyclic linkages. The process is known to a person skilled in the art. The chlorine-assisted process may produce a dispersant that is a polyisobutylene succinimide having a carbocyclic ring present on 50 mole % or more, or 60 to 100 mole % of the dispersant molecules. Both the thermal and chlorine-assisted processes are described in greater detail in U.S. Pat. No. 7,615,521, columns 4-5 and preparative examples A and B.

[0113] The dispersant may be used alone or as part of a mixture of non-borated and borated dispersants. If a mixture of dispersants is used, there may be two to five, or two to three or two dispersants.

[0114] The polyolefin dispersant may comprise a polyalphaolefins (PAO) containing dispersant selected from the group consisting of a polyalphaolefin succinimide, a polyalphaolefin succinamide, a polyalphaolefin acid ester, a polyalphaolefin oxazoline, a polyalphaolefin imidazoline, a polyalphaolefin succinamide imidazoline, and combinations thereof

[0115] Polyalphaolefins (PAO) useful as feedstock in forming the PAO containing dispersants are those derived from oligomerization or polymerization of ethylene, propylene, and α-olefins. Suitable α-olefins include 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tetradecene, and 1-octadecene. Feedstocks containing a mixture of two or more of the foregoing monomers as well as other hydrocarbons are typically employed when manufacturing PAOs commercially. The PAO may take the form of dimers, trimers, tetramers, polymers, and the like.

[0116] The PAO may be reacted with maleic anhydride (MA) to form the polyalphaolefin succinic anhydride (PAO-SA) and subsequently the anhydride may reacted with one or more of polyamines, aminoalcohols, and alcohols/polyols to form polyalphaolefin succinimide, polyalphaolefin succinamide, polyalphaolefin succinic acid ester, polyalphaolefin oxazoline, polyalphaolefin imidazoline, polyalphaolefin-succinamide-imidazoline, and mixtures thereof.

[0117] The polyolefin 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 1 wt % to 6 wt % of the lubricating composition.

Polymeric Viscosity Modifier

[0118] The lubricating composition may contain a polymeric viscosity modifier, a dispersant viscosity modifier, or combinations thereof. The dispersant viscosity modifier may be generally understood to be a functionalized, i.e. derivatized, form of a polymer similar to that of the polymeric viscosity modifier.

[0119] The polymeric viscosity modifier may be an olefin (co)polymer, a poly(meth)acrylate (PMA), or mixtures thereof. In one embodiment, the polymeric viscosity modifier is an olefin (co)polymer.

[0120] The olefin polymer may be derived from isobutylene or isoprene. In one embodiment, the olefin polymer is prepared from ethylene and a higher olefin within the range of C3-C10 alpha-mono-olefins, for example, the olefin polymer may be prepared from ethylene and propylene.

[0121] In one embodiment, the olefin polymer may be a polymer of 15 to 80 mole percent of ethylene, for example, 30 mol percent to 70 mol percent ethylene and from and from 20 to 85 mole percent of C3 to C10 mono-olefins, such as propylene, for example, 30 to 70 mol percent propylene or higher mono-olefins. Terpolymer variations of the olefin copolymer may also be used and may contain up to 15 mol percent of a non-conjugated diene or triene. Non-conjugated dienes or trienes may have 5 to about 14 carbon atoms. The non-conjugated diene or triene monomers may be characterized by the presence of a vinyl group in the structure and can include cyclic and bicycle compounds. Representative dienes include 1,4-hexadiene, 1,4-cyclohexadiene, dicyclopentadiene, 5-ethyldiene-2-norbornene, 5-methylene-2-norbornene, 1,5-heptadiene, and 1,6-octadiene.

[0122] In one embodiment, the olefin copolymer may be a copolymer of ethylene, propylene, and butylene. The polymer may be prepared by polymerizing a mixture of monomers comprising ethylene, propylene and butylene. These polymers may be referred to as copolymers or terpolymers. The terpolymer may comprise from about 5 mol % to about 20 mol %, or from about 5 mol % to about 10 mol % structural units derived from ethylene; from about 60 mol % to about 90 mol %, or from about 60 mol % to about 75 mol structural units derived from propylene; and from about 5 mol % to about 30 mol %, or from about 15 mol % to about 30 mol % structural units derived from butylene. The butylene may comprise any isomers or mixtures thereof, such as n-butylene, iso-butylene, or a mixture thereof. The butylene may comprise butene-1. Commercial sources of butylene may comprise butene-1 as well as butene-2 and butadiene. The butylene may comprise a mixture of butene-1 and isobutylene wherein the weight ratio of butene-1 to isobutylene is about 1:0.1 or less. The butylene may comprise butene-1 and be free of or essentially free of isobutylene.

