IMPROVED ANTI-WEAR PERFORMANCE OF LUBRICANTS USING CARBON NANOPLATELETS

FIELD OF THE INVENTION

[0001] This disclosure relates to lubricating engines using formulated lubricating oils to reduce wear and improve engine fuel efficiency. The formulated lubricating oils contain a lubricating oil base stock as a major component, an antiwear additive as a first minor component, and carbon nanoplatelets, e.g., nanographene platelets (NGPs), as a second minor component. The carbon nanoplatelets are dispersed in the lubricating oil such that the lubricating oil exhibits improved antiwear performance and improved engine fuel efficiency. A synergy exists between carbon nanoplatelets and other major components of lubricants, especially with zinc dialkyldithiophosphate (ZDDP) or other phosphate antiwear additives, that helps to form nano-composite wear resistant and low friction tribofilm both on ferrous and non-ferrous surfaces (e.g., carbon coatings, ceramic coatings, polymeric coatings, and the like) of engines/machines.

BACKGROUND

[0002] Fuel efficiency requirements for passenger vehicles are becoming increasingly more stringent. New legislation in the United States and European Union within the past few years has set fuel economy and emissions targets not readily achievable with today's vehicle and lubricant technology. In order to improve lubricant fuel economy performance, reduction of viscosity is typically the best path; however, present day lubricant oils with a HTHS (ASTM D4683) viscosity of less than 2.6 cP at 150°C would not be expected to be able to provide acceptable passenger vehicle engine durability performance.

[0003] HTHS is the measure of a lubricant's viscosity under conditions that

simulate severe engine operation. Under high temperatures and high stress conditions, lubricant degradation can occur. As this happens, the viscosity of the lubricant decreases which may lead to increased engine wear. Antiwear additives are typically added to lubricant formulations to reduce engine wear. Illustrative antiwear additives include, for example, ZDDP, zinc dithiocarbamates, molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, other organo molybdenum-nitrogen complexes, sulfurized olefins, etc.

[0004] ZDDP is an antiwear additive almost universally used in engine lubricants for the last 60 years. See Spikes, H., 2004, The History and Mechanisms of ZDDP, Tribology Letters, 17(3), p. 469-489. ZDDP provides wear protection under mild wear conditions.

[0005] In recent years, studies have been performed using nanoscale platelets or nanoparticles in lubricants as they hold the promise to reduce friction and wear. For example, the fullerene-like carbon/WS_2/MoS_2 nano-balls dispersed in lubricants were thought to provide rolling effect. However, they were found to be exfoliated or decomposed at the tribological contact and thereby were less likely to provide rolling effect. These decomposed or exfoliated nanoplatelets have weak Van der Waals' interactions between the atoms of two adjacent surfaces and are supposed to provide low friction. However, neither the fullerene-like nano-balls nor the exfoliated carbon nanoplatelets can deliver friction coefficients lower than 0.05 on ferrous surfaces. This was probably because the hard nanoparticles acted as abrasive particles leading to abrasive wear on the relatively soft ferrous surfaces. Resulting iron oxide abrasive wear debris has high friction.

[0006] Fuel economy improvement strongly depends on the reduction of lubricant viscosity. This leads the contact conditions to be more severe and thereby results in more engine wear. There is a need to develop improved antiwear technologies for the low viscosity lubricants that afford fuel economy improvement.

[0007] Despite the advances in lubricant oil formulation technology, there exists a need for a low viscosity engine oil lubricant that provides superior antiwear performance with improved fuel economy, and has the capability to do so with or without conventional antiwear additives, e.g., ZDDP.

SUMMARY

[0008] This disclosure relates in part to a method for improving antiwear performance of a lubricating oil, and thereby improving fuel efficiency, in an engine lubricated with a lubricating oil by using carbon nanoplatelets, e.g., NGPs, dispersed in the lubricating oil, sufficient for the lubricating oil to exhibit improved antiwear performance.

[0009] This disclosure also relates in part to a method of improving wear protection in an engine lubricated with a lubricating oil. The method comprises using as the lubricating oil a formulated oil comprising a lubricating oil base stock as a major component, an antiwear additive as a first minor component, and carbon nanoplatelets as a second minor component. The carbon nanoplatelets are dispersed in said lubricating oil base stock. Wear protection is improved as compared to wear protection achieved using a lubricating oil not containing carbon nanoplatelets as a second minor component.

[0010] This disclosure further relates in part to a method for improving wear protection in an engine lubricated with a lubricating oil by using as the lubricating oil a formulated oil having a HTHS viscosity of less than 4.0 cP at 150°C. The formulated oil has a composition comprising a major amount of a lubricating oil base stock, a minor amount of an antiwear additive, and a minor amount of carbon nanoplatelets. The carbon nanoplatelets are dispersed in the lubricating oil base stock sufficient for the formulated oil to pass wear protection requirements of one or more engine tests selected from TU3M, Sequence IIIG, Sequence IVA and

OM646LA.

[0011] This disclosure yet further relates in part to a method for improving wear protection in an engine lubricated with a lubricating oil by using as the lubricating oil a formulated oil having a HTHS viscosity of less than 4.0 cP at 150°C. The formulated oil has a composition comprising a major amount of a lubricating oil base stock and a minor amount of carbon nanoplatelets. The carbon nanoplatelets are dispersed in the lubricating oil base stock sufficient for the formulated oil to pass wear protection requirements of one or more engine tests selected from TU3M, Sequence IIIG, Sequence IVA and OM646LA.

[0012] This disclosure also relates in part to a lubricating engine oil having a composition comprising a lubricating oil base stock as a major component, an antiwear additive as a first minor component, and carbon nanoplatelets as a second minor component. The carbon nanoplatelets are dispersed in the lubricating oil base stock sufficient for the lubricating engine oil to exhibit improved wear protection as compared to wear protection achieved using a lubricating oil not containing carbon nanoplatelets as a second minor component.

[0013] This disclosure further relates in part to a lubricating engine oil having a composition comprising a major amount of a lubricating oil base stock, a minor amount of an antiwear additive, and a minor amount of carbon nanoplatelets. The lubricating engine oil has a HTHS viscosity of less than 4.0 cP at 150°C. The carbon nanoplatelets are dispersed in the lubricating oil base stock sufficient for the lubricating engine oil to pass wear protection requirements of one or more engine tests selected from TU3M, Sequence IIIG, Sequence IVA and OM646LA.

[0014] This disclosure yet further relates in part to a lubricating engine oil having a composition comprising a major amount of a lubricating oil base stock and a minor amount of carbon nanoplatelets. The lubricating engine oil has a HTHS viscosity of less than 4.0 cP at 150°C. The carbon nanoplatelets are

dispersed in the lubricating oil base stock sufficient for the lubricating engine oil to pass wear protection requirements of one or more engine tests selected from TU3M, Sequence IIIG, Sequence IVA and OM646LA.

[0015] In accordance with this disclosure, an engine oil lubricant provides superior antiwear performance and effectively improves fuel economy, and has the capability to do so with or without antiwear additives, e.g., ZDDP. Engine wear protection is maintained even at lower HTHS viscosities, e.g., 2.6 cP or lower at 150°C.

[0016] Other objects and advantages of the present disclosure will become apparent from the detailed description that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] Fig. 1 graphically depicts friction performance on a diamond-like carbon (DLC) coating using nanographene platelets (NGP) in polyalphaolefin (PAO), in particular, the friction coefficient as a function of time for PAO6 and PAO6 + NGP.

[0018] Fig. 2 depicts wear results measured from a DLC coating using an optical profilometer for PAO6 and PAO6 + NGP.

[0019] Fig. 3 graphically depicts results of Stribeck tests on fresh surfaces (friction as a function of speed). Tests were performed on fresh surfaces from high speed (3000 mm/s) to low speed (3 mm/s) at 50% slide to roll ratio (SRR), 1 GPa pressure and 100°C.

[0020] Fig. 4 depicts 2D and 3D maps of wear tracks for PAO base stock.

[0021] Fig. 5 depicts 2D and 3D maps of wear tracks for 0.5% graphene in

PAO base stock.

[0022] Fig. 6 depicts 2D and 3D maps of wear tracks for 0.75% ZDDP in PAO base stock.

[0023] Fig. 7 depicts 2D and 3D maps of wear tracks for 0.5% graphene and 0.75% ZDDP in PAO base stock.

[0024] Fig. 8 graphically depicts friction results from 4 hour wear tests, in particular, friction coefficients as a function of time for PAO base stock, 0.5% graphene in PAO base stock, 0.75% ZDDP in PAO base stock, and 0.5% graphene and 0.75% ZDDP in PAO base stock. Tests were performed at 50 mm/s speed, 50% slide to roll ratio (SRR), 1 GPa pressure and 100°C for 4 hours.

[0025] Fig. 9 graphically depicts the friction performance of graphene on a hydrogenated DLC coating.

[0026] Fig. 10 graphically depicts the friction performance of graphene and the effect of DLC coating type, i.e., hydrogenated DLC coating or non-hydrogenated DLC coating.

[0027] Fig. 11 graphically depicts the friction performance of graphene and the effect of base stocks, i.e., PAO and PEG.

[0028] Fig. 12 graphically depicts the friction performance of graphene and the effect of graphene concentration.

[0029] Fig. 13 graphically depicts the friction performance of graphene and the effect of base stock viscosity.

[0030] Fig. 14 graphically depicts the friction performance of graphene in PAO and a fully formulated oil.

DETAILED DESCRIPTION

[0031] All numerical values within the detailed description and the claims herein are modified by "about" or "approximately" the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

[0032] It has now been found that improved wear protection and fuel efficiency can be attained in an engine lubricated with a lubricating oil by using as the lubricating oil a formulated oil having a HTHS viscosity of less than 4.0 cP at 150°C. The formulated oil comprises a major amount of a lubricating oil base stock and a minor amount of carbon nanoplatelets, e.g., NGP materials. The carbon nanoplatelets are dispersed in the lubricating oil base stock sufficient for the lubricating engine oil to pass wear protection requirements of one or more engine tests selected from TU3M, Sequence IIIG, Sequence IVA and OM646LA. The lubricating oils of this disclosure are particularly advantageous as passenger vehicle engine oil (PVEO) products.

