

METHOD FOR IMPROVING ENGINE FUEL EFFICIENCY

FIELD OF THE DISCLOSURE

[0001] This disclosure relates to improving friction reduction and fuel efficiency, while maintaining or improving wear protection, in an engine lubricated with a lubricating oil by including a detergent mixture containing at least one low total base number (TBN) detergent, in the lubricating oil.

BACKGROUND OF THE DISCLOSURE

[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.

[0003] To address these increasing standards, automotive original equipment manufacturers are demanding better fuel economy as a lubricant-related performance characteristic, while maintaining deposit control and oxidative stability requirements. One well known way to increase fuel economy is to decrease the viscosity of the lubricating oil. However, this approach is now reaching the limits of current equipment capabilities and specifications. At a given viscosity, it is well known that adding organic or organo-metallic friction modifiers reduces the surface friction of the lubricating oil and allows for better fuel economy. However these additives often bring with them detrimental effects such as increased deposit formation, seals impacts, or they out-compete the anti-wear components for limited surface sites, thereby not allowing the formation of an anti-wear film, causing increased wear.

[0004] Contemporary lubricants such as engine oils use mixtures of additives such as dispersants, detergents, inhibitors, viscosity index improvers and the like to provide engine cleanliness and durability under a wide range of performance conditions of temperature, pressure, and lubricant service life.

[0005] Lubricating oil compositions use a variety of detergents to minimize varnish, ring zone deposits, and rust by solubilizing oil insoluble particles. Overbased detergents are used to help neutralize acids that accumulate in lubricating oil during use.

[0006] A typical detergent is an anionic material that contains a long chain oleophilic portion of the molecule and a smaller anionic or oleophobic 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 counter ion is typically an alkaline earth or alkali metal. Salts that contain a substantially stoichiometric amount of the metal are described as neutral salts and have a total base number (TBN; measured by ASTM D2896, TBN is defined as mg KOH/g) of from about 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). The resulting overbased detergent is an overbased detergent that will typically have a TBN of 150 or higher, often 250 to 450 or more.

[0007] U.S. Patent No. 7,704,930 discloses a detergent additive for lubricating oil compositions that comprises at least two detergents with substantially different total base number (TBN). The detergent additive comprises at least two of the following: a detergent of greater than about 200 TBN, a detergent of about 100 to 200 TBN, and a detergent of less than about 100 TBN. All three detergents may be used. The detergents include salicylate detergents. U.S. Patent No. 7,704,930 discloses lubricating oil compositions containing such detergents and at least one of Group II base stock, Group III base stock, Group IV base stock, and wax isomerates, and mixtures thereof.

[0008] With engines increasingly demanding higher performance, there is a need for detergents that provide increased friction reduction, detergent film maintenance, and engine cleanliness.

[0009] Despite the advances in lubricant oil formulation technology, there exists a need for an engine oil lubricant that effectively improves friction reduction and fuel economy while maintaining or improving anti-wear performance.

SUMMARY OF THE DISCLOSURE

[0010] This disclosure relates in part to a method for improving friction reduction and fuel efficiency, while maintaining or improving wear protection, in an engine lubricated with a lubricating oil by including a detergent mixture containing at least one low TBN detergent, in the lubricating oil.

[0011] This disclosure also relates in part to a method for improving friction reduction and fuel efficiency, while maintaining or improving wear protection, in an engine lubricated with a lubricating oil by using as the lubricating oil a formulated oil. The formulated oil has a composition comprising a lubricating oil base stock as a major component; and a detergent mixture comprising a first detergent having a TBN of less than about 100, more preferably a detergent having a TBN of less than about 80, and at least one other detergent different from said first detergent, as a minor component. The composition contains greater than about 4 weight percent of the first detergent, based on the total weight of the formulated oil. Friction reduction and fuel efficiency are improved and wear protection is maintained or improved as compared to friction reduction, fuel efficiency and wear protection achieved using a lubricating engine oil containing a detergent mixture having other than the first detergent having a TBN of less than about 100.

[0012] This disclosure further relates in part to a lubricating engine oil having a composition comprising a lubricating oil base stock as a major component; and a detergent mixture comprising a first detergent having a TBN of less than about 100, and at least one other detergent different from said first detergent, as a minor component. The composition contains greater than about 4 weight percent of the first detergent, based on the total weight of the lubricating engine oil. The composition is sufficient for the lubricating engine oil to exhibit improved friction reduction and fuel efficiency and improved or maintained wear protection as compared to friction reduction, fuel efficiency and wear protection achieved using a lubricating engine oil containing a detergent mixture having other than the first detergent having a TBN of less than about 100.

[0013] It has been surprisingly found that, in accordance with this disclosure, improvements in friction reduction and fuel economy are obtained without sacrificing engine durability by including a detergent mixture containing at least one low TBN (i.e., less than about 100) detergent in the lubricating oil.

[0014] Other objects and advantages of the present disclosure will become apparent from the detailed description that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] Fig. 1 shows 0W-20 synthetic oil formulations having varying calcium salicylate type.

[0016] Fig. 2 shows MTM Stribeck curves from the no detergent finished oil performance in MTM Stribeck test at 140°C.

[0017] Fig. 3 shows MTM Stribeck curves from the baseline 0W-20 finished oil performance in MTM Stribeck test at 140°C.