[0123] In one embodiment, the olefin copolymer may be a copolymer of ethylene and butylene. The polymer may be prepared by polymerizing a mixture of monomers comprising ethylene and butylene wherein, the monomer composition is free of or substantially free of propylene monomers (i.e. contains less than 1 weight percent of intentionally added monomer). The copolymer may comprise 30 to 50 mol percent structural units derived from butylene; and from about 50 mol percent to 70 mol percent structural units derived from ethylene. The butylene may comprise a mixture of butene-1 and isobutylene wherein the weight ratio of butene-1 to isobutylene is about 1:0.1 or less. The butylene may comprise butene-1 and be free of or essentially free of isobutylene.

[0124] Useful olefin polymers, in particular, ethylene-α-olefin copolymers have a number average molecular weight ranging from 4500 to 500,000, for example, 5000 to 100,000, or 7500 to 60,000, or 8000 to 45,000.

[0125] The formation of functionalized ethylene-α-olefin copolymer is well known in the art, for instance those described in U.S. Pat. No. 7,790,661 column 2, line 48 to column 10, line 38. Additional detailed descriptions of similar functionalized ethylene-α-olefin copolymers are found in International Publication WO2006/015130 or U.S. Pat. Nos. 4,863,623; 6,107,257; 6,107,258; 6,117,825; and 7,790,661. In one embodiment the functionalized ethylene-α-olefin copolymer 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 paragraphs [0065] to [0073]).

[0126] In one embodiment, the lubricating composition comprises a dispersant viscosity modifier (DVM). The DVM may comprise an olefin polymer that has been modified by the addition of a polar moiety.

[0127] The olefin polymers are functionalized by modifying the polymer by the addition of a polar moiety. In one useful embodiment, the functionalized copolymer is the reaction product of an olefin polymer grafted with an acylating agent. In one embodiment, the acylating agent may be an ethylenically unsaturated acylating agent. Useful acylating agents are typically α,β unsaturated compounds having at least one ethylenic bond (prior to reaction) and at least one, for example two, carboxylic acid (or its anhydride) groups or a polar group which is convertible into said carboxyl groups by oxidation or hydrolysis. The acylating agent grafts onto the olefin polymer to give two carboxylic acid functionalities. Examples of useful acylating agents include maleic anhydride, chlormaleic anhydride, itaconic anhydride, or the reactive equivalents thereof, for example, the corresponding dicarboxylic acids, such as maleic acid, fumaric acid, cinnamic acid, (meth)acrylic acid, the esters of these compounds and the acid chlorides of these compounds.

[0128] In one embodiment, the functionalized ethylene-α-olefin copolymer comprises an olefin copolymer grafted with the acyl group which is further functionalized with a hydrocarbyl amine, a hydrocarbyl alcohol group, amino- or hydroxy- terminated polyether compounds, and mixtures thereof.

[0129] Amine functional groups may be added to the olefin polymer by reacting the olefin copolymer (typically, an ethylene-α-olefin copolymer, such as an ethylene-propylene copolymer) with an acylating agent (typically maleic anhydride) and a hydrocarbyl amine having a primary or secondary amino group. In one embodiment, the hydrocarbyl amine may be selected from aromatic amines, aliphatic amines, and mixtures thereof.

[0130] In one embodiment, the hydrocarbyl amine component may comprise at least one aromatic amine containing at least one amino group capable of condensing with said acyl group to provide a pendant group and at least one additional group comprising at least one nitrogen, oxygen, or sulfur atom, wherein said aromatic amine is selected from the group consisting of (i) a nitro-substituted aniline, (ii) an amine comprising two aromatic moieties linked by a C(O)NR— group, a —C(O)O— group, an —O— group, an N═N— group, or an —SO2— group where R is hydrogen or hydrocarbyl, one of said aromatic moieties bearing said condensable amino group, (iii) an aminoquinoline, (iv) an aminobenzimidazole, (v) an N,N-dialkylphenylenediamine, (vi), an aminodiphenylamine (also N,N-phenyldiamine), and (vii) a ring-substituted benzyl amine.

[0131] In one embodiment, the hydrocarbyl amine component may comprise at least one aliphatic amine containing at least one amino group capable of condensing with said acyl group to provide a pendant group and at least one additional group comprising at least one nitrogen, oxygen, or sulfur atom. Suitable aliphatic amines include polyethylene polyamines (such as tetraethylene pentamine (TEPA), triethylene tetra amine (TETA), pentaethylene hexamine (PEHA), and polyamine bottoms), N,N-dimethylaminopropylamine (DMAPA), N-(aminopropyl)morpholine, N,N-dilsostearylaminopropylamine, ethanolamine, and combinations thereof.