[0033] This disclosure provides a method of enhancing the wear performance of lubricants using NGP materials. The addition of NGP dispersed in a lubricant base stock significantly reduces wear. Furthermore, when NGP is added to an oil containing the antiwear additive zinc dialkyldithiophosphate (ZDDP), the resulting tribofilm film growth on ferrous surfaces is enhanced. More specifically, NGP helps increase the uniformity, surface coverage and rate of film growth of the ZDDP film. This is a synergistic effect between NGP and ZDDP. This mechanism can be extended to other antiwear additives and especially those based on phosphorus chemistry that typically form thick films on wear surfaces. The improvement in antiwear film formation will result in a more robust wear performance.

[0034] In accordance with this disclosure, there is provided an option to either

replace ZDDP with a relatively unreactive compound or improve the effectiveness of the current antiwear technologies. This is important for several reasons. Currently the phosphorus levels of automotive engine oils is limited in order to prevent poisoning emissions catalysts. There is a constant interest from OEMs to further reduce the phosphorus content of engine oils and this disclosure provides a method of meeting that demand. Also, a core strategy for improving fuel economy is to reduce the lubricant viscosity. This makes the lubrication conditions more severe and would require new methods to maintain or improve the wear performance of future lubricant products.

[0035] In accordance with this disclosure, the wear advantage can be realized by the addition of NGP to any lubricating base stock or combinations of base stocks. In addition, the mechanism of wear film enhancement applies in the presence of any additive that produces a thick phosphate glass tribofilm. This covers a wide class of phosphorus antiwear chemistry used in a number of different lubricant products. Beneficial effects may also be realized for other non-phosphorus based additives.

[0036] The lubricating oils of this disclosure provide excellent engine protection including anti-wear performance. This benefit can be demonstrated for the lubricating oils of this disclosure in the Sequence IIIG/IIIGA (ASTM D7320), Sequence IVA (ASTM D6891), PSA TU3MS (CEC L-038-94), MB OM646LA (CEC L-099-08), and Caterpillar 1M-PC (ASTM D6618) engine tests at HTHS viscosities less than 2.6 cP (at 150°C). The lubricating oils of this disclosure provide improved fuel efficiency. A lower HTHS viscosity engine oil generally provides superior fuel economy to a higher HTHS viscosity product. This benefit can be demonstrated for the lubricating oils of this disclosure in the MB M111 Fuel Economy (CEC L-054-96) and Sequence VID Fuel Economy (ASTM D7589) engine tests. By providing outstanding engine protection at very low HTHS viscosities, this disclosure provides improved fuel economy without

sacrificing engine durability.

[0037] The engine lubricating oils of this disclosure include both low viscosity fuel economy oils, e.g., passenger vehicle lubricants (PVL) and commercial vehicle lubricants (CVL), and also high viscosity and high performance industrial oils.

[0038] The low viscosity fuel economy, engine lubricating oils of the present disclosure have a HTHS viscosity of less than 2.6 cP at 150°C, preferably less than 2.4 cP at 150°C, and more preferably less than 2.2 cP at 150°C. The low viscosity fuel economy, lubricating engine oils of this disclosure have a composition sufficient to pass wear protection requirements of one or more engine tests selected from TU3M, Sequence IIIG, Sequence IVA, OM646LA and others.

[0039] The high viscosity and high performance industrial oils of this disclosure have a kinematic viscosity at 40°C of from 12 cSt to 800 cSt depending on the ISO VG grade. The kinematic viscosity is determined by the capillary tube viscometer test method as described in ASTM D445 and ISO 3104. For most industrial oils, it is common to measure kinematic viscosity at 40°C because this is the basis for the ISO viscosity grading system (ISO 3448).

[0040] The lubricating engine oils of this disclosure can also be useful for applications irrespective of viscosity grade and/or base stock type. For example, the lubricating engine oils of this disclosure can be useful in marine, aviation, and industrial engine and machine components.

Lubricating Oil Base Stocks

[0041] A wide range of lubricating base oils is known in the art. Lubricating base oils that are useful in the present disclosure are both natural oils, and synthetic oils, and unconventional oils (or mixtures thereof) can be used

unrefined, refined, or rerefined (the latter is also known as reclaimed or reprocessed oil). Unrefined oils are those obtained directly from a natural or synthetic source and used without added purification. These include shale oil obtained directly from retorting operations, petroleum oil obtained directly from primary distillation, and ester oil obtained directly from an esterification process. Refined oils are similar to the oils discussed for unrefined oils except refined oils are subjected to one or more purification steps to improve at least one lubricating oil property. One skilled in the art is familiar with many purification processes. These processes include solvent extraction, secondary distillation, acid extraction, base extraction, filtration, and percolation. Rerefined oils are obtained by processes analogous to refined oils but using an oil that has been previously used as a feed stock.

[0042] Groups I, II, III, IV and V are broad base oil stock categories developed and defined by the American Petroleum Institute (API Publication 1509; www.API.org) to create guidelines for lubricant base oils. Group I base stocks have a viscosity index of between 80 to 120 and contain greater than 0.03% sulfur and/or less than 90% saturates. Group II base stocks have a viscosity index of between 80 to 120, and contain less than or equal to 0.03% sulfur and greater than or equal to 90% saturates. Group III stocks have a viscosity index greater than 120 and contain less than or equal to 0.03 % sulfur and greater than 90% saturates. Group IV includes polyalphaolefins (PAO). Group V base stock includes base stocks not included in Groups I-IV. The table below summarizes properties of each of these five groups.

	Base Oil Properties		
	Saturates	Sulfur	Viscosity Index
Group I	<90 and/or	>0.03% and	≥80 and <120
Group II	≥90 and	≤0.03% and	≥80 and <120
Group III	≥90 and	≤0.03% and	≥120

Group IV	Includes polyalphaolefins (PAO) and GTL products
Group V	All other base oil stocks not included in Groups I, II, III or IV

[0043] Natural oils include animal oils, vegetable oils (castor oil and lard oil, for example), and mineral oils. Animal and vegetable oils possessing favorable thermal oxidative stability can be used. Of the natural oils, mineral oils are preferred. Mineral oils vary widely as to their crude source, for example, as to whether they are paraffinic, naphthenic, or mixed paraffinic-naphthenic. Oils derived from coal or shale are also useful. Natural oils vary also as to the method used for their production and purification; for example, their distillation range and whether they are straight run or cracked, hydrorefined, or solvent extracted.

[0044] Group II and/or Group III hydroprocessed or hydrocracked basestocks, including synthetic oils such as polyalphaolefins, alkyl aromatics and synthetic esters are also well known basestock oils.

[0045] Synthetic oils include hydrocarbon oil. Hydrocarbon oils include oils such as polymerized and interpolymerized olefins (polybutylenes, polypropylenes, propylene isobutylene copolymers, ethylene-olefin copolymers, and ethylene-alphaolefin copolymers, for example). Polyalphaolefin (PAO) oil base stocks are commonly used synthetic hydrocarbon oil. By way of example, PAOs derived from C_8, C_{10}, C_{12}, C_{14} olefins or mixtures thereof may be utilized. See U.S. Patent Nos. 4,956,122; 4,827,064; and 4,827,073.

[0046] The number average molecular weights of the PAOs, which are known materials and generally available on a major commercial scale from suppliers such as ExxonMobil Chemical Company, Chevron Phillips Chemical Company, BP, and others, typically vary from 250 to 3,000, although PAO's may be made in viscosities up to 100 cSt (100°C). The PAOs are typically comprised of relatively low molecular weight hydrogenated polymers or oligomers of alphaolefins which

include, but are not limited to, C_2 to C_{32} alphaolefins with the C_8 to C_{16} alphaolefins, such as 1-octene, 1-decene, 1-dodecene and the like, being preferred. The preferred polyalphaolefins are poly-1-octene, poly-1-decene and poly-1-dodecene and mixtures thereof and mixed olefin-derived polyolefins. However, the dimers of higher olefins in the range of C_{14} to C_{18} may be used to provide low viscosity basestocks of acceptably low volatility. Depending on the viscosity grade and the starting oligomer, the PAOs may be predominantly trimers and tetramers of the starting olefins, with minor amounts of the higher oligomers, having a viscosity range of 1.5 to 12 cSt.

[0047] The PAO fluids may be conveniently made by the polymerization of an alphaolefin in the presence of a polymerization catalyst such as the Friedel-Crafts catalysts including, for example, aluminum trichloride, boron trifluoride or complexes of boron trifluoride with water, alcohols such as ethanol, propanol or butanol, carboxylic acids or esters such as ethyl acetate or ethyl propionate. For example the methods disclosed by U.S. Patent Nos. 4,149,178 or 3,382,291 may be conveniently used herein. Other descriptions of PAO synthesis are found in the following U.S. Patent Nos. 3,742,082; 3,769,363; 3,876,720; 4,239,930; 4,367,352; 4,413,156; 4,434,408; 4,910,355; 4,956,122; and 5,068,487. The dimers of the C_{14} to C_{18} olefins are described in U.S. Patent No. 4,218,330.