[0018] Fig. 4 shows MTM Stribeck curves from the all mid-TBN detergent finished oil performance in MTM Stribeck test at 140°C.

[0019] Fig. 5 shows MTM Stribeck curves from the all low TBN detergent finished oil performance in MTM Stribeck test at 140°C.

[0020] Fig. 6 shows MTM Stribeck curves from the high/low mix TBN detergent finished oil performance in MTM Stribeck test at 140°C.

[0021] Fig. 7 shows MTM Stribeck curves from the low TBN calcium sulfonate/high TBN calcium salicylate detergent finished oil performance in MTM Stribeck test at 140°C.

[0022] Fig. 8 shows MTM Stribeck curves from the all low TBN calcium phenate detergent finished oil performance in MTM Stribeck test at 140°C.

[0023] Fig. 9 shows a comparison of HFRR friction traces as a function of temperature for the baseline oil and the balanced high/low TBN salicylate detergent mix finished oils, indicating significant improvement in friction at typical Sequence VID engine oil sump temperatures (black vertical line).

[0024] Fig. 10 shows integrated Stribeck friction coefficients by run and average over all runs for Figs. 2 through 8.

[0025] Fig. 11 shows average integrated Stribeck friction coefficients for formulations with a range of low TBN detergent concentrations.

[0026] Fig. 12 shows Sequence IIIG, VW TDi-2, OM 646, and Sequence VID engine test results on the baseline and example lubricant oil with higher levels of low TBN detergent.

[0027] Fig. 13 shows a comparison of average integrated Stribeck friction coefficients for formulations with high TBN detergent and with or without low TBN detergent in a range of base stock groups.

[0028] Fig. 14 shows a comparison of average integrated Stribeck friction coefficients for formulations with mid TBN detergent and with or without low TBN detergent in a range of base stock groups.

[0029] Fig. 15 shows that average integrated Stribeck friction coefficient for samples with concentrations of high TBN detergent from 2.5 to 7.5 weight percent in Group II, III, and IV base stocks.

DETAILED DESCRIPTION

[0030] It has now been found that improved friction reduction and fuel efficiency can be attained, while wear protection is maintained or improved, in an engine lubricated with a lubricating oil by using as the lubricating oil a formulated oil that has one or more low base number detergents. The formulated oil comprises a lubricating oil base stock as a major component, and a metal dialkyl dithio phosphate, a first detergent having a TBN of less than about 100, optionally a second detergent having a TBN between about 100 and about 200, optionally a third detergent having a TBN of greater than about 200, and a viscosity index improver, as minor components. The lubricating oils of this disclosure are particularly advantageous as passenger vehicle engine oil (PVEO) products.

[0031] The lubricating oils of this disclosure provide excellent engine protection including friction reduction and anti-wear performance. This benefit has been demonstrated for the lubricating oils of this disclosure in the Sequence IIIG/IIIGA (ASTM D7320), Sequence IVA (ASTM D6891), and MB OM646LA (CEC L-099-08) engine tests. 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 has been 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.

[0032] The 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.

Lubricating Oil Base Stocks

[0033] 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.

[0034] 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 about 80 to 120 and contain greater than about 0.03% sulfur and/or less than about 90% saturates. Group II base stocks have a viscosity index of between about 80 to 120, and contain less than or equal to about 0.03% sulfur and greater than or equal to about 90% saturates. Group III stocks have a viscosity index greater than about 120 and contain less than or equal to about 0.03 % sulfur and greater than about 90% saturates. Group IV 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		

[0035] 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.

[0036] 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.

[0037] 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 C₈, C₁₀, C₁₂, C₁₄ olefins or mixtures thereof may be utilized. See U.S. Patent Nos. 4,956,122; 4,827,064; and 4,827,073.

[0038] 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 about 250 to about 3,000, although PAO's may be made in viscosities up to about 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, C₂ to about C₃₂ alphaolefins with the C₈ to about C₁₆ 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 C₁₄ to C₁₈ 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.

[0039] The PAO fluids may be conveniently made by the polymerization of an α -olefin 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.

[0040] Other useful lubricant oil base stocks include wax isomerate base stocks and base oils, comprising hydroisomerized waxy stocks (e.g. waxy stocks such as gas oils, slack waxes, fuels hydrocracker bottoms, etc.), hydroisomerized Fischer-Tropsch waxes, Gas-to-Liquids (GTL) base stocks and base oils, and other wax isomerate hydroisomerized base stocks and base oils, or mixtures thereof Fischer-Tropsch waxes, the high boiling point residues of Fischer-Tropsch synthesis, are highly paraffinic hydrocarbons with very low sulfur content. The hydroprocessing used for the production of such base stocks may use an amorphous hydrocracking/hydroisomerization catalyst, such as one of the specialized lube hydrocracking (LHDC) catalysts or a crystalline hydrocracking/hydroisomerization catalyst, preferably a zeolitic catalyst. For example, one useful catalyst is ZSM-48 as described in U.S. Patent No. 5,075,269, the disclosure of which is incorporated herein by reference in its entirety. Processes for making hydrocracked/hydroisomerized distillates and hydrocracked/hydroisomerized waxes are described, for example, in U.S. Patent Nos. 2,817,693; 4,975,177; 4,921,594 and 4,897,178 as well as in British Patent Nos. 1,429,494; 1,350,257; 1,440,230 and 1,390,359. Each of the aforementioned patents is incorporated herein in their entirety. Particularly favorable processes are described in European Patent Application Nos. 464546 and 464547, also incorporated herein by reference. Processes using Fischer-Tropsch wax feeds are described in U.S. Patent Nos. 4,594,172 and 4,943,672, the disclosures of which are incorporated herein by reference in their entirety.