[0132] In another one embodiment, the polar moiety added to the functionalized ethylene-α-olefin copolymer may be derived from a hydrocarbyl alcohol group, containing at least one hydroxy group capable of condensing with said acyl group to provide a pendant group and at least one additional group comprising at least one nitrogen, oxygen, or sulfur atom. The alcohol functional groups may be added to the olefin polymer by reacting the olefin copolymer with an acylating agent (typically maleic anhydride) and a hydrocarbyl alcohol. The hydrocarbyl alcohol may be a polyol compound. Suitable hydrocarbyl polyols include ethylene glycol and propylene glycol, trimethylol propane (TMP), pentaerythritol, and mixtures thereof.

[0133] In another one embodiment, the polar moiety added to the functionalized ethylene-α-olefin copolymer may be amine-terminated polyether compounds, hydroxy-terminated polyether compounds, and mixtures thereof. The hydroxy terminated or amine terminated polyether may be selected from the group comprising polyethylene glycols, polypropylene glycols, mixtures of one or more amine terminated polyether compounds containing units derived from ethylene oxides, propylene oxides, butylene oxides or some combination thereof, or some combination thereof. Suitable polyether compounds include Synalox® line of polyalkylene glycol compounds, the UCON™ OSP line of polyether compounds available from Dow Chemical, Jeffamine® line of polyether amines available from Huntsman.

[0134] In one embodiment, lubricating composition may comprise a poly(meth)acrylate polymeric viscosity modifier. As used herein, the term "(meth)acrylate" and its cognates means either methacrylate or acrylate, as will be readily understood.

[0135] In one embodiment, the poly(meth)acrylate polymer is prepared from a monomer mixture comprising (meth)acrylate monomers having alkyl groups of varying length. The (meth)acrylate monomers may contain alkyl groups that are straight chain or branched chain groups. The alkyl groups may contain 1 to 24 carbon atoms, for example 1 to 20 carbon atoms.

[0136] The poly(meth)acrylate polymers described herein are formed from monomers derived from saturated alcohols, such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, 2-methylpentyl (meth)acrylate, 2-propylheptyl (meth)acrylate, 2-butyloctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, nonyl (meth)acrylate, isooctyl (meth)acrylate, isononyl (meth)acrylate, 2-tert-butylheptyl (meth)acrylate, 3-isopropylheptyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, 5-methylundecyl (meth)acrylate, dodecyl (meth)acrylate, 2-methyldodecyl (meth)acrylate, tridecyl (meth)acrylate, 5-methyltridecyl (meth)acrylate, tetradecyl (meth)acrylate, pentadecyl (meth)acrylate, hexadecyl (meth)acrylate, 2-methylhexadecyl (meth)acrylate, heptadecyl (meth)acrylate, 5-isopropylheptadecyl (meth)acrylate, 4-tert-butyloctadecyl (meth)acrylate, 5-ethyloctadecyl (meth)acrylate, 3-isopropyl-octadecyl-(meth)acrylate, octadecyl (meth)acrylate, nonadecyl (meth)acrylate, eicosyl (meth)-acrylate, (meth)acrylates derived from unsaturated alcohols, such as oleyl (meth)acrylate; and cycloalkyl (meth)acrylates, such as 3-vinyl-2-butylcyclohexyl (meth) acrylate or bornyl (meth)acrylate.

[0137] Other examples of monomers include alkyl (meth) acrylates with long-chain alcohol-derived groups which may be obtained, for example, by reaction of a (meth)acrylic acid (by direct esterification) or methyl (meth)acrylate (by transesterification) with long-chain fatty alcohols, in which reaction a mixture of esters such as (meth)acrylate with alcohol groups of various chain lengths is generally obtained. These fatty alcohols include Oxo Alcohol® 7911, Oxo Alcohol® 7900 and Oxo Alcohol® 1100 of Monsanto; Alphanol® 79 of ICI; Nafol® 1620, Alfol® 610 and Alfol® 810 of Condea (now Sasol); Epal® 610 and Epal® 810 of Ethyl Corporation; Linevol® 79, Linevol® 911 and Dobanol® 25 L of Shell AG; Lial® 125 of Condea Augusta, Milan; Dehydad® and Lorol® of Henkel KGaA (now Cognis) as well as Linopol® 7-11 and Acropol® 91 of Ugine Kuhlmann.

[0138] In one embodiment, the poly(meth)acrylate polymer comprises a dispersant monomer; dispersant monomers include those monomers which may copolymerize with (meth)acrylate monomers and contain one or more heteroatoms in addition to the carbonyl group of the (meth)acrylate. The dispersant monomer may contain a nitrogen-containing group, an oxygen-containing group, or mixtures thereof.