[0048] The hydrocarbyl aromatics can be used as base oil or base oil component and can be any hydrocarbyl molecule that contains at least 5% of its weight derived from an aromatic moiety such as a benzenoid moiety or naphthenoid moiety, or their derivatives. These hydrocarbyl aromatics include alkyl benzenes, alkyl naphthalenes, alkyl diphenyl oxides, alkyl naphthols, alkyl diphenyl sulfides, alkylated bis-phenol A, alkylated thiodiphenol, and the like. The aromatic can be mono-alkylated, dialkylated, polyalkylated, and the like. The aromatic can be mono- or poly-functionalized. The hydrocarbyl groups can also be comprised of mixtures of alkyl groups, alkenyl groups, alkynyl, cycloalkyl

groups, cycloalkenyl groups and other related hydrocarbyl groups. The hydrocarbyl groups can range from C_6 up to C_{60} with a range of C_8 to C_{20} often being preferred. A mixture of hydrocarbyl groups is often preferred, and up to three such substituents may be present. The hydrocarbyl group can optionally contain sulfur, oxygen, and/or nitrogen containing substituents. The aromatic group can also be derived from natural (petroleum) sources, provided at least 5% of the molecule is comprised of an above-type aromatic moiety. Viscosities at 100°C of approximately 3 cSt to 50 cSt are preferred, with viscosities of approximately 3.4 cSt to 20 cSt often being more preferred for the hydrocarbyl aromatic component. In one embodiment, an alkyl naphthalene where the alkyl group is primarily comprised of 1-hexadecene is used. Other alkylates of aromatics can be advantageously used. Naphthalene or methyl naphthalene, for example, can be alkylated with olefins such as octene, decene, dodecene, tetradecene or higher, mixtures of similar olefins, and the like. Useful concentrations of hydrocarbyl aromatic in a lubricant oil composition can be 2% to 25%, preferably 4% to 20%, and more preferably 4% to 15%, depending on the application.

[0049] Esters comprise a useful base stock. Additive solvency and seal compatibility characteristics may be secured by the use of esters such as the esters of dibasic acids with monoalkanols and the polyol esters of monocarboxylic acids. Esters of the former type include, for example, the esters of dicarboxylic acids such as phthalic acid, succinic acid, alkyl succinic acid, alkenyl succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acid, alkenyl malonic acid, etc., with a variety of alcohols such as butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, etc. Specific examples of these types of esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, etc.

[0050] Particularly useful synthetic esters are those which are obtained by reacting one or more polyhydric alcohols, preferably the hindered polyols (such as the neopentyl polyols, e.g., neopentyl glycol, trimethylol ethane, 2-methyl-2-propyl-1,3-propanediol, trimethylol propane, pentaerythritol and dipentaerythritol) with alkanoic acids containing at least 4 carbon atoms, preferably C_5 to C_{30} acids such as saturated straight chain fatty acids including caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, and behenic acid, or the corresponding branched chain fatty acids or unsaturated fatty acids such as oleic acid, or mixtures of any of these materials.

[0051] Suitable synthetic ester components include the esters of trimethylol propane, trimethylol butane, trimethylol ethane, pentaerythritol and/or dipentaerythritol with one or more monocarboxylic acids containing from 5 to 10 carbon atoms. These esters are widely available commercially, for example, the Mobil P-41 and P-51 esters of ExxonMobil Chemical Company).

[0052] Other useful fluids of lubricating viscosity include non-conventional or unconventional base stocks that have been processed, preferably catalytically, or synthesized to provide high performance lubrication characteristics.

[0053] Non-conventional or unconventional base stocks/base oils include one or more of a mixture of base stock(s) derived from one or more Gas-to-Liquids (GTL) materials, as well as isomerate/isodewaxate base stock(s) derived from natural wax or waxy feeds, mineral and or non-mineral oil waxy feed stocks such as slack waxes, natural waxes, and waxy stocks such as gas oils, waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, or other mineral, mineral oil, or even non-petroleum oil derived waxy materials such as waxy materials received from coal liquefaction or shale oil, and mixtures of such base stocks.

[0054] GTL materials are materials that are derived via one or more synthesis,

combination, transformation, rearrangement, and/or degradation/deconstructive processes from gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks such as hydrogen, carbon dioxide, carbon monoxide, water, methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane, butylenes, and butynes. GTL base stocks and/or base oils are GTL materials of lubricating viscosity that are generally derived from hydrocarbons; for example, waxy synthesized hydrocarbons, that are themselves derived from simpler gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks. GTL base stock(s) and/or base oil(s) include oils boiling in the lube oil boiling range (1) separated/fractionated from synthesized GTL materials such as, for example, by distillation and subsequently subjected to a final wax processing step which involves either or both of a catalytic dewaxing process, or a solvent dewaxing process, to produce lube oils of reduced/low pour point; (2) synthesized wax isomerates, comprising, for example, hydrodewaxed or hydroisomerized cat and/or solvent dewaxed synthesized wax or waxy hydrocarbons; (3) hydrodewaxed or hydroisomerized cat and/or solvent dewaxed Fischer-Tropsch (F-T) material (i.e., hydrocarbons, waxy hydrocarbons, waxes and possible analogous oxygenates); preferably hydrodewaxed or hydroisomerized/followed by cat and/or solvent dewaxing dewaxed F-T waxy hydrocarbons, or hydrodewaxed or hydroisomerized/followed by cat (or solvent) dewaxing dewaxed, F-T waxes, or mixtures thereof.

[0055] GTL base stock(s) and/or base oil(s) derived from GTL materials, especially, hydrodewaxed or hydroisomerized/followed by cat and/or solvent dewaxed wax or waxy feed, preferably F-T material derived base stock(s) and/or base oil(s), are characterized typically as having kinematic viscosities at 100°C of from 2 mm^2/s to 50 mm^2/s (ASTM D445). They are further characterized typically as having pour points of -5°C to -40°C or lower (ASTM D97). They are also characterized typically as having viscosity indices of 80 to 140 or greater

(ASTM D2270).

[0056] In addition, the GTL base stock(s) and/or base oil(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stock(s) and/or base oil(s) typically have very low sulfur and nitrogen content, generally containing less than 10 ppm, and more typically less than 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock(s) and/or base oil(s) obtained from F-T material, especially F-T wax, is essentially nil. In addition, the absence of phosphorous and aromatics make this materially especially suitable for the formulation of low SAP products.

[0057] The term GTL base stock and/or base oil and/or wax isomerate base stock and/or base oil is to be understood as embracing individual fractions of such materials of wide viscosity range as recovered in the production process, mixtures of two or more of such fractions, as well as mixtures of one or two or more low viscosity fractions with one, two or more higher viscosity fractions to produce a blend wherein the blend exhibits a target kinematic viscosity.

[0058] The GTL material, from which the GTL base stock(s) and/or base oil(s) is/are derived is preferably an F-T material (i.e., hydrocarbons, waxy hydrocarbons, wax).

[0059] In addition, the GTL base stock(s) and/or base oil(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stock(s) and/or base oil(s) and hydrodewaxed, or hydroisomerized/cat (and/or

solvent) dewaxed base stock(s) and/or base oil(s) typically have very low sulfur and nitrogen content, generally containing less than 10 ppm, and more typically less than 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock(s) and/or base oil(s) obtained from F-T material, especially F-T wax, is essentially nil. In addition, the absence of phosphorous and aromatics make this material especially suitable for the formulation of low sulfur, sulfated ash, and phosphorus (low SAP) products.

[0060] Base oils for use in the formulated lubricating oils useful in the present disclosure are any of the variety of oils corresponding to API Group I, Group II, Group III, Group IV, and Group V oils and mixtures thereof, preferably API Group II, Group III, Group IV, and Group V oils and mixtures thereof, more preferably the Group III to Group V base oils due to their exceptional volatility, stability, viscometric and cleanliness features. Minor quantities of Group I stock, such as the amount used to dilute additives for blending into formulated lube oil products, can be tolerated but should be kept to a minimum, i.e. amounts only associated with their use as diluents/carrier oil for additives used on an "as-received" basis. Even in regard to the Group II stocks, it is preferred that the Group II stock be in the higher quality range associated with that stock, i.e. a Group II stock having a viscosity index in the range $100 < VI < 120$.

[0061] The base oil constitutes the major component of the engine oil lubricant composition of the present disclosure and typically is present in an amount ranging from 50 to 99 weight percent, preferably from 70 to 95 weight percent, and more preferably from 85 to 95 weight percent, based on the total weight of the composition. The base oil may be selected from any of the synthetic or natural oils typically used as crankcase lubricating oils for spark-ignited and compression-ignited engines. The base oil conveniently has a kinematic viscosity, according to ASTM standards, of 2.5 cSt to 12 cSt (or mm^2/s) at 100°C and

preferably of 2.5 cSt to 9 cSt (or mm^2/s) at 100°C. Mixtures of synthetic and natural base oils may be used if desired.

Carbon Nanoplatelets

[0062] Carbon nanoplatelets, e.g., nanographene platelets (NGP), are an essential component of the lubricating oils of this disclosure. The carbon nanoplatelets dispersed in a lubricating oil, e.g., polyalphaolefin (PAO), base stock provide excellent wear protection on diamond-like carbon (DLC) surfaces and ferrous surfaces under boundary lubrication conditions. The carbon nanoplatelets are conventional materials known in the art.

[0063] The carbon nanoplatelets, e.g., graphite and graphene, useful in this disclosure are well suited for tribological applications since lubrication takes place at the nanoscale level. To achieve boundary lubrication, for instance, the carbon nanoplatelets can form a thin carpet with the thickness of just one or two molecules to separate the surface asperities. For anti-wear lubrication, the carbon nanoplatelets can chemically attach to the metal surface, forming a thin barrier film. In extreme pressure lubrication, the carbon nanoplatelets can react chemically with the metal surface, forming a sacrificial film of metallic salts to prevent catastrophic wear. The carbon nanoplatelets have a high surface affinity and chemical reactivity. Their small sizes enable them to fill in the surface irregularities giving improved smoothness or penetrate wear crevices and thereby provides low friction.

[0064] The carbon nanoplatelets typically have a thickness of from 0.5 nm to 50 nm and a length and width of from 500 nm to 50 microns. For instance, the carbon nanoplatelets can have a thickness of from 5 nm to 25 nm and a length and width of from 1 micron to 5 microns. The carbon nanoplatelets are commercially available and can be prepared by conventional methods.

[0065] The aspect ratio (i.e. ratio of longest dimension to shortest dimension) of the carbon nanoplatelets can vary over a wide range. The aspect ratio can range from 50 to 50,000. Typically the aspect ratio of the carbon nanoplatelets can range from 500 to 10,000, for instance from 600 to 8000, or from 800 to 6000.