[0041] Gas-to-Liquids (GTL) base oils, Fischer-Tropsch wax derived base oils, and other wax-derived hydroisomerized (wax isomerate) base oils be advantageously used in the instant disclosure, and may have useful kinematic viscosities at 100°C of about 3 cSt to about 50 cSt, preferably about 3 cSt to about 30 cSt, more preferably about 3.5 cSt to about 25 cSt, as exemplified by GTL 4 with kinematic viscosity of about 4.0 cSt at 100°C and a viscosity index of about 141. These Gas-to-Liquids (GTL) base oils, Fischer-Tropsch wax derived base oils, and other wax-derived hydroisomerized base oils may have useful pour points of about -20°C or lower, and under some conditions may have advantageous pour points of about -25°C or lower, with useful pour points of about -30°C to about -40°C or lower. Useful compositions of Gas-to-Liquids (GTL) base oils, Fischer-Tropsch wax derived base oils, and wax-derived hydroisomerized base oils are recited in U.S. Patent Nos. 6,080,301; 6,090,989, and 6,165,949 for example, and are incorporated herein in their entirety by reference.

[0042] The hydrocarbyl aromatics can be used as base oil or base oil component and can be any hydrocarbyl molecule that contains at least about 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 about C₆ up to about C₆₀ with a range of about C₈ to about C₂₀ often being preferred. A mixture of hydrocarbyl groups is often preferred, and up to about 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 about 5% of the molecule is comprised of an above-type aromatic moiety. Viscosities at 100°C of approximately 3 cSt to about 50 cSt are preferred, with viscosities of approximately 3.4 cSt to about 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 about 2% to about 25%, preferably about 4% to about 20%, and more preferably about 4% to about 15%, depending on the application.

[0043] Alkylated aromatics such as the hydrocarbyl aromatics of the present disclosure may be produced by well-known Friedel-Crafts alkylation of aromatic compounds. See Friedel-Crafts and Related Reactions, Olah, G. A. (ed.), Inter-science Publishers, New York, 1963. For example, an aromatic compound, such as benzene or naphthalene, is alkylated by an olefin, alkyl halide or alcohol in the presence of a Friedel-Crafts catalyst. See Friedel-Crafts and Related Reactions, Vol. 2, part 1, chapters 14, 17, and 18, See Olah, G. A. (ed.), Inter-science Publishers, New York, 1964. Many homogeneous or heterogeneous, solid catalysts are known to one skilled in the art. The choice of catalyst depends on the reactivity of the starting materials and product quality requirements. For example, strong acids such as AlCl_3 , BF_3 , or HF may be used. In some cases, milder catalysts such as FeCl_3 or SnCl_4 are preferred. Newer alkylation technology uses zeolites or solid super acids.

[0044] By using a first detergent having a TBN of less than about 100, optionally a second detergent having a TBN between about 100 and about 200, and optionally a third detergent having a TBN of greater than about 200, in lubricating oils in accordance with this disclosure, in the presence of the hydrocarbyl aromatics, the lubricating oils may exhibit improved cleanliness, film forming and friction reducing properties.

[0045] The mixture of the detergent components in combination with hydrocarbyl aromatic of this disclosure can be used at a total concentration of about 5% to about 45% in a paraffinic lubricating oil base stock or a mixture of lubricating oil base stocks having a combined viscosity index of approximately 110 or greater or more preferably 115 or greater. Concentrations of such components can more preferably range from approximately 5% to about 30%, or more preferably from about 6% to about 25% by weight. Group II and/or Group III hydroprocessed or hydrocracked base stocks, wax isomerate base stock, or their synthetic counterparts such as polyalphaolefin lubricating

oils can often be preferred as lubricating base stocks when used in conjunction with the components of this disclosure. At least about 20% of the total composition should consist of such Group II base stock, Group III base stock or wax isomerate base stock, with at least about 30%, on occasion being more preferable, and at least about 80% on occasion being even more preferable. In one embodiment, gas to liquid base stocks are preferentially used with the components of this disclosure as a portion or all of the base stocks used to formulate the finished lubricant. A mixture of all or some of such base stocks can be used to advantage and can often be preferred. In an embodiment, the components of this disclosure are added to lubricating systems comprised of primarily Group II, base stock or Group III base stocks derived from hydrotreating, hydrocracking, hydroisomerization, and/or wax isomerate base stock derived from gas to liquid processes with up to lesser quantities of alternate fluids.

[0046] In an embodiment, the components of this disclosure are added to lubricating systems comprised of primarily Group II base stock, Group III base stock, or wax isomerate base stock with up to lesser quantities of co-base stocks. These co-base stocks include polyalphaolefin oligomeric low and medium and high viscosity oils, dibasic acid esters, polyol esters, other hydrocarbon oils, supplementary hydrocarbyl aromatics and the like. These co-base stocks can also include some quantity of decene-derived trimers and tetramers, and also some quantity of Group I base stocks, provided that the above Group II base stock, Group III type base stock, and wax isomerate base stock predominate and make up at least about 50% of the total base stocks contained in fluids comprised of the elements of this disclosure.