[0139] The oxygen-containing compound may include hydroxyalkyl(meth)acrylates such as 3-hydroxypropyl (meth)acrylate, 3,4-dihydroxybutyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl(meth)acrylate, 2,5-dimethyl-1,6-hexanediol (meth)acrylate, 1,10-decanediol(meth)acrylate, carbonyl-containing (meth)acrylates such as 2-carboxyethyl(meth)acrylate, carboxymethyl (meth)acrylate, oxazolidinylethyl(meth)acrylate, N-(methacryloyloxy)formamide, acetonyl(meth)acrylate, N-methacryloylmorpholine, N-methacryloyl-2-pyrrolidinone, N-(2-methacryloyl-oxyethyl)-2-pyrrolidinone, N-(3-methacryloyloxypropyl)-2-pyrrolidinone, N-(2-methacryloyloxypentadecyl)-2-pyrrolidinone, N-(3-methacryloyloxy-heptadecyl)-2-pyrrolidinone; glycol di(meth)acrylates such as 1,4-butanediol(meth)acrylate, 2-butoxyethyl(meth)acrylate, 2-ethoxyethoxymethyl(meth) acrylate, 2-ethoxyethyl(meth)acrylate, or mixtures thereof.

[0140] The nitrogen-containing compound may be a (meth)acrylamide or a nitrogen containing (meth)acrylate monomer. Examples of a suitable nitrogen-containing compound include N,N-dimethylacrylamide, N-vinyl carbonamides such as N-vinyl-formamide, vinyl pyridine, N-vinylacetoamide, N-vinyl propionamides, N-vinyl hydroxyacetoamide, N-vinyl imidazole, N-vinyl pyrrolidinone, N-vinyl caprolactam, dimethylaminoethyl acrylate (DMAEA), dimethylaminoethyl methacrylate (DMAEMA), dimethylaminobutyl acrylamide, dimethylaminopropyl meth-acrylate (DMAPMA), dimethylaminopropyl acrylamide, dimethyl-aminopropyl methacrylamide, dimethylaminoethyl acrylamide or mixtures thereof.

[0141] Dispersant monomers may be present in an amount up to 5 mol percent of the monomer composition of the (meth)acrylate polymer. In one embodiment, the poly(meth) acrylate is present in an amount 0 to 5 mol percent, 0.5 to 4 mol percent, or 0.8 to 3 mol percent of the polymer composition. In one embodiment, the poly(meth)acrylate is free of or substantially free of dispersant monomers.

[0142] In one embodiment, the poly(meth)acrylate comprises a block copolymer or tapered block copolymer. Block copolymers are formed from a monomer mixture comprising one or more (meth)acrylate monomers, wherein, for example, a first (meth)acrylate monomer forms a discrete block of the polymer joined to a second discrete block of the polymer formed from a second (meth)acrylate monomer. While block copolymers have substantially discrete blocks formed from the monomers in the monomer mixture, a tapered block copolymer may be composed of, at one end, a relatively pure first monomer and, at the other end, a relatively pure second monomer. The middle of the tapered block copolymer is more of a gradient composition of the two monomers.

[0143] In one embodiment, the poly(meth)acrylate polymer (P) is a block or tapered block copolymer that comprises at least one polymer block (B_1) that is insoluble or substantially insoluble in the base oil and a second polymer block (B_2) that is soluble or substantially soluble in the base oil.

[0144] In one embodiment, the poly(meth)acrylate polymers may have an architecture selected from linear, branched, hyper-branched, cross-linked, star (also referred to as "radial"), or combinations thereof. Star or radial refers to multi-armed polymers. Such polymers include (meth) acrylate-containing polymers comprising 3 or more arms or branches, which, in some embodiments, contain at least about 20, or at least 50 or 100 or 200 or 350 or 500 or 1000 carbon atoms. The arms are generally attached to a multivalent organic moiety which acts as a "core" or "coupling agent." The multi-armed polymer may be referred to as a radial or star polymer, or even a "comb" polymer, or a polymer otherwise having multiple arms or branches as described herein.

[0145] Linear poly(meth)acrylates, random, block or otherwise, may have weight average molecular weight (M_w) of 1000 to 400,000 Daltons, 1000 to 150,000 Daltons, or 15,000 to 100,000 Daltons. In one embodiment, the poly (meth)acrylate may be a linear block copolymer with a Mw of 5,000 to 40,000 Daltons, or 10,000 to 30,000 Daltons.

[0146] Radial, cross-linked or star copolymers may be derived from linear random or di-block copolymers with molecular weights as described above. A star polymer may have a weight average molecular weight of 10,000 to 1,500,000 Daltons, or 40,000 to 1,000,000 Daltons, or 300,000 to 850,000 Daltons.

[0147] The lubricating compositions may comprise 0.05 weight % to 2 weight %, or 0.08 weight % to 1.8 weight %, or 0.1 to 1.2 weight % of the one or more polymeric viscosity modifiers and/or dispersant viscosity modifiers as described herein

Other Performance Additives

[0148] Various embodiments of the compositions disclosed herein may optionally comprise one or more additional performance additives. These additional performance additives may include one or more metal deactivators, friction modifiers, corrosion inhibitors, extreme pressure agents, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents, and any combination or mixture thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives, and often a package of multiple performance additives

[0149] In one embodiment, a lubricating composition further comprises a friction modifier. Examples of friction modifiers include long chain fatty acid derivatives of amines, fatty esters, or epoxides; fatty imidazolines such as condensation products of carboxylic acids and polyalkylene-polyamines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrimides; or fatty alkyl tartramides. The term fatty, as used herein, can mean having a C8-22 linear alkyl group.