[0066] The NGP materials typically have a thickness varying from 0.45 nm to 100 nm. The carbon nanoplatelets exhibit high thermal conductivity. For example, the thermal conductivity of graphene is 5300 $Wm^{-1}K^{-1}$ while it is only approximately 0.1 $Wm^{-1}K^{-1}$ for most of the mineral and synthetic hydrocarbon based lubricants. Hence the use of graphene in lubricants will provide an increase of heat transfer compared to the existing lubricants. In addition, the elastic modulus of the nanoscale carbon platelets is also as high as 1 TPa. Lubricants containing nanoscale carbon platelets can provide more load-bearing capability than the conventional lubricants by forming a graphene/antiwear composite tribofilm.

[0067] The graphene nanoplatelets can be monolayer, e.g., a single layer of graphite, or mixtures of xp3 diamond and xp2 graphite in thicker layers or stacks. The stacks can typically be at least 15 nm thick and the platelets can have an aspect ratio of 1000:1. The graphene nanoplatelets are commercially available and can be prepared by conventional methods. See "Processing of nanographene platelets (NGPs) and NGP nanocomposites; a review" B.Z. Jang and A. Zhamu, J Mater Sci (2008) 43:5092-5101, which is incorporated herein by reference.

[0068] The NGP materials can be platelets, sheets, or ribbons composed of one or multiple layers of graphene plane, with a thickness that can be as small as 0.34 nm (one carbon atom thick). A single-layer graphene is composed of carbon atoms forming a 2-D hexagonal lattice through strong in-plane covalent bonds. In a multi-layer NGP, several graphene planes are weakly bonded together through van der Waals forces in the thickness-direction. Multi-layer NGPs can have a thickness up to 100 nm, but typically less than 10 nm.

[0069] The NGP materials may be considered a two-dimensional carbon material. An NGP is essentially composed of a sheet of graphene plane or multiple sheets of graphene plane stacked and bonded together. Each graphene plane, also referred to as a graphene sheet or basal plane, comprises a two-dimensional hexagonal structure of carbon atoms. Each platelet has a length and a width parallel to the graphite plane and a thickness orthogonal to the graphite plane. The thickness of an NGP, by definition, is 100 nanometers (nm) or smaller, but typically thinner than 15 nm with a single-sheet NGP being as thin as 0.34 nm. The length and width of a NGP are typically between 0.5 μm and 20 μm, but could be longer or shorter.

[0070] The NGP materials can exhibit the high intrinsic strength and thermal conductivity. The NGP materials also have exceptional elastic modulus (approximately 1 TPa or 1,000 GPa) and high electrical conductivity (up to 20,000 S/cm).

[0071] There are several unique features of NGPs that make them an ideal candidate for a lubricant additive. For lubricant applications, the ultra-high thermal conductivity of NGPs is desirable since, in most of the friction-reducing or anti-wear applications, adequate heat dissipation is an important requirement. The notion that NGPs can be as thin as one carbon atom size (<0.34 nm) suggests that NGPs could form a molecular sized lubricating film between two working parts, effectively reducing friction and wear. Furthermore, a graphene plane is a structure of extended carbon hexagons or an extended fused-ring aromatic structure, which is more thermally and chemically stable than most of the organic molecules. This implies that graphene is capable of providing long-term, stable protection against friction and wear of working parts. The unique plate-like geometry enables NGPs to slide over one another, providing stable fluid properties (e.g., viscosity remains relatively stable with respect to shear rate or

service time). This same geometry also enables a large proportion of NGPs (e.g., up to 75% by weight) to be dispersed in a fluid.

[0072] For certain applications, the nano graphene platelets preferably have a length or width greater than 1 μm. For other applications (e.g., in re-circulating systems), nano graphene platelets preferably have a length or width less than 500 nm to avoid the potential issue of clogging the ultra-small gaps through which the lubricant must flow freely. Preferably, the lubricating fluid is a type of oil having a molecular weight of from 250 to 2,000 g/mole.

[0073] It is important that the carbon nanoplatelets are dispersed in the lubricating oil sufficient for the lubricating oil to exhibit improved antiwear performance. Carbon nanoplatelets useful in this disclosure are described, for example in U.S. Patent Application Publication No. 2011/0046027 and H.D. Huang et al., "An investigation on tribological properties of graphite nanosheets as oil additive, Wear 261 (2006), 140-144, which are incorporated herein by reference.

[0074] The carbon nanoplatelets are typically used in amounts of from 0.1 weight percent to 10 weight percent, preferably from 0.1 weight percent to 7.5 weight percent, and more preferably from 0.1 weight percent to 5.0 or 3.0 weight percent, based on the total weight of the lubricating oil, although more or less can often be used advantageously. The amount used should be sufficient to achieve greater or equal wear resistance than the wear resistance obtained with ZDDP antiwear additive.

Antiwear Additives

[0075] A metal alkylthiophosphate and more particularly a metal dialkyl dithio phosphate in which the metal constituent is zinc, or zinc dialkyl dithio phosphate (ZDDP) is a component of the lubricating oils of this disclosure. ZDDP can be

primary, secondary or mixtures thereof. ZDDP compounds generally are of the formula $Zn[SP(S)(OR^1)(OR^2)]_2$ where R^1 and R^2 are C_1-C_{18} alkyl groups, preferably C_2-C_{12} alkyl groups. These alkyl groups may be straight chain or branched.

[0076] Preferable zinc dithiophosphates which are commercially available include secondary zinc dithiophosphates such as those available from for example, The Lubrizol Corporation under the trade designations "LZ 677A", "LZ 1095" and "LZ 1371", from for example Chevron Oronite under the trade designation "OLOA 262" and from for example Afton Chemical under the trade designation "HITEC 7169".

[0077] The ZDDP is typically used in amounts of from 0.4 weight percent to 1.2 weight percent, preferably from 0.5 weight percent to 1.0 weight percent, and more preferably from 0.6 weight percent to 0.8 weight percent, based on the total weight of the lubricating oil, although more or less can often be used advantageously. Preferably, the ZDDP is a secondary ZDDP and present in an amount of from 0.6 to 1.0 weight percent of the total weight of the lubricating oil.

[0078] ZDDP is one of the most successful antiwear additives ever used in lubricants. This additive is fairly cost effective and provides exceptionally durable antiwear tribofilms on ferrous surfaces under extreme lubrication conditions. ZDDP forms protective films on ferrous surfaces within a very short period of time. This additive forms pad-like polymeric tribofilms at the rubbing contact and thus prevents wear. It is believed that ZDDP undergoes thermal decomposition at the tribological contact followed by the reactions with reactive iron surfaces or iron oxides that forms glassy phosphate films. These films contain minimal iron meaning that the formation of tribofilm requires minimal loss of iron from the rubbed surfaces. The chain lengths of the phosphate decreases with the depth of the tribofilm and the layers near the surface were mostly dominated by iron sulphides and iron oxides.

[0079] Using an optical interferometry technique, it has been demonstrated that the formation of ZDDP tribofilm takes several tens of minutes. The friction coefficients during the film formation period initially increases and then gradually decreases and finally reaches to steady sate. The increase of friction is a result of initial wear (adhesive/abrasive wear) that generates enough nascent iron to react with the thermally decomposed ZDDP. As soon as the ZDDP tribofilm starts to dominate the contact between two interacting surfaces, friction starts to decrease. Since the film formation of ZDDP is primarily influenced by the initial wear, the nature of wear influences the uniformity as well as growth rate of ZDDP tribofilm to a great extent.

[0080] Uniform antiwear tribofilms are desirable over the non-uniform patchy tribofilms. This is because the uniform tribofilm can resist the applied load more uniformly and thereby generates distributed stresses within the tribofilm. In contrast, in the case of non-uniform tribofilms, the applied load is mainly taken by the high spots resulting in more concentrated stresses and thereby causing more failure of tribofilms. This disclosure reveals that NGP materials enable the formation of uniform ZDDP tribofilms by controlling the initial wear process.

Other Additives

[0081] The formulated lubricating oil useful in the present disclosure may additionally contain one or more of the other commonly used lubricating oil performance additives including but not limited to dispersants, detergents, corrosion inhibitors, rust inhibitors, metal deactivators, other anti-wear agents and/or extreme pressure additives, anti-seizure agents, wax modifiers, viscosity index improvers, viscosity modifiers, fluid-loss additives, seal compatibility agents, friction modifiers, lubricity agents, anti-staining agents, chromophoric agents, defoamants, demulsifiers, emulsifiers, densifiers, wetting agents, gelling agents, tackiness agents, colorants, and others. For a review of many commonly used additives, see Klamann in Lubricants and Related Products, Verlag Chemie,

Deerfield Beach, FL; ISBN 0-89573-177-0. Reference is also made to "Lubricant Additives" by M.W. Ranney, published by Noyes Data Corporation of Parkridge, NJ (1973).

[0082] The types and quantities of performance additives used in combination with the instant disclosure in lubricant compositions are not limited by the examples shown herein as illustrations.

Dispersants

[0083] During engine operation, oil-insoluble oxidation byproducts are produced. Dispersants help keep these byproducts in solution, thus diminishing their deposition on metal surfaces. Dispersants used in the formulation of the lubricating oil may be ashless or ash-forming in nature. Preferably, the dispersant is ashless. So-called ashless dispersants are organic materials that form substantially no ash upon combustion. For example, non-metal-containing or borated metal-free dispersants are considered ashless. In contrast, metal-containing detergents discussed above form ash upon combustion.

[0084] Suitable dispersants typically contain a polar group attached to a relatively high molecular weight hydrocarbon chain. The polar group typically contains at least one element of nitrogen, oxygen, or phosphorus. Typical hydrocarbon chains contain 50 to 400 carbon atoms.