[0047] 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.

[0048] 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 about 4 carbon atoms, preferably C₅ to C₃₀ 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.

[0049] 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 about 5 to about 10 carbon atoms. These esters are widely available commercially, for example, the Mobil P-41 and P-51 esters of ExxonMobil Chemical Company).

[0050] 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.

[0051] 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.

[0052] 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.

[0053] 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 about 2 mm²/s to about 50 mm²/s (ASTM D445). They are further characterized typically as having pour points of -5°C to about -40°C or lower (ASTM D97). They are also characterized typically as having viscosity indices of about 80 to about 140 or greater (ASTM D2270).

[0054] 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 about 10 ppm, and more typically less than about 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 SAP products.

[0055] 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.

[0056] 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).

[0057] 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 about 10 ppm, and more typically less than about 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.

[0058] 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 diluent/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 $100 < VI < 120$.

[0059] 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 about 50 to about 99 weight percent, preferably from about 70 to about 95 weight percent, and more preferably from about 85 to about 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 about 2.5 cSt to about 12 cSt (or mm^2/s) at 100°C and preferably of about 2.5 cSt to about 9 cSt (or mm^2/s) at 100°C . Mixtures of synthetic and natural base oils may be used if desired.

Detergent Mixture

[0060] A detergent mixture is an essential component in the lubricating oils of this disclosure. The detergent mixture comprises at least one alkali or alkaline earth metal salt of sulfates, phenates, carboxylates, phosphates, and salicylates, and having a TBN of less than about 100, and at least one other detergent, different from the first detergent. 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.

[0061] The lubricating oils of this disclosure contain a detergent mixture in which the detergent mixture can be selected from the following: a mixture of a first detergent

having a TBN of less than about 100 and at least one second detergent, different from said first detergent, having a TBN of less than about 100; a mixture of a first detergent having a TBN of less than about 100 and at least one second detergent having a TBN between about 100 and about 200; a mixture of a first detergent having a TBN of less than about 100 and at least one second detergent having a TBN greater than about 200; and a mixture of a first detergent having a TBN of less than about 100, at least one second detergent having a TBN between about 100 and about 200, and at least one third detergent having a TBN greater than about 200.

[0062] In an embodiment, the present disclosure concerns a detergent mixture additive useful in lubricating oil compositions comprising a salicylate detergent mixture comprising two or more salicylate detergents having a TBN of less than about 100 (different from each other), a mixture comprising one or more salicylate detergents having a TBN of less than about 100 and one or more salicylate detergents having a TBN between about 100 and about 200, a mixture comprising one or more salicylate detergents having a TBN of less than about 100 and one or more salicylate detergents having a TBN greater than about 200, and a mixture comprising one or more salicylate detergents having a TBN of less than about 100, one or more salicylate detergents having a TBN between about 100 and about 200, and one or more salicylate detergents having a TBN greater than about 200. By using at least one low TBN detergent or mixtures of at least one low TBN detergent together with at least one of high and/or medium TBN detergents, unexpected improved cleanliness, film forming and friction reducing properties are seen. These improvements are particularly significant within concentration ranges when test results are compared to the individual components, or to properties that should be provided by an arithmetic mean of such components. In one preferred mode, mixtures of low and medium TBN detergents are used. Preferably the detergent mixture is a salicylate detergent mixture, more preferably a calcium salicylate detergent mixture.

[0063] Within the scope of the present disclosure, a low TBN detergent is defined as having a TBN of less than about 100. A medium TBN detergent is defined as having a TBN of between about 100 and 200. A high TBN detergent is defined as having a TBN of greater than about 200.

[0064] Low TBN refers to neutral to low-overbased detergents, medium TBN refers to medium overbased-detergents and high TBN refers to high-overbased detergents. These terms are used descriptively to describe the general differences between the total base numbers (TBN) of the detergents used and are meant to describe in general terms the differences between the contained calcium levels and the presence or absence and/or the degree of overbasing derived by the carbonation of the calcium salicylate in the presence of excess (over and beyond stoichiometric quantities) of calcium bases to form overbased calcium carbonate complexed calcium salicylate detergents.

[0065] Salts that contain a substantially stoichiometric 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, borated, mildly overbased, or highly overbased.

[0066] It is desirable for at least some detergent used in the detergent mixture 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 about 1.05:1 to 50:1 on an equivalent basis. More preferably, the ratio is from about 4:1 to about 25:1. The resulting detergent is an overbased detergent that will typically have a TBN of about 150 or higher, often about 250 to 450 or more. Preferably, the overbasing cation is sodium, calcium, or magnesium. A mixture of detergents of differing TBN and differing metal can be used in the present disclosure.

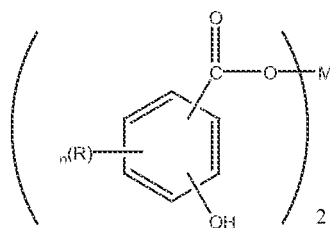
[0067] Preferred detergents include at least one alkali or alkaline earth metal salts of sulfonates, phenates, carboxylates, phosphates, and salicylates, having a TBN of less than about 100, e.g., calcium salicylate. Preferred mixtures include at least one alkali or alkaline earth metal salts of sulfonates, phenates, carboxylates, phosphates, and salicylates, having a TBN of less than about 100, together with at least one of alkali or alkaline earth metal salts of sulfonates, phenates, carboxylates, phosphates, and salicylates, having a TBN of less than about 100 (different from the first detergent),

having a TBN between about 100 and about 200, or a TBN greater than about 200, e.g., a mixture of magnesium sulfonate and calcium salicylate.