[0150] Friction modifiers may also encompass materials such as sulfurized fatty compounds and olefins, molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, sunflower oil or monoester of a polyol and an aliphatic carboxylic acid.

[0151] In one embodiment the friction modifier may be selected from the group consisting of long chain fatty acid derivatives of amines, long chain fatty esters, or long chain fatty epoxides; fatty imidazolines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrimides; and fatty alkyl tartramides. The friction modifier may be present at 0 wt % to 6 wt %, or 0.05 wt % to 4 wt %, or 0.1 wt % to 2 wt % of the lubricating composition.

[0152] In one embodiment, the friction modifier may be a long chain fatty acid ester. In another embodiment the long chain fatty acid ester may be a mono-ester or a diester or a mixture thereof, and in another embodiment, the long chain fatty acid ester may be a triglyceride.

[0153] In one embodiment, a lubricating composition may further comprise a molybdenum compound. The molybdenum compound may be selected from the group consisting of molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, amine salts of molybdenum compounds, and mixtures thereof. The molybdenum compound may provide the lubricating composition with 0 to 1000 ppm, or 5 to 1000 ppm, or 10 to 750 ppm, or 5 ppm to 300 ppm, or 20 ppm to 250 ppm of molybdenum

[0154] Other performance additives such as corrosion inhibitors include those described in paragraphs 5 to 8 of U.S. Application US05/038319, published as WO2006/047486, octyl octanamide, condensation products of dodecenyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine. In one embodiment, the corrosion inhibitors include the Synalox® (a registered trademark of The Dow Chemical Company) corrosion inhibitor. The Synalox® corrosion inhibitor may be a homopolymer or copolymer of propylene oxide. The Synalox® corrosion inhibitor is described in more detail in a product brochure with Form No. 118-01453-0702 AMS, published by The Dow Chemical Company. The product brochure is entitled "SYNALOX Lubricants, High-Performance Polyglycols for Demanding Applications."

[0155] The lubricating composition may further include metal deactivators, including derivatives of benzotriazoles (typically tolyltriazole), dimercaptothiadiazole derivatives, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, or 2-alkyldithiobenzothiazoles; foam inhibitors, including copolymers of ethyl acrylate and 2-ethylhexylacrylate and copolymers of ethyl acrylate and 2-ethylhexylacrylate and vinyl acetate; demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers; and pour point depressants, including esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides.

[0156] Pour point depressants that may be useful in the lubricating compositions disclosed herein further include polyalphaolefins, esters of maleic anhydride-styrene, poly(meth)acrylates, polyacrylates or polyacrylamides.

[0157] In different embodiments the lubricating composition may have a composition as described in the following table:

	Embodiments (wt %)		
Additive	A	B	C
Antiwear Agents	0.15 to 6	0.2 to 4	0.5 to 2
Ashless Antioxidants	1.2 to 7	1.2 to 5	2 to 5
Metal Detergents	0.2 to 8	0.2 to 4	0.5 to 2
Polyolefin Dispersants	0.8 to 8	1 to 6	1.5 to 4
Viscosity Modifier	0 or 0.1 to 4.5	0.5 to 4	0.8 to 2.5
Dispersant Viscosity Modifier	0 or 0.1 to 4.5	0 or 0.1 to 2.5	0.5 to 1.6
Friction Modifier	0 or 0.05 to 4	0.05 to 3	0.1 to 2
Any Other Performance Additive	0 or 0.05 to 10	0 or 0.05 to 8	0 or 0.05 to 6
Oil of Lubricating Viscosity	Balance to 100%		

[0158] The instant compositions provide a surprising ability to prevent damage to an engine operating at high brake mean effective pressure or alternatively at high effective compression ratio. This is accomplished while maintaining fuel economy performance, low sulfated ash levels, improved deposit control, and other limitations, required by increasingly stringent government regulations.

Industrial Application

[0159] As described above, the instant disclosure includes a method for lubricating a high efficiency internal combustion engine comprising supplying to the internal combustion engine a lubricating composition as disclosed herein. Generally, the lubricant is added to the lubricating system of the internal combustion engine, which then delivers the lubricating composition to the critical parts of the engine, during its operation, that require lubrication

[0160] The lubricating compositions described above may be utilized in an internal combustion engine. The engine components may have a surface of steel or aluminum (typically a surface of steel), and may also be coated for example with a diamond-like carbon (DLC) coating.