[0085] Chemically, many dispersants may be characterized as phenates, sulfonates, sulfurized phenates, salicylates, naphthenates, stearates, carbamates, thiocarbamates, phosphorus derivatives. A particularly useful class of dispersants are the alkenylsuccinic derivatives, typically produced by the reaction of a long chain hydrocarbyl substituted succinic compound, usually a hydrocarbyl substituted succinic anhydride, with a polyhydroxy or polyamino compound. The long chain hydrocarbyl group constituting the oleophilic portion of the molecule

which confers solubility in the oil, is normally a polyisobutylene group. Many examples of this type of dispersant are well known commercially and in the literature. Exemplary U.S. patents describing such dispersants are U.S. Patent Nos. 3,172,892; 3,215,707; 3,219,666; 3,316,177; 3,341,542; 3,444,170; 3,454,607; 3,541,012; 3,630,904; 3,632,511; 3,787,374 and 4,234,435. Other types of dispersant are described in U.S. Patent Nos. 3,036,003; 3,200,107; 3,254,025; 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,413,347; 3,697,574; 3,725,277; 3,725,480; 3,726,882; 4,454,059; 3,329,658; 3,449,250; 3,519,565; 3,666,730; 3,687,849; 3,702,300; 4,100,082; 5,705,458. A further description of dispersants may be found, for example, in European Patent Application No. 0 471 071, to which reference is made for this purpose.

[0086] Hydrocarbyl-substituted succinic acid and hydrocarbyl-substituted succinic anhydride derivatives are useful dispersants. In particular, succinimide, succinate esters, or succinate ester amides prepared by the reaction of a hydrocarbon-substituted succinic acid compound preferably having at least 50 carbon atoms in the hydrocarbon substituent, with at least one equivalent of an alkylene amine are particularly useful.

[0087] Succinimides are formed by the condensation reaction between hydrocarbyl substituted succinic anhydrides and amines. Molar ratios can vary depending on the polyamine. For example, the molar ratio of hydrocarbyl substituted succinic anhydride to TEPA can vary from 1:1 to 5:1. Representative examples are shown in U.S. Patent Nos. 3,087,936; 3,172,892; 3,219,666; 3,272,746; 3,322,670; and 3,652,616, 3,948,800; and Canada Patent No. 1,094,044.

[0088] Succinate esters are formed by the condensation reaction between hydrocarbyl substituted succinic anhydrides and alcohols or polyols. Molar ratios can vary depending on the alcohol or polyol used. For example, the condensation

product of a hydrocarbyl substituted succinic anhydride and pentaerythritol is a useful dispersant.

[0089] Succinate ester amides are formed by condensation reaction between hydrocarbyl substituted succinic anhydrides and alkanol amines. For example, suitable alkanol amines include ethoxylated polyalkylpolyamines, propoxylated polyalkylpolyamines and polyalkenylpolyamines such as polyethylene polyamines. One example is propoxylated hexamethylenediamine. Representative examples are shown in U.S. Patent No. 4,426,305.

[0090] The molecular weight of the hydrocarbyl substituted succinic anhydrides used in the preceding paragraphs will typically range between 800 and 2,500. The above products can be post-reacted with various reagents such as sulfur, oxygen, formaldehyde, carboxylic acids such as oleic acid. The above products can also be post reacted with boron compounds such as boric acid, borate esters or highly borated dispersants, to form borated dispersants generally having from 0.1 to 5 moles of boron per mole of dispersant reaction product.

[0091] Mannich base dispersants are made from the reaction of alkylphenols, formaldehyde, and amines. See U.S. Patent No. 4,767,551, which is incorporated herein by reference. Process aids and catalysts, such as oleic acid and sulfonic acids, can also be part of the reaction mixture. Molecular weights of the alkylphenols range from 800 to 2,500. Representative examples are shown in U.S. Patent Nos. 3,697,574; 3,703,536; 3,704,308; 3,751,365; 3,756,953; 3,798,165; and 3,803,039.

[0092] Typical high molecular weight aliphatic acid modified Mannich condensation products useful in this disclosure can be prepared from high molecular weight alkyl-substituted hydroxyaromatics or $HN®_2$ group-containing reactants.

[0093] Hydrocarbyl substituted amine ashless dispersant additives are well known to one skilled in the art; see, for example, U.S. Patent Nos. 3,275,554; 3,438,757; 3,565,804; 3,755,433, 3,822,209, and 5,084,197.

[0094] Preferred dispersants include borated and non-borated succinimides, including those derivatives from mono-succinimides, bis-succinimides, and/or mixtures of mono- and bis-succinimides, wherein the hydrocarbyl succinimide is derived from a hydrocarbylene group such as polyisobutylene having a Mn of from 500 to 5000 or a mixture of such hydrocarbylene groups. Other preferred dispersants include succinic acid-esters and amides, alkylphenol-polyamine-coupled Mannich adducts, their capped derivatives, and other related components. Such additives may be used in an amount of 0.1 to 20 weight percent, preferably 0.5 to 8 weight percent.

Detergents

[0095] A typical detergent is an anionic material that contains a long chain hydrophobic portion of the molecule and a smaller anionic or oleophobic hydrophilic portion of the molecule. The anionic portion of the detergent is typically derived from an organic acid such as a sulfur acid, carboxylic acid, phosphorous acid, phenol, or mixtures thereof. The counterion is typically an alkaline earth or alkali metal.

[0096] Salts that contain a substantially stochiometric amount of the metal are described as neutral salts and have a total base number (TBN, as measured by ASTM D2896) of from 0 to 80. Many compositions are overbased, containing large amounts of a metal base that is achieved by reacting an excess of a metal compound (a metal hydroxide or oxide, for example) with an acidic gas (such as carbon dioxide). Useful detergents can be neutral, mildly overbased, or highly overbased.

[0097] It is desirable for at least some detergent to be overbased. Overbased detergents help neutralize acidic impurities produced by the combustion process and become entrapped in the oil. Typically, the overbased material has a ratio of metallic ion to anionic portion of the detergent of 1.05:1 to 50:1 on an equivalent basis. More preferably, the ratio is from 4:1 to 25:1. The resulting detergent is an overbased detergent that will typically have a TBN of 150 or higher, often 250 to 450 or more. Preferably, the overbasing cation is sodium, calcium, or magnesium. A mixture of detergents of differing TBN can be used in the present disclosure.

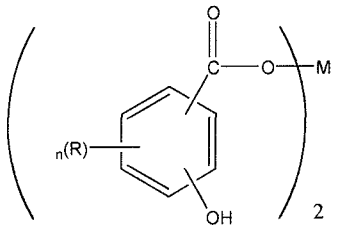
[0098] Preferred detergents include the alkali or alkaline earth metal salts of sulfonates, phenates, carboxylates, phosphates, and salicylates, e.g., a mixture of magnesium sulfonate and calcium salicylate.

[0099] Sulfonates may be prepared from sulfonic acids that are typically obtained by sulfonation of alkyl substituted aromatic hydrocarbons. Hydrocarbon examples include those obtained by alkylating benzene, toluene, xylene, naphthalene, biphenyl and their halogenated derivatives (chlorobenzene, chlorotoluene, and chloronaphthalene, for example). The alkylating agents typically have 3 to 70 carbon atoms. The alkaryl sulfonates typically contain 9 to 80 carbon or more carbon atoms, more typically from 16 to 60 carbon atoms.

[00100] Alkaline earth phenates are another useful class of detergent. These detergents can be made by reacting alkaline earth metal hydroxide or oxide (CaO, $Ca(OH)_2$, BaO, $Ba(OH)_2$, MgO, $Mg(OH)_2$, for example) with an alkyl phenol or sulfurized alkylphenol. Useful alkyl groups include straight chain or branched C_1-C_{30} alkyl groups, preferably C_4-C_{20}. Examples of suitable phenols include isobutylphenol, 2-ethylhexylphenol, nonylphenol, dodecyl phenol, and the like. It should be noted that starting alkylphenols may contain more than one alkyl substituent that are each independently straight chain or branched. When a non-sulfurized alkylphenol is used, the sulfurized product may be obtained by methods

well known in the art. These methods include heating a mixture of alkylphenol and sulfurizing agent (including elemental sulfur, sulfur halides such as sulfur dichloride, and the like) and then reacting the sulfurized phenol with an alkaline earth metal base.

[00101] Metal salts of carboxylic acids are also useful as detergents. These carboxylic acid detergents may be prepared by reacting a basic metal compound with at least one carboxylic acid and removing free water from the reaction product. These compounds may be overbased to produce the desired TBN level. Detergents made from salicylic acid are one preferred class of detergents derived from carboxylic acids. Useful salicylates include long chain alkyl salicylates. One useful family of compositions is of the formula



where R is an alkyl group having 1 to 30 carbon atoms, n is an integer from 1 to 4, and M is an alkaline earth metal. Preferred R groups are alkyl chains of at least C_{11}, preferably C_{13} or greater. R may be optionally substituted with substituents that do not interfere with the detergent's function. M is preferably, calcium, magnesium, or barium. More preferably, M is calcium.

[00102] Hydrocarbyl-substituted salicylic acids may be prepared from phenols by the Kolbe reaction (see U.S. Patent No. 3,595,791). The metal salts of the hydrocarbyl-substituted salicylic acids may be prepared by double decomposition of a metal salt in a polar solvent such as water or alcohol.

[00103] Alkaline earth metal phosphates are also used as detergents and are known in the art.

[00104] Detergents may be simple detergents or what is known as hybrid or complex detergents. The latter detergents can provide the properties of two detergents without the need to blend separate materials. See U.S. Patent No. 6,034,039.

[00105] Preferred detergents include calcium phenates, calcium sulfonates, calcium salicylates, magnesium phenates, magnesium sulfonates, magnesium salicylates and other related components (including borated detergents) in any combination. A preferred detergent includes magnesium sulfonate and calcium salicylate.

[00106] The detergent concentration in the lubricating oils of this disclosure can range from 1.0 to 6.0 weight percent, preferably 2.0 to 5.0 weight percent, and more preferably from 2.0 weight percent to 4.0 weight percent, based on the total weight of the lubricating oil.

Antioxidants

[00107] Antioxidants retard the oxidative degradation of base oils during service. Such degradation may result in deposits on metal surfaces, the presence of sludge, or a viscosity increase in the lubricant. One skilled in the art knows a wide variety of oxidation inhibitors that are useful in lubricating oil compositions. See, Klamann in Lubricants and Related Products, op cite, and U.S. Patent Nos. 4,798,684 and 5,084,197, for example.

