

LOW VISCOSITY ENGINE OIL WITH SUPERIOR
ENGINE WEAR PROTECTION

FIELD OF THE INVENTION

[0001] This invention relates to a lubricant oil composition having a sulfated ash content of about 0.6 wt% and a high-temperature high-shear (HTHS) viscosity of lower than 2.9 cP at 150°C that provides excellent engine wear protection and improved fuel efficiency and use thereof.

BACKGROUND OF THE INVENTION

[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 high temperature high-shear (HTHS) viscosity of less than 2.9 cP at 150°C would not be expected to be able to provide acceptable passenger vehicle diesel engine durability performance.

[0003] HTHS is the measure of a lubricant's viscosity under severe engine conditions. Under high temperatures and high stress conditions viscosity index improver degradation can occur. As this happens, the viscosity of the oil decreases which may lead to increased engine wear. HTHS is measured using ASTM D4683, which is incorporated herein by reference.

[0004] In view of the more strict requirements, manufacturers are moving towards the use of diesel engines. Diesel engines are more prone to filter

plugging due to high sulfated ash content of the lubricant. For this reason, diesel engine vehicle manufacturers generally recommend lubricants with reduced sulfated ash levels.

[0005] Despite the advances in lubricant oil formulation technology, there remains a need for an engine oil lubricant that effectively improves fuel economy while providing superior antiwear performance.

SUMMARY OF THE INVENTION

[0006] In accordance with a first aspect of the invention, there is provided an engine oil lubricant composition comprising a major amount of base oil and an effective amount of a zinc dialkyl dithio phosphate, a polymeric viscosity index improver and a mixture of alkaline earth metal detergents. The engine oil lubricant composition has a sulfated ash content of less than about 0.8 wt% and an HTHS of less than about 2.9 cP at 150°C.

[0007] In another aspect of the invention, there is provided a method for improving fuel