[0161] An aluminum surface may be comprised of an aluminum alloy that may be a eutectic or hyper-eutectic aluminum alloy (such as those derived from aluminum silicates, aluminum oxides, or other ceramic materials). The aluminum surface may be present on a cylinder bore, cylinder block, or piston ring having an aluminum alloy, or aluminum composite.

[0162] The internal combustion engine may be fitted with an emission control system or a turbocharger. Examples of the emission control system include diesel particulate filters (DPF), or systems employing selective catalytic reduction (SCR).

[0163] The internal combustion engine described herein is distinct from a gas turbine. In an internal combustion engine, individual combustion events translate from a linear reciprocating force into a rotational torque through the rod and crankshaft. In contrast, in a gas turbine (which may also be referred to as a jet engine) a continuous combustion process generates a rotational torque continuously without translation, and can also develop thrust at the exhaust outlet. These differences in operation conditions of a gas turbine and internal combustion engine result in different operating environments and stresses.

[0164] The lubricant composition for an internal combustion engine may be suitable for any engine lubricant irrespective of the sulfur, phosphorus or sulfated ash (ASTM D-874) content. The sulfur content of the engine oil lubricant may be 1 wt % or less, or 0.8 wt % or less, or 0.5 wt % or less, or 0.3 wt % or less. In one embodiment, the sulfur content may be in the range of 0.001 wt % to 0.5 wt %, or 0.01 wt % to 0.3 wt %. The phosphorus content may be 0.2 wt % or less, or 0.12 wt % or less, or 0.1 wt % or less, or 0.085 wt % or less, or 0.08 wt % or less, or even 0.06 wt % or less, 0.055 wt % or less, or 0.05 wt % or less. In one embodiment the phosphorus content may be 100 ppm to 1000 ppm, or 200 ppm to 600 ppm. The total sulfated ash content may be 2 wt % or less, or 1.5 wt % or less, or 1.1 wt % or less, or 1 wt % or less, or 0.8 wt % or less, or 0.5 wt % or less, or 0.4 wt % or less. In one embodiment, the sulfated ash content may be 0.05 wt % to 0.9 wt %, or 0.1 wt % to 0.2 wt % or to 0.45 wt %.

[0165] In one embodiment, the lubricating composition may be an engine oil, wherein the lubricating composition may be characterized as having at least one of (i) a sulfur content of 0.5 wt % or less, (ii) a phosphorus content of 0.1 wt % or less, (iii) a sulfated ash content of 1.5 wt % or less, or combinations thereof.

EXAMPLES

[0166] Embodiments will be further illustrated by the following examples, which set forth particularly advantageous embodiments. While the examples are provided to illustrate certain embodiments, they are not intended to limiting.

Lubricating Compositions

[0167] A series of OW-20 engine lubricants in Group III base oil of lubricating viscosity are prepared containing the anti-wear additives described above as well as conventional additives including polymeric viscosity modifier, ashless succinimide dispersant, overbased detergents, antioxidants (combination of phenolic ester and diarylamine), as well as other performance additives as follows (Table 1). The phosphorus, sulfur and ash contents of each of the examples are also presented in the table in part to show that each example has a similar amount of these materials and so provide a proper comparison between the comparative and examples according to embodiments described herein.

TABLE 1

Lubricating Oil Composition Formulations[1]

	EX1	EX2	EX3	EX4
C3/6 Secondary ZDDP	0.79	0.79	0.79	0.79
Ashless Antiwear[2]	0	0.48	0	0.48
Overbased Calcium Sulfonate[3]	0.74	0.74	0.58	0.58
PIBsuccinimide dispersant[4]	2	2	2	2
Na Sulfonate	0.16	0.16	0	0
Overbased Mg Sulfonate	0	0	0.58	0.58
Ashless Antioxidant[5]	1.5	1.5	1.45	1.45
PMA VI Improver[6]	2.1	2.1	0	0
E-P VI Improver[7]	0	0	0.5	0.5
Additional Additives[8]	0.28	0.28	0.25	0.25

[1] All amounts shown above are in weight percent and are on an oil-free basis unless otherwise noted.

[2] Oleyl tartrimide

[3] Combination of 500 and 700 TBN (oil free) overbased calcium sulfonates

[4] PIBsuccinimide prepared from 2000 Mn PIB with oil free TBN of 27 mg KOH/g

[5] Combination of alkylated diarylamine, hindered phenol, and sulfurized olefin antioxidants

[6] High VI Mw polymethacrylate

[7] Ethylene-propylene copolymer

[8] The Additional Additives used in the examples include friction modifier, pourpoint depressants, anti-foam agents, emulsifier, titanium alkoxide, and includes some amount of diluent oil

[0168] Testing

[0169] Using advanced power-cylinder simulation tools, current engine technologies can be simulated and extrapolated forward into the realm of future combustion conditions. This simulation allows for the measurement of the impact of lubricant compositions to reduce transmitted force and therefore tribocouple stress over a wide range of operating conditions. Under conditions designed to simulate modern and future high compression engines it was found that LZ surface active additive systems can have a large impact in reducing tribocouple stress and decreasing friction power loss, particularly during the power-stroke. Ring on Bore Testing

[0170] Increasing compression ratio means combustion pressures will essentially rise. Increased combustion pressures result in higher piston ring loading on the cylinder bore wall and so the two are physically linked. Using knowledge of contact dynamics and geometry it is possible to perform calculations to relate combustion pressures to dynamic load in the ring-on-bore apparatus.