[00108] Useful antioxidants include hindered phenols. These phenolic antioxidants may be ashless (metal-free) phenolic compounds or neutral or basic metal salts of certain phenolic compounds. Typical phenolic antioxidant compounds are the hindered phenolics which are the ones which contain a sterically hindered hydroxyl group, and these include those derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or

p-position to each other. Typical phenolic antioxidants include the hindered phenols substituted with C_6+ alkyl groups and the alkylene coupled derivatives of these hindered phenols. Examples of phenolic materials of this type 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-t-butyl-4-heptyl phenol; and 2-methyl-6-t-butyl-4-dodecyl phenol. Other useful hindered mono-phenolic antioxidants may include for example hindered 2,6-di-alkyl-phenolic proprionic ester derivatives. Bis-phenolic antioxidants may also be advantageously used in combination with the instant disclosure. Examples of ortho-coupled phenols include: 2,2′-bis(4-heptyl-6-t-butyl-phenol); 2,2′-bis(4-octyl-6-t-butyl-phenol); and 2,2′-bis(4-dodecyl-6-t-butyl-phenol). Para-coupled bisphenols include for example 4,4′-bis(2,6-di-t-butyl phenol) and 4,4′-methylene-bis(2,6-di-t-butyl phenol).

[00109] Non-phenolic oxidation inhibitors which may be used include aromatic amine antioxidants and these may be used either as such or in combination with phenolics. Typical examples of non-phenolic antioxidants include: alkylated and non-alkylated aromatic amines such as aromatic monoamines of the formula $R^8R^9R^{10}N$ where R^8 is an aliphatic, aromatic or substituted aromatic group, R^9 is an aromatic or a substituted aromatic group, and R^{10} is H, alkyl, aryl or $R^{11}S(O)_XR^{12}$ where R^{11} is an alkylene, alkenylene, or aralkylene group, R^{12} is a higher alkyl group, or an alkenyl, aryl, or alkaryl group, and x is 0, 1 or 2. The aliphatic group R^8 may contain from 1 to 20 carbon atoms, and preferably contains from 6 to 12 carbon atoms. The aliphatic group is a saturated aliphatic group. Preferably, both R^8 and R^9 are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring aromatic group such as naphthyl. Aromatic groups R^8 and R^9 may be joined together with other groups such as S.

[00110] Typical aromatic amines antioxidants have alkyl substituent groups of at least 6 carbon atoms. Examples of aliphatic groups include hexyl, heptyl, octyl,

nonyl, and decyl. Generally, the aliphatic groups will not contain more than 14 carbon atoms. The general types of amine antioxidants useful in the present compositions include diphenylamines, phenyl naphthylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more aromatic amines are also useful. Polymeric amine antioxidants can also be used. Particular examples of aromatic amine antioxidants useful in the present disclosure include: p,p′-dioctyldiphenylamine; t-octylphenyl-alpha-naphthylamine; phenyl-alphanaphthylamine; and p-octylphenyl-alpha-naphthylamine.

[00111] Sulfurized alkyl phenols and alkali or alkaline earth metal salts thereof also are useful antioxidants.

[00112] Preferred antioxidants include hindered phenols, arylamines. These antioxidants may be used individually by type or in combination with one another. Such additives may be used in an amount of 0.01 to 5 weight percent, preferably 0.01 to 1.5 weight percent, more preferably zero to less than 1.5 weight percent, most preferably zero.

Pour Point Depressants (PPDs)

[00113] Conventional pour point depressants (also known as lube oil flow improvers) may be added to the compositions of the present disclosure if desired. These pour point depressant may be added to lubricating compositions of the present disclosure to lower the minimum temperature at which the fluid will flow or can be poured. Examples of suitable pour point depressants include polymethacrylates, polyacrylates, polyarylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, and terpolymers of dialkylfumarates, vinyl esters of fatty acids and allyl vinyl ethers. U.S. Patent Nos. 1,815,022; 2,015,748; 2,191,498; 2,387,501; 2,655, 479; 2,666,746; 2,721,877; 2,721,878; and 3,250,715 describe useful pour point

depressants and/or the preparation thereof. Such additives may be used in an amount of 0.01 to 5 weight percent, preferably 0.01 to 1.5 weight percent.

Seal Compatibility Agents

[00114] Seal compatibility agents help to swell elastomeric seals by causing a chemical reaction in the fluid or physical change in the elastomer. Suitable seal compatibility agents for lubricating oils include organic phosphates, aromatic esters, aromatic hydrocarbons, esters (butylbenzyl phthalate, for example), and polybutenyl succinic anhydride. Such additives may be used in an amount of 0.01 to 3 weight percent, preferably 0.01 to 2 weight percent.

Antifoam Agents

[00115] Anti-foam agents may advantageously be added to lubricant compositions. These agents retard the formation of stable foams. Silicones and organic polymers are typical anti-foam agents. For example, polysiloxanes, such as silicon oil or polydimethyl siloxane, provide antifoam properties. Anti-foam agents are commercially available and may be used in conventional minor amounts along with other additives such as demulsifiers; usually the amount of these additives combined is less than 1 weight percent and often less than 0.1 weight percent.

Friction Modifiers

[00116] A friction modifier is any material or materials that can alter the coefficient of friction of a surface lubricated by any lubricant or fluid containing such material(s). Friction modifiers, also known as friction reducers, or lubricity agents or oiliness agents, and other such agents that change the ability of base oils, formulated lubricant compositions, or functional fluids, to modify the coefficient of friction of a lubricated surface may be effectively used in combination with the

base oils or lubricant compositions of the present disclosure if desired. Friction modifiers that lower the coefficient of friction are particularly advantageous in combination with the base oils and lube compositions of this disclosure. Friction modifiers may include metal-containing compounds or materials as well as ashless compounds or materials, or mixtures thereof. Metal-containing friction modifiers may include metal salts or metalligand complexes where the metals may include alkali, alkaline earth, or transition group metals. Such metal-containing friction modifiers may also have low-ash characteristics. Transition metals may include Mo, Sb, Sn, Fe, Cu, Zn, and others. Ligands may include hydrocarbyl derivative of alcohols, polyols, glycerols, partial ester glycerols, thiols, carboxylates, carbamates, thiocarbamates, dithiocarbamates, phosphates, thiophosphates, dithiophosphates, amides, imides, amines, thiazoles, thiadiazoles, dithiazoles, diazoles, triazoles, and other polar molecular functional groups containing effective amounts of O, N, S, or P, individually or in combination. In particular, Mo-containing compounds can be particularly effective such as for example Mo-dithiocarbamates, Mo(DTC), Mo-dithiophosphates, Mo(DTP), Mo-amines, Mo (Am), Mo-alcoholates, Mo-alcohol-amides, etc. See U.S. Patent Nos. 5,824,627, 6,232,276, 6,153,564, 6,143,701, 6,110,878, 5,837,657, 6,010,987, 5,906,968, 6,734,150, 6,730,638, 6,689,725, 6,569,820; WO 99/66013; WO 99/47629; and WO 98/26030.

[00117] Ashless friction modifiers may also include lubricant materials that contain effective amounts of polar groups, for example, hydroxyl-containing hydrocarbyl base oils, glycerides, partial glycerides, glyceride derivatives, and the like. Polar groups in friction modifiers may include hydrocarbyl groups containing effective amounts of O, N, S, or P, individually or in combination. Other friction modifiers that may be particularly effective include, for example, salts (both ash-containing and ashless derivatives) of fatty acids, fatty alcohols, fatty amides, fatty esters, hydroxyl-containing carboxylates, and comparable synthetic long-chain hydrocarbyl acids, alcohols, amides, esters, hydroxy

carboxylates, and the like. In some instances fatty organic acids, fatty amines, and sulfurized fatty acids may be used as suitable friction modifiers.

[00118] Useful concentrations of friction modifiers may range from 0.01 weight percent to 10-15 weight percent or more, often with a preferred range of 0.1 weight percent to 5 weight percent. Concentrations of molybdenum-containing materials are often described in terms of Mo metal concentration. Advantageous concentrations of Mo may range from 10 ppm to 3000 ppm or more, and often with a preferred range of 20-2000 ppm, and in some instances a more preferred range of 30-1000 ppm. Friction modifiers of all types may be used alone or in mixtures with the materials of this disclosure. Often mixtures of two or more friction modifiers, or mixtures of friction modifier(s) with alternate surface active material(s), are also desirable.

Viscosity Index Improvers

[00119] Viscosity index improvers (also known as VI improvers, viscosity modifiers, and viscosity improvers) can be included in the lubricant compositions of this disclosure. Preferably, the method of this disclosure obtains improvements in fuel economy without sacrificing durability by a reduction of high-temperature high-shear (HTHS) viscosity to a level lower than 2.6 cP through reduction or removal of viscosity index improvers or modifiers.

[00120] Viscosity index improvers provide lubricants with high and low temperature operability. These additives impart shear stability at elevated temperatures and acceptable viscosity at low temperatures.

[00121] Suitable viscosity index improvers include high molecular weight hydrocarbons, polyesters and viscosity index improver dispersants that function as both a viscosity index improver and a dispersant. Typical molecular weights of

these polymers are between 10,000 to 1,500,000, more typically 20,000 to 1,200,000, and even more typically between 50,000 and 1,000,000.

[00122] Examples of suitable viscosity index improvers are linear or star-shaped polymers and copolymers of methacrylate, butadiene, olefins, or alkylated styrenes. Polyisobutylene is a commonly used viscosity index improver. Another suitable viscosity index improver is polymethacrylate (copolymers of various chain length alkyl methacrylates, for example), some formulations of which also serve as pour point depressants. Other suitable viscosity index improvers include copolymers of ethylene and propylene, hydrogenated block copolymers of styrene and isoprene, and polyacrylates (copolymers of various chain length acrylates, for example). Specific examples include styrene-isoprene or styrene-butadiene based polymers of 50,000 to 200,000 molecular weight.