[0068] 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 about 3 to 70 carbon atoms. The alkaryl sulfonates typically contain about 9 to about 80 carbon or more carbon atoms, more typically from about 16 to 60 carbon atoms.

[0069] 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.

[0070] 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 a hydrogen atom or an alkyl group having 1 to about 30 carbon atoms, n is an integer from 1 to 4, and M is an alkaline earth metal. Often, preferred R groups are alkyl chains of at least C₁₁, preferably C₁₃ or greater, or mixtures thereof. 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.

[0071] 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.

[0072] Alkaline earth metal phosphates are also used as detergents and are known in the art.

[0073] 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.

[0074] Preferred detergents include at least one of calcium phenates, calcium sulfonates, calcium salicylates, magnesium phenates, magnesium sulfonates, magnesium salicylates and other related components (including borated detergents) having a TBN less than about 100. A preferred detergent mixture includes at least one of calcium phenates, calcium sulfonates, calcium salicylates, magnesium phenates, magnesium sulfonates, magnesium salicylates and other related components (including borated detergents) having a TBN less than about 100, together with at least one of calcium phenates, calcium sulfonates, calcium salicylates, magnesium phenates, magnesium sulfonates, magnesium salicylates and other related components (including borated

detergents) having a TBN less than about 100 (different from the first detergent), having a TBN between about 100 and about 200, or a TBN greater than about 200, e.g., a mixture of magnesium sulfonate and calcium salicylate.

[0075] The detergent concentration in the lubricating oils of this disclosure can range from about 1.0 to about 10.0 weight percent, preferably about 2.0 to 8.0 weight percent, and more preferably from about 2.0 weight percent to about 5.0 weight percent, based on the total weight of the lubricating oil. The concentration of the low TBN detergent is preferably greater than about 4.0 weight percent, more preferably from greater than about 4.0 weight percent to about 8.0 weight percent, and most preferably from about 4.1 weight percent to about 6.0 weight percent, based on the total weight of the lubricating oil. These ranges are supported by the average integrated Stribeck friction coefficients in Figure 11. The concentration of the medium TBN detergent is preferably from 0.1 about 4.0 weight percent, more preferably from about 0.2 weight percent to about 3.8 weight percent, and most preferably from about 0.25 weight percent to about 3.75 weight percent, based on the total weight of the lubricating oil. The concentration of the high TBN detergent is preferably from 0.1 about 4.0 weight percent, more preferably from about 0.2 weight percent to about 3.8 weight percent, and most preferably from about 0.25 weight percent to about 3.75 weight percent, based on the total weight of the lubricating oil.

[0076] As used herein, the detergent concentrations are given on an “as delivered” basis. Typically, the active detergent is delivered with a process oil. The “as delivered” detergent typically contains from about 20 weight percent to about 80 weight percent, or from about 40 weight percent to about 60 weight percent, of active detergent in the “as delivered” detergent product. Illustrative commercially available detergent products useful in this disclosure include, for example, Infineum™ M7125, C9340, M7102 and C9012; OLOA™ 216M and 219M; Na-Sul™ 729; Lobase™ C4506; and Hybase™ MS-100.

Other Additives

[0077] 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 anti-wear agents, dispersants, other detergents, corrosion inhibitors, rust inhibitors, metal deactivators, 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); see also U.S. Patent No. 7,704,930, the disclosure of which is incorporated herein in its entirety.

[0078] 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.

Anti-wear Additive

[0079] 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 an essential 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.

[0080] 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".

[0081] The ZDDP is typically used in amounts of from about 0.4 weight percent to about 1.2 weight percent, preferably from about 0.5 weight percent to about 1.0 weight percent, and more preferably from about 0.6 weight percent to about 0.8 weight percent, based on the total weight of the lubricating oil, although more or less can often be used advantageously. Preferably, the ZDDP is a secondary ZDDP and present in an amount of from about 0.6 to 1.0 weight percent of the total weight of the lubricating oil.

[0082] As used herein, the ZDDP concentrations are given on an "as delivered" basis. Typically, ZDDP is delivered with a process oil. The "as delivered" ZDDP typically contains from about 20 weight percent to about 80 weight percent, or from about 40 weight percent to about 60 weight percent, of ZDDP in the "as delivered" product.

Viscosity Index Improvers

[0083] Viscosity index improvers (also known as VI improvers, viscosity modifiers, and viscosity improvers) can be included in the lubricant compositions of this disclosure.

[0084] 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.

[0085] 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 about 10,000 to 1,500,000, more typically about 20,000 to 1,200,000, and even more typically between about 50,000 and 1,000,000.

[0086] 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.

[0087] 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".

[0088] In an embodiment of this disclosure, the viscosity index improvers may be used in an amount of less than about 2.0 weight percent, preferably less than about 1.0 weight percent, and more preferably less than about 0.5 weight percent, based on the total weight of the formulated oil or lubricating engine oil.