[0171] The ring on bore apparatus consists of a section of piston ring cut from actual engine hardware which is reciprocated against a section of cylinder bore material removed from the same engine, and in the presence of the lubricant under investigation. This approach allows in-cylinder dynamics to be closely replicated. The test is carried out at 1000 rpm and 100° C.; and is designed to simulate typical engine conditions. Dynamic loading is increased incrementally to simulate engines with increased combustion pressure. Steady-state load (applied during the three pumping strokes) is set at 25N for every experiment as this simulates ring tension only and is typical of in-cylinder dynamics.

[0172] The experiment starts at low loads which simulate low power gasoline engines. The dynamic load is ramped up incrementally while holding all other experimental conditions constant. Dynamic load (simulating combustion pressure) is increased from low to high, to simulate current engines, high efficiency engines, and above where current engines can operate. This procedure is repeated identically using lubricants of differing composition to allow for scientific comparison to be made.

TABLE 2

Power Loss Testing: Peak Transmitted Force

	Peak Combustion Load (N)								
	75	100	125	150	175	200	225	250	275
EX1 (N)	8.63	11.7	14.6	18	20.9	24.2	27.4	30.8	33.9
EX2 (N)	7.16	9.15	12	14.4	16.6	20.2	22.9	25.2	28.2

[0173] The data indicates that in this simulation of a high compression engine (as indicated by the increase in peak combustion load), the lubricating composition with the boosted anti-wear system reduced force transmission from the piston ring to the power cylinder surface. This reduced force reduces stress in the tribocouple, and so limits the propensity for contact derived wear to occur.

[0174] Additional testing was carried out to evaluate the impact of viscosity on efficiency in simulated high compression regimes. Experiments were conducted to evaluate the ability of viscous fluids in reducing peak powerstroke friction power loss. Performance gains can be realized by interposing a viscous film in the power-cylinder tribocouple during the power-stroke.

[0175] The 'Approximate SAE' grade viscosity fluids tested show the propensity of the fluid element to offset the transition from fluid lubrication regimes to the regimes of contact. This results in a net reduction of transmitted force during the power-stroke. These experiments were carried using synthetic Group V polyalphaolefin base oil with a kinematic viscosity of ~8 cSt. The base oil is heated while transmitted force under dynamic conditions is measured. This creates a sweep of all SAE grade viscosities and their performance (Table 3).

TABLE 3

Viscosity Impact on Power Losses

Viscosity (mPas)	Simulated SAE Grade	Temperature (C.)	PowerStroke Mean Dynamic FF (N)
82.36		20	1.37
51.02		30	1.47
32.42		40	1.73
21.99	60	50	2.23
15.6	50	60	2.64
11.77	40	70	3.16
9.22	30	80	3.17
7.32	20	90	3.36
6.09	16	100	3.42
5.42	12	110	3.66
4.47		120	3.69
3.93	8	130	3.79
3.43		140	4

[0176] Table 3 demonstrates that increasing viscosity between the ranges of SAE 8 to SAE 60^{+} provides reduced transmitted force for the tribocouple under dynamic conditions specifically designed to mechanically simulate combustion event tribology for high efficiency engines. This result shows that increased viscosity during the combustion event reduces friction powerloss of the high efficiency engine, further contributing to the engines efficiency. The result also suggests that the durability of the power-cylinder tribocouple is improved, primarily due to the reduced surface stress imparted by the surface-separating fluid lubricant layer which exists for longer duration during the combustion event.

[0177] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. The products formed thereby, including the products formed upon employing lubricant composition in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the disclosed embodiments; the lubricating compositions disclosed herein encompass lubricant compositions prepared by admixing the components described above.

[0178] Each of the documents referred to above is incorporated herein by reference, as is the priority document and all related applications, if any, which this application claims the benefit of Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, byproducts, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the disclosed lubricating compositions may be used together with ranges or amounts for any of the other elements.

[0179] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include i) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring); (ii) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this disclosure, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulphoxy); (iii) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this disclosure, contain other than carbon in a ring or chain otherwise composed of carbon atoms.

[0180] Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

[0181] While the instant disclosure has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the instant disclosure is intended to cover such modifications as fall within the scope of the appended claims.