[00123] Olefin copolymers, are commercially available from Chevron Oronite Company LLC under the trade designation "PARATONE®" (such as "PARATONE® 8921" and "PARATONE® 8941"); from Afton Chemical Corporation under the trade designation "HiTEC®" (such as "HiTEC® 5850B"); and from The Lubrizol Corporation under the trade designation "Lubrizol® 7067C". Polyisoprene polymers are commercially available from Infineum International Limited, e.g. under the trade designation "SV200"; diene-styrene copolymers are commercially available from Infineum International Limited, e.g. under the trade designation "SV 260".

[00124] In an embodiment of this disclosure, the viscosity index improvers may be used in an amount of less than 2.0 weight percent, preferably less than 1.0 weight percent, and more preferably less than 0.5 weight percent, based on the total weight of the formulated oil or lubricating engine oil.

[00125] In another embodiment of this disclosure, the viscosity index improvers may be used in an amount of from 0.0 to 2.0 weight percent, preferably 0.0 to 1.0

weight percent, and more preferably 0.0 to 0.5 weight percent, based on the total weight of the formulated oil or lubricating engine oil.

[00126] When lubricating oil compositions contain one or more of the additives discussed above, the additive(s) are blended into the composition in an amount sufficient for it to perform its intended function. Typical amounts of such additives useful in the present disclosure are shown in Table A below.

[00127] It is noted that many of the additives are shipped from the additive manufacturer as a concentrate, containing one or more additives together, with a certain amount of base oil diluents. Accordingly, the weight amounts in the table below, as well as other amounts mentioned in this specification, are directed to the amount of active ingredient (that is the non-diluent portion of the ingredient). The weight percent (wt%) indicated below is based on the total weight of the lubricating oil composition.

TABLE 1

Typical Amounts of Other Lubricating Oil Components

Compound	Approximate wt% (Useful)	Approximate wt% (Preferred)
Dispersant	0.1-20	0.1-8
Detergent	1.0-6.0	2.0-4.0
Friction Modifier	0.01-5	0.01-1.5
Antioxidant	0.1-5	0.1-1.5
Pour Point Depressant (PPD)	0.0-5	0.01-1.5
Anti-Foam Agent	0.001-3	0.001-0.15
Viscosity Index Improver (solid polymer basis)	0.0-2	0.0-1

[00128] The foregoing additives are all commercially available materials. These additives may be added independently but are usually precombined in packages which can be obtained from suppliers of lubricant oil additives. Additive packages with a variety of ingredients, proportions and characteristics are available and selection of the appropriate package will take the requisite use of the ultimate composition into account.

[00129] The following non-limiting examples are provided to illustrate the disclosure.

EXAMPLES

Example 1

[00130] This example demonstrates the effect of nanographene platelets (NGP) on the tribological performance of DLC coating under boundary lubrication conditions. Experiments were conducted using a high-frequency reciprocating

rig, HFRR (PCS Instruments, Inc., London, UK) to understand the tribological (friction and wear) performance of DLC coatings under lubricated conditions. A 6 mm diameter steel ball was rubbed against a flat disc. Both the ball and the flat disc were made of 440C tool steel and coated with DLC. The HFRR tests reported herein were run at 100°C for 4 hours with 400g applied load, and 1mm stroke length at a frequency of 60 Hz. The apparatus was instrumented to measure friction force via a bi-directional load cell which was connected to a computer program that controlled the time elapsed and number of points in each data set. The specimens were removed from the apparatus after the test and cleaned using acetone and heptane to remove residual oils. The loss of material in the wear track was measured using an optical profilometer. The calculated lambda ratio (the ratio of film thickness to surface roughness) for the given experimental parameters was less than unity suggesting that the experiments were conducted under boundary lubrication. The lubricant used for the results shown in Figs. 1 and 2 contained 5mg NGP in 5g PAO of viscosity grade 6. Fig. 1 graphically depicts friction performance on a diamond-like carbon (DLC) coating using nanographene platelets (NGP) in polyalphaolefin (PAO), in particular, the friction coefficient as a function of time for PAO6 and PAO6 + NGP. Fig. 2 depicts wear results measured from a DLC coating using an optical profilometer for PAO6 and PAO6 + NGP.

[00131] The friction results presented in Fig. 1 show that PAO + NGP provided super low friction (<0.02) under boundary lubrication conditions which was more than 50% lower than PAO alone, and that the frictional stability given by PAO + NGP was much better than PAO alone.

[00132] DLC coatings generally provide lower friction than ferrous surfaces. This is because of the weak Van der Waals' interactions between the sp^2 carbon atoms of two adjacent surfaces. When the graphene nanoplatelets are used on

DLC coatings, this effect is significantly amplified at the interfaces and hence enhanced low friction is obtained.

[00133] The wear results measured from the DLC coating using optical profilometer are shown in Fig. 2. Fig. 2 shows that PAO alone yielded 0.6 μm loss of coating while it was only 0.1 μm for the NGP-containing PAO. The use of NGP in PAO provided 5-6 times lower wear on DLC coating than PAO alone. The improved load bearing capability of NGP may be the reason for showing such a different wear result. The marked increase of durability and reduction of friction demonstrate the ability of the PAO + NGP/DLC combination to offer significant improvement in fuel efficiency, emission reduction and component durability for machines/engines.

Example 2

[00134] In this example, the friction and wear tests were conducted in a Mini Traction Machine (MTM) for all lubricant formulations. This machine has a ball-on-disc arrangement where the speeds of ball and disc can be controlled independently. This helps simulate the sliding/rolling contact conditions. The rolling/sliding type of contact is commonly found in many machine/engine components such as gears and cams. A standard steel ball was loaded against a standard steel disc with 37 N load that exerted approximately 1 GPa Hertzian contact pressure. The lubricant temperature was 100°C while the mean entrainment speed and slide-roll-ratio (SRR) were 50 mm/s and 50% respectively. The test sequence involved a Stribeck test followed by a 4-hour wear test. The test specimen and lubricant were not changed between the Stribeck and wear tests. It is noted that the long duration wear tests were conducted to achieve the steady state friction response as well as ZDDP film formation. The specimens were removed from the apparatus and cleaned using first with acetone and then with heptane to remove the residual oils. A stylus profilometer was used to generate

the 2D and 3D maps of the wear tracks (tribofilms). The following four lubricant formulations were used:

a. PAO Base Stock (viscosity grade 6),

b. 0.5% Graphene in Base Stock

c. 0.75% ZDDP in Base Stock Blend, and

d. 0.5% Graphene, 0.75% ZDDP in Base Stock Blend

[00135] The Stribeck friction results are shown in Fig. 3. Fig. 3 graphically depicts results of Stribeck tests on fresh surfaces (friction as a function of speed). Tests were performed on fresh surfaces from high speed (3000 mm/s) to low speed (3 mm/s) at 50% slide to roll ratio (SRR), 1 GPa pressure and 100°C. In this test, the mean entrainment speed was varied from 3000 mm/s to 3 mm/s to change the lubrication regime while the load (37 N) and temperature (100°C) were kept constant. A full lubricant film was developed between the disc and ball starting with the highest speed (3000 mm/s). The friction coefficient at this speed was sufficiently low and identical for all blends as expected. It is noted that the friction in this lubrication regime is primarily governed by the rheological properties of base stock. The lubricant film thickness decreases with the decrease of speed. As soon as the film thickness goes below the roughness of the interacting surfaces, the surface friction (asperity/asperity interactions) starts to dominate resulting in friction increase. The lubrication regime provided under this type of conditions is called boundary lubrication regime.

[00136] The friction response in the boundary lubrication conditions is influenced by the surface active lubricant components. In this example, it was observed that the PAO base stock provided the highest friction coefficient under these conditions (low speed) while adding ZDDP in base stock provided slightly lower friction than PAO. In contrast, graphene nanoplatelets dispersed in base

stock revealed significantly low friction. While ZDDP tribofilms are typically rough and result in high boundary friction, adding graphene with ZDDP did not hinder the low friction performance of graphene.

[00137] The wear tracks generated by all lubricant formulations are shown in Figs. 4, 5, 6 and 7. Fig. 4 depicts 2D and 3D maps of wear tracks for PAO base stock. Fig. 5 depicts 2D and 3D maps of wear tracks for 0.5% graphene in PAO base stock. Fig. 6 depicts 2D and 3D maps of wear tracks for 0.75% ZDDP in PAO base stock. Fig. 7 depicts 2D and 3D maps of wear tracks for 0.5% graphene and 0.75% ZDDP in PAO base stock. It is evident from the images that PAO having no additive provided the highest wear as expected. Adding graphene in PAO significantly improved the wear performance giving mild polishing and abrasive wear. In contrast, ZDDP provided a non-uniform tribofilm showing no measurable wear while the growth as well as uniformity of ZDDP tribofilm significantly improved in the presence of graphene.

[00138] ZDDP tribofilm usually forms within the first 60 minutes and during this period of time friction coefficients initially increase and then decrease. This is commonly known as the sign of incubation friction response. The initial increase of friction is primarily because of the initial metal/metal contact that often results in adhesive/abrasive type of wear. As soon as the ZDDP tribofilm starts to grow, the extent of metal/metal contact decreases resulting in a friction drop which finally reaches to a steady state. The steady state friction response correlates with the formation of stable ZDDP tribofilm. The friction response is shown in Fig. 8 and ZDDP film growth shown in Fig. 6. However, no incubation friction response was observed when graphene was used with ZDDP; rather the friction coefficients reached to a steady state within 10-15 minutes. This suggests that the stable ZDDP tribofilms presumably formed within the first 10-15 minutes in the presence of graphene. Fig. 8 graphically depicts friction results from 4 hour wear tests, in particular, friction coefficients as a function of time for PAO base

stock, 0.5% graphene in PAO base stock, 0.75% ZDDP in PAO base stock, and 0.5% graphene and 0.75% ZDDP in PAO base stock. Tests were performed at 50 mm/s speed, 50% slide to roll ratio (SRR), 1 GPa pressure and 100°C for 4 hours.