[0089] In another embodiment of this disclosure, the viscosity index improvers may be used in an amount of from 0.25 to about 2.0 weight percent, preferably 0.15 to about 1.0 weight percent, and more preferably 0.05 to about 0.5 weight percent, based on the total weight of the formulated oil or lubricating engine oil.

Dispersants

[0090] 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.

[0091] 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.

[0092] 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. 471 071, to which reference is made for this purpose.

[0093] 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.

[0094] 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 about 1:1 to about 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.

[0095] 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.

[0096] 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.

[0097] 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 about 0.1 to about 5 moles of boron per mole of dispersant reaction product.

[0098] 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.

[0099] 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.

[00100] 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.

[00101] 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 about 500 to about 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 about 0.1 to 20 weight percent, preferably about 0.5 to 8 weight percent.

Antioxidants

[00102] 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.

[00103] 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 C₆+ alkyl groups and the alkylene coupled

derivatives of these hindered phenols. Examples of phenolic materials of this type 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-t-butyl-4-heptyl phenol; and 2-methyl-6-t-butyl-4-dodecyl phenol. Other useful hindered mono-phenolic antioxidants may include for example hindered 2,6-di-alkyl-phenolic propionic ester derivatives. Bis-phenolic antioxidants may also be advantageously used 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).

[00104] 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 about 20 carbon atoms, and preferably contains from about 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.

[00105] Typical aromatic amines antioxidants have alkyl substituent groups of at least about 6 carbon atoms. Examples of aliphatic groups include hexyl, heptyl, octyl, nonyl, and decyl. Generally, the aliphatic groups will not contain more than about 14 carbon atoms. The general types of amine antioxidants useful in the present compositions include diphenylamines, phenyl naphthylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more aromatic amines are also useful. Polymeric amine antioxidants can also be used. Particular examples of aromatic amine antioxidants useful in the present disclosure include: p,p'-dioctyldiphenylamine;

t-octylphenyl-alpha-naphthylamine; phenyl-alphanaphthylamine; and p-octylphenyl-alpha-naphthylamine.

[00106] Sulfurized alkyl phenols and alkali or alkaline earth metal salts thereof also are useful antioxidants.

[00107] 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 about 0.01 to 5 weight percent, preferably about 0.01 to 1.5 weight percent, more preferably zero to less than 1.5 weight percent, most preferably zero.

Pour Point Depressants (PPDs)

[00108] 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 about 0.01 to 5 weight percent, preferably about 0.01 to 1.5 weight percent.

Seal Compatibility Agents

[00109] 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 about 0.01 to 3 weight percent, preferably about 0.01 to 2 weight percent.

Anti-foam Agents

[00110] 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 anti-foam 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

[00111] 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.

[00112] 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, 32iluent carboxylates, and the like. In some instances fatty organic acids, fatty amines, and sulfurized fatty acids may be used as suitable friction modifiers.

[00113] Useful concentrations of friction modifiers may range from about 0.01 weight percent to 10-15 weight percent or more, often with a preferred range of about 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 about 10 ppm to 3000 ppm or more, and often with a preferred range of about 20-2000 ppm, and in some instances a more preferred range of about 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.

Inhibitors and Anti-rust Additives

[00114] Anti-rust additives (or corrosion inhibitors) are additives that protect lubricated metal surfaces against chemical attack by water or other contaminants. A wide variety of these are commercially available.

[00115] One type of anti-rust additive is a polar compound that wets the metal surface preferentially, protecting it with a film of oil. Another type of anti-rust additive absorbs

water by incorporating it in a water-in-oil emulsion so that only the oil touches the metal surface. Yet another type of anti-rust additive chemically adheres to the metal to produce a non-reactive surface. Examples of suitable additives include zinc dithiophosphates, metal phenolates, basic metal sulfonates, fatty acids and amines. Such additives may be used in an amount of about 0.01 to 5 weight percent, preferably about 0.01 to 1.5 weight percent.

[00116] 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 1 below.

[00117] 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
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	0.1-2	0.1-1
Anti-wear	0.4-1.2	0.5-1
Inhibitor and Anti-rust (solid polymer basis)	0.01-5	0.01-1.5

[00118] 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.

[00119] The following non-limiting examples are provided to illustrate the disclosure.

Examples

[00120] A fully formulated 0W-20 synthetic oil containing calcium salicylate and magnesium sulfonate detergents was used as a baseline oil, against which all other oils were compared. Friction measurements by mini-traction machine (MTM) in Stribeck mode at 140°C, 1 GPa load, and 50% slide to roll ratio were carried out on all oils. High frequency reciprocating rig (HFRR) measurements were carried out on all oils using a temperature ramp mode from room temperature to 195°C. These two types of measurements provided an indication of the frictional performance of lubricants. Engine testing in the Sequence IIIG (D7320), VID (D7589), VW TDi2, and OM646 LA were

carried out to ascertain wear, deposit formation and fuel economy performance of select oils.

[00121] Lubricant oils were formulated containing no magnesium sulfonate, and varying amounts of calcium salicylate or calcium sulfonate. Calculated total base number was held constant for Figs. 3-9, but the total soap to calcium ratio was varied. Oil containing no detergent was also blended to allow for comparisons of impact of detergent on friction.

[00122] Fig. 1 shows 0W-20 synthetic oil formulations having varying calcium salicylate type and amount as a replacement for magnesium sulfonate.