1. A method of lubricating an internal combustion engine, comprising supplying to a sump-lubricated, high efficiency, gasoline-fueled internal combustion engine a lubricating composition comprising (a) an oil of lubricating viscosity, (b) an anti-wear agent in an amount 0.15 weight percent to 6 weight percent of the composition, (c) an ashless antioxidant in an amount 1.2 weight to 7 weight percent of the composition, and (d) a metal-containing detergent in an amount to deliver 0.2 weight percent sulfated ash up to 1.5 weight percent sulfated ash to the composition, (e) an ashless polyolefin dispersant in an amount 0.8 weight percent to 8 weight percent of the composition, and (f) a polymeric viscosity modifier, dispersant viscosity modifier, or mixtures thereof in an amount 0.1 weight percent to 4.5 weight percent of the composition.

2. The method of claim **1**, wherein the internal combustion engine is operated at an effective compression ratio of at least 15:1.

3. The method of claim **1**, wherein the internal combustion engine is operated under a load with a brake mean effective pressure (BMEP) of greater than or equal to 18 bars.

4. The method of claim **1**, wherein the gasoline has an octane rating of at least 95 by the (R+M)/2 method.

5. The method of claim **1**, wherein the internal combustion engine is spark ignited.

6. The method of claim **1**, wherein the internal combustion engine is compression ignited.

7. The method of claim[[s]] 1 to 6, wherein the internal combustion engine is a gasoline direct injection (GDI) engine.

8. The method of claim **1**, wherein the internal combustion engine is equipped with a turbocharger, a super charger, an air booster, or combinations thereof.

9. The method of claim **1**, wherein the internal combustion engine is operated with variable valve timing.

10. The method of claim **1**, wherein the internal combustion engine is operated with an air-fuel equivalence ratio (X) of less than 1.2.

11. The method of claim **1**, wherein the internal combustion engine is operated at speeds less than or equal to 3000 rpm.

12. The method of any of claim **1**, wherein the anti-wear additive comprises a phosphorus-containing additive, a phosphorus-free additive, or combinations thereof.

13. The method of claim **12**, wherein the phosphorus-containing additive is selected from metal dialkyldithiophosphates, amino phosphate salts, hydrocarbyl phosphites, hydrocarbyl phosphines, hydrocarbyl phosphonates, and combinations thereof.

14. The method of claim **12**, wherein the phosphorus-free anti-wear additive is selected from hydrocarbyl esters, amides, or imides of hydroxy-substituted carboxylic acid acids and mixtures thereof.

15. The method of claim **1**, wherein the metal detergent is a selected from a neutral alkaline earth metal detergent, an overbased alkaline earth metal detergent, and combinations thereof.

16. The method of claim **15**, wherein the alkaline earth metal detergent comprises calcium detergents, magnesium detergent, and mixtures thereof.

17. The method of claim **1**, wherein the oil of lubricating viscosity has a kinematic viscosity of at least 4.2 m^2/s at 100 ° C.

18. The method of claim **1**, wherein the lubricant composition has a viscosity grade according to SAE J300 of XW-YY, wherein X is 0, 5, 10 or 15, and YY is 8, 12, 16, 20, 30, or 40.

19. A method of operating an internal combustion engine, comprising supplying to a sump-lubricated, high efficiency, gasoline-fueled internal combustion engine a lubricating composition comprising (a) an oil of lubricating viscosity, (b) an anti-wear agent in an amount 0.15 weight percent to 6 weight percent of the composition, (c) an ashless antioxidant in an amount 1.2 weight to 7 weight percent of the composition, and (d) a metal-containing detergent in an amount to deliver 0.2 weight percent sulfated ash up to 1.5 weight percent sulfated ash to the composition, (e) an ashless polyolefin dispersant in an amount 0.8 weight percent to 8 weight percent of the composition, and (f) a polymeric viscosity modifier, dispersant viscosity modifier, or mixtures thereof in an amount 0.1 weight percent to 4.5 weight percent of the composition.

20. A method of reducing friction power loss in a sump-lubricated, high efficiency, gasoline-fueled internal combustion engine comprising operating said engine and lubricating said engine with a lubricant composition comprising (a) an oil of lubricating viscosity, (b) an anti-wear agent in an amount 0.15 weight percent to 6 weight percent of the composition, (c) an ashless antioxidant in an amount 1.2 weight to 7 weight percent of the composition, and (d) a metal-containing detergent in an amount to deliver 0.2 weight percent sulfated ash up to 1.5 weight percent sulfated ash to the composition, (e) an ashless polyolefin dispersant in an amount 0.8 weight percent to 8 weight percent of the composition, and (f) a polymeric viscosity modifier, dispersant viscosity modifier, or mixtures thereof in an amount 0.1 weight percent to 4.5 weight percent of the composition.

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