[00139] The formation of ZDDP tribofilm requires reactive surfaces as generated by wear at the tribological contacts. In the case of ZDDP alone (Fig. 6), the presence of sharp spikes along the wear track suggests that the film formation was limited to those sites only while a large portion of the contact area had no or less tribofilm. In contrast, the presence of graphene greatly suppressed any possible aggressive or non-uniform wear as evidenced by having no incubation friction response. The anti-friction/antiwear properties of graphene may be responsible for this phenomenon. The controlled and limited wear provided by graphene created the reactive sites more uniformly all over the contact region and thus promoted the growth of consistent ZDDP tribofilm within a very short period of time (10-15 minutes).

[00140] Fig. 9 graphically depicts the friction performance of NGP on a hydrogenated DLC coating. NGP + PAO provided significantly low boundary friction (0.02) on a hydrogenated DLC coating under pure sliding contact. NGP + PAO provided approximately 60% lower friction and 80% lower wear on a hydrogenated DLC coating than PAO alone.

[00141] Fig. 10 graphically depicts the friction performance of NGP and the effect of DLC coating type, i.e., hydrogenated DLC coating or non-hydrogenated DLC coating. NGP + PAO provided significantly low boundary friction on a hydrogenated DLC coating (0.04) and on a non-hydrogenated DLC coating (0.02) under mixed rolling/sliding contact. NGP-containing lubricants provide low friction on hydrogenated, non-hydrogenated and metal-doped DLC coatings.

[00142] Fig. 11 graphically depicts the friction performance of NGP and the effect of base stocks, i.e., PAO and PEG. NGP + PAO and NGP + PEG provided

85% and 75% lower boundary friction than PAO and PEG respectively under mixed rolling/sliding contact. NGP dispersed in various characteristically different base stocks gives significantly low friction. NGP-containing lubricants provide significantly low friction on ferrous surfaces.

[00143] Fig. 12 graphically depicts the friction performance of NGP and the effect of NGP concentration. A low concentration of NGP in a base stock can provide a significantly low friction.

[00144] Fig. 13 graphically depicts the friction performance of NGP and the effect of base stock viscosity. NGP dispersed over a wide range of base stock viscosity provides a significantly low boundary friction.

[00145] Fig. 14 graphically depicts the friction performance of NGP in PAO and a fully formulated oil. NGP dispersed in a fully formulated oil showed a 40% lower friction than the fully formulated oil alone. NGP shows positive friction response when added with fully formulated oils.

[00146] The Mini Traction Machine (MTM) was used in Example 2 for measuring the frictional properties of lubricated contacts under mixed rolling and sliding conditions. Many tribological contacts such as contacts between engine valve train components and gear contacts are operated under mixed rolling/sliding conditions. MTM can simulate such contacts and provide traction mapping and Stribeck curves for lubricants commonly used in engine oils. This machine was manufactured by PCS Instruments (UK).

[00147] The High Frequency Reciprocating Rig (HFRR) was used in Example 1 for measuring the friction properties of lubricated contacts under pure sliding conditions. This machine is suitable for boundary friction measurements of engine oils, greases and other compounds. This rig is also used as a wear tested to characterize antiwear performance of lubricants. This machine was manufactured

by PCS Instruments (UK) and it the industry standard test for diesel fuel lubricity and conforms to ASTM D6079, CEC F-06-A, ISO 12156, EN 590, JPI-5S-50 and IP 450.

[00148] The NGP used in the examples was less than 10 nm thick. The average dimensions of length and width were approximately 0.6 micrometers. The high aspect ratio of NGP gives high specific surface area (surface coverage) and thereby provides excellent low friction surface when used as a lubricant/lubricant additive. The thermal conductivity of NGP is up to 5300 W/(mK) which is 5 time higher than copper. Hence, NGP used in lubricants will significantly enhance capability to transfer heat from the engine combustion cycle.

[00149] The use of NGP in lubricants can provide a positive effect on energy efficiency for several reasons. The NGP provides significantly low boundary friction which is 40% lower than that provided by current oil formulations. The effectiveness of NGP is friction reduction in low viscosity lubricants will significantly improve fuel economy. It is noted that the improvement in fuel economy using lubricants primarily depends on lubricant viscosity. High engine wear given by low viscosity fuel economy lubricants actually limits their use in engines. A significant improvement in both energy efficiency and engine durability can be achieved using the combination of wear resistant DLC-coated engine components and NGP-containing low viscosity lubricants.

[00150] As used herein, lubrication of tribo-components occurs when the interacting surfaces are separated by lubricant films. The applied load is carried by pressure generated within the fluid and the frictional resistance to motion arises entirely from the shearing of viscous fluid. When the interacting surfaces are completely separated lubricant films, it is called hydrodynamic lubrication (HL). In this lubrication regime, the friction loss is mainly governed by the rheological properties of lubricants. In the boundary lubrication (BL) regime, the surfaces are not entirely separated by lubricant films and asperity-asperity contact occurs. In

this lubrication regime, the friction is mostly controlled by the antifriction and load carrying capability of lubricants and also by the nature of the mating surfaces.

[00151] All patents and patent applications, test procedures (such as ASTM methods, UL methods, and the like), and other documents cited herein are fully incorporated by reference to the extent such disclosure is not inconsistent with this disclosure and for all jurisdictions in which such incorporation is permitted.

[00152] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated. While the illustrative embodiments of the disclosure have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the disclosure. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present disclosure, including all features which would be treated as equivalents thereof by those skilled in the art to which the disclosure pertains.

[00153] The present disclosure has been described above with reference to numerous embodiments and specific examples. Many variations will suggest themselves to those skilled in this art in light of the above detailed description. All such obvious variations are within the full intended scope of the appended claims.

CLAIMS:

1. A method of improving wear protection in an engine lubricated with a lubricating oil, said method comprising using as the lubricating oil a formulated oil comprising a lubricating oil base stock as a major component, an antiwear additive as a first minor component, and carbon nanoplatelets as a second minor component; wherein said carbon nanoplatelets are dispersed in said lubricating oil base stock; and wherein wear protection is improved as compared to wear protection achieved using a lubricating oil not containing carbon nanoplatelets as a second minor component.

2. A method for improving wear protection in an engine lubricated with a lubricating oil by using as the lubricating oil a formulated oil having a HTHS viscosity of less than 4.0 cP at 150°C, said formulated oil having a composition comprising a major amount of a lubricating oil base stock, a minor amount of an antiwear additive, and a minor amount of carbon nanoplatelets; wherein said carbon nanoplatelets are dispersed in said lubricating oil base stock sufficient for the formulated oil to pass wear protection requirements of one or more engine tests selected from TU3M, Sequence IIIG, Sequence IVA and OM646LA.

3. A method for improving wear protection in an engine lubricated with a lubricating oil by using as the lubricating oil a formulated oil having a HTHS viscosity of less than 4.0 cP at 150°C, said formulated oil having a composition comprising a major amount of a lubricating oil base stock and a minor amount of carbon nanoplatelets; wherein said carbon nanoplatelets are dispersed in said lubricating oil base stock sufficient for the formulated oil to pass wear protection requirements of one or more engine tests selected from TU3M, Sequence IIIG, Sequence IVA and OM646LA.

4. The method of claims 1-2 wherein the antiwear additive comprises zinc dialkyldithiophosphate (ZDDP), and the carbon nanoplatelets comprise nanographene platelets (NGP).

5. The method of claim 3 wherein said nanographene platelets have an average thickness less than 10 nm, and a length or width less than 500 nm.

6. The method of claims 1-5 wherein the engine comprises one or more components and/or surfaces that are lubricated with the lubricating oil, wherein the one or more components and/or surfaces are coated with a ferrous or non-ferrous coating, a diamond-like carbon (DLC) coating, a ceramic coating, or a polymeric coating.

7. The method of claims 1-6 wherein the lubricating oil base stock comprises a Group I, Group II, Group III, Group IV or Group V base oil.

8. The method of claims 1-7 wherein the oil base stock is present in an amount of from 70 weight percent to 95 weight percent, the antiwear additive is present in an amount of from 0.4 weight percent to 1.2 weight percent, and the carbon nanoplatelets are present in an amount of from 0.1 weight percent to 10 weight percent, based on the total weight of the formulated oil.

9. A lubricating engine oil having a composition comprising a lubricating oil base stock as a major component, an antiwear additive as a first minor component, and carbon nanoplatelets as a second minor component; wherein said carbon nanoplatelets are dispersed in said lubricating oil base stock sufficient for the lubricating engine oil to exhibit improved wear protection as compared to wear protection achieved using a lubricating oil not containing carbon nanoplatelets as a second minor component.

10. A lubricating engine oil having a composition comprising a major amount of a lubricating oil base stock, a minor amount of an antiwear additive, and a minor amount of carbon nanoplatelets; wherein said lubricating engine oil has a HTHS viscosity of less than 4.0 cP at 150°C; and wherein said carbon nanoplatelets are dispersed in said lubricating oil base stock sufficient for the lubricating engine oil to pass wear protection requirements of one or more engine tests selected from TU3M, Sequence IIIG, Sequence IVA and OM646LA.

11. A lubricating engine oil having a composition comprising a major amount of a lubricating oil base stock and a minor amount of carbon nanoplatelets; wherein said lubricating engine oil has a HTHS viscosity of less than 4.0 cP at 150°C; and wherein said carbon nanoplatelets are dispersed in said lubricating oil base stock sufficient for the lubricating engine oil to pass wear protection requirements of one or more engine tests selected from TU3M, Sequence IIIG, Sequence IVA and OM646LA.

12. The lubricating engine oil of claims 9-10 wherein the antiwear additive comprises zinc dialkyldithiophosphate (ZDDP), and the carbon nanoplatelets comprise nanographene platelets (NGP).

13. The lubricating engine oil of claim 12 wherein said nanographene platelets have an average thickness less than 10 nm, and a length or width less than 500 nm.

14. The lubricating engine oil of claims 9-13 wherein the lubricating oil base stock comprises a Group I, Group II, Group III, Group IV or Group V base oil.