[00123] MTM Stribeck curves from the formulations shown in Fig. 1, show decreased friction with increasing low TBN salicylate in comparison to the baseline. Fig. 2 shows the no detergent finished oil performance in MTM Stribeck test at 140°C, while Fig. 3 shows the baseline 0W-20 finished oil performance. Figs. 4 and 5 show the effect of increasing soap content on friction under the same conditions, while Fig. 6 shows the engine test lubricant oil formulation with balanced high/low salicylate detergent loading. Figs. 7 and 8 show the effect of using an alternative low TBN detergent, such as calcium sulfonate or calcium phenate at high treat rates, respectively, indicating the concept is more general than salicylate chemistries alone.

[00124] Fig. 9 shows a comparison of HFRR friction traces as a function of temperature for the baseline oil and the high TBN salicylate detergent/Low TBN salicylate detergent mix (sample number 11-31703).

[00125] Fig. 2 shows no detergent finished oil formulation MTM Stribeck curves. Fig. 3 shows baseline finished oil formulation MTM Stribeck curves. Fig. 4 shows all mid-TBN calcium salicylate detergent finished oil MTM Stribeck curves. Fig. 5 shows all low TBN calcium salicylate detergent finished oil MTM Stribeck curves. Fig. 6 shows balanced high/low TBN calcium salicylate detergent mix finished oil MTM Stribeck curves. Fig. 7 shows balanced high TBN Ca salicylate/low TBN Ca sulfonate detergent mix finished oil MTM Stribeck curves. Fig. 8 shows all calcium phenate

detergent finished oil MTM Stribeck curves. **Fig. 9** shows a comparison of HFRR friction traces as a function of temperature for the baseline oil and the balanced high/low TBN salicylate detergent mix finished oils, indicating significant improvement in friction at typical Sequence VID engine oil sump temperatures (black vertical line).

[00126] Such low friction, as demonstrated in **Figs. 4-8** (disclosure) in comparison to **Fig. 3** (baseline oil), is unusual in that it allows for a significant improvement in piston cleanliness, while providing increased fuel economy, as measured by the Sequence IIIG and VID stationary engine tests, respectively. These results are achieved by skewing the detergent mix (and therefore ratio of high: medium: low TBN detergents) of such patents as U.S. Patent No. 7,704,930 to a higher level of low TBN detergent than previously thought useful or necessary and, resulting in a parallel increase in soap content of the finished oil. Another way to interpret the results shown in **Figs. 2** through **8** is by integration of the area under the individual curves, shown in **Fig. 10**. The trapezoidal integration rule is applied such that

$$\begin{aligned} \text{Integrated Stribeck Friction Coefficient} \approx & \sum_{i=3}^{3000} ((\log(\text{speed}(b)) - \log(\text{speed}(a))) \\ & \times (\text{traction coefficient}(a) + \text{traction coefficient}(b))/2) \end{aligned}$$

where a and b denote a pair of subsequent measurement points between 3 mm/s and 3000 mm/s. Such integration indicates that, by employing certain versions of the disclosure, one is able to decrease the integrated Stribeck friction coefficient in the MTM by over half (see highlighted values in the improvement versus baseline row for sample numbers 11-62083, 11-62086, and 11-70505 in **Fig. 10**, below, noting that a larger negative number indicates lower integrated Stribeck friction).

[00127] **Fig. 10** shows integrated Stribeck friction coefficients by run and average over all runs for **Figs. 2** through **8**.

[00128] Sequence IIIG, VW TDi-2, OM 646, and Sequence VID engine test results on the baseline and example lubricant oil with higher levels of low TBN detergent are provided in **Fig. 12**. . The data shows a significant increase in piston cleanliness as

measured in the Sequence IIIG, OM646, and VW TDI-2. A beneficial decrease in the low temperature viscosity, as measured by the Sequence IIIGA, and a significant beneficial increase in phosphorus retention, as measured by the Sequence IIIGB, are also observed. The Sequence VID results clearly indicate a significant increase in all the measured fuel economy parameters of the test. The testing of one version of the disclosure (sample number 11-70505) also indicates that the typical tradeoff between better fuel economy and wear is avoided. This phenomenon is observed in several industry wear tests, including the Sequence VIII, IVA, and OM646 LA engine tests, results for which are also shown in Fig. 11, which indicate equivalent, or in the case of OM646 LA inlet and outlet camshaft wear, improved, performance.

[00129] **Fig. 12** shows engine test comparisons of baseline versus lubricant oil formulations. The baseline formulation listed in **Fig. 11** differs from sample number 10-115372 by an increase in molybdenum content of 1.5 times the content in sample number 10-115372.

[00130] The reduction in the average integrated Stribeck friction coefficient with the introduction of low TBN detergent into formulations with high TBN detergent occurs in every base stock group, as shown in **Fig. 13**. The low TBN detergent varied in concentration from 0.0 weight percent in the baseline formulations to 5.0 weight percent.

[00131] The reduction in the average integrated Stribeck friction coefficient with the introduction of low TBN detergent into formulations with mid TBN detergent occurs in Group II, III, and IV base stock groups, as shown in **Fig. 14**. The low TBN detergent varied in concentration from 0.0 weight percent in the baseline formulations to 5.0 weight percent.

[00132] **Fig. 15** shows that the concentration of the high TBN detergent in a range of 2.5 to 7.5 weight percent in Group II, III, and IV base stocks does not have an impact the average integrated Stribeck friction coefficient. Thus comparative example supports that the reduction in the average integrated Stribeck friction coefficient is attributable to the concentration of the low TBN detergent rather than a change in the concentration of the high or mid TBN detergent.

[00133] 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.

[00134] 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.

[00135] 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 for improving friction reduction and fuel efficiency, while maintaining or improving wear protection, in an engine lubricated with a lubricating oil by using as the lubricating oil a formulated oil, said formulated oil having a composition comprising a lubricating oil base stock as a major component; and a detergent mixture comprising a first detergent having a TBN of less than about 100, and at least one other detergent different from said first detergent, as a minor component; wherein said composition contains greater than about 4 weight percent of the first detergent, based on the total weight of the formulated oil; and wherein friction reduction and fuel efficiency are improved and wear protection is maintained or improved as compared to friction reduction, fuel efficiency and wear protection achieved using a lubricating engine oil containing a detergent mixture having other than the first detergent having a TBN of less than about 100.

2. The method of claim 1 wherein the lubricating oil base stock comprises a Group I, Group II, Group III, Group IV or Group V base oil.

3. The method of claim 1 wherein the detergent mixture comprises said first detergent having a TBN of less than about 100 and at least one second detergent, different from said first detergent, having a TBN of less than about 100; said first detergent having a TBN of less than about 100 and at least one second detergent having a TBN between about 100 and about 200; said first detergent having a TBN of less than about 100 and at least one second detergent having a TBN greater than about 200; said first detergent having a TBN of less than about 100, at least one second detergent having a TBN between about 100 and about 200, and at least one third detergent having a TBN greater than about 200.

4. The method of claim 3 wherein the first detergent, second detergent and third detergent are selected from metallic salicylates, sulfates, phenates, carboxylates, phosphates and sulfonates, and wherein the metallic salicylates, sulfates, phenates, carboxylates, phosphates and sulfonates are selected from alkali metals and alkaline earth metals.

5. The method of claim 3 wherein the first detergent, second detergent and third detergent are selected from metallic salicylates, sulfates, phenates, carboxylates, phosphates and sulfonates, and wherein the metallic salicylates, sulfates, phenates, carboxylates, phosphates and sulfonates are selected from calcium and magnesium.

6. The method of claims 1-5 wherein first detergent is calcium salicylate or calcium sulfonate.

7. The method of claims 1-6 wherein wherein the oil base stock is present in an amount of from about 70 weight percent to about 95 weight percent, and the detergent mixture is present in an amount greater than about 4 weight percent to about 8 weight percent, based on the total weight of the formulated oil.

8. The method of claims 1-7 wherein, in friction measurements of the lubricating oil by mini-traction machine (MTM) in Stribeck mode at 140°C, the integrated Stribeck friction coefficient of the lubricating oil in the MTM is reduced as compared to the integrated Stribeck friction coefficient of a lubricating oil containing a detergent mixture having other than the first detergent having a TBN of less than about 100.

9. A lubricating engine oil having a composition comprising a lubricating oil base stock as a major component; and a detergent mixture comprising a first detergent having a TBN of less than about 100, and at least one other detergent different from said first detergent, as a minor component; wherein said composition contains greater than about 4 weight percent of the first detergent, based on the total weight of the formulated oil; and wherein said composition is sufficient for the lubricating engine oil to exhibit improved friction reduction and fuel efficiency and improved or maintained wear protection as compared to friction reduction, fuel efficiency and wear protection achieved using a lubricating engine oil containing a detergent mixture having other than the first detergent having a TBN of less than about 100.

10. The lubricating engine oil of claim 9 wherein the lubricating oil base stock comprises a Group I, Group II, Group III, Group IV or Group V base oil.

11. The lubricating engine oil of claim 9 wherein the detergent mixture comprises said first detergent having a TBN of less than about 100 and at least one second detergent, different from said first detergent, having a TBN of less than about 100; said first detergent having a TBN of less than about 100 and at least one second detergent having a TBN between about 100 and about 200; said first detergent having a TBN of less than about 100 and at least one second detergent having a TBN greater than about 200; said first detergent having a TBN of less than about 100, at least one second detergent having a TBN between about 100 and about 200, and at least one third detergent having a TBN greater than about 200.

12. The lubricating engine oil of claim 11 wherein the first detergent, second detergent and third detergent are selected from metallic salicylates, sulfates, phenates, carboxylates, phosphates and sulfonates, and wherein the metallic salicylates, sulfates, phenates, carboxylates, phosphates and sulfonates are selected from alkali metals and alkaline earth metals.

13. The lubricating engine oil of claim 11 wherein the first detergent, second detergent and third detergent are selected from metallic salicylates, sulfates, phenates, carboxylates, phosphates and sulfonates, and wherein the metallic salicylates, sulfates, phenates, carboxylates, phosphates and sulfonates are selected from calcium and magnesium.

14. The lubricating engine oil of claims 9-13 wherein first detergent is calcium salicylate or calcium sulfonate.

15. The lubricating engine oil of claims 9-14 wherein the oil base stock is present in an amount of from about 70 weight percent to about 95 weight percent, and the detergent mixture is present in an amount greater than about 4 weight percent to about 8 weight percent, based on the total weight of the formulated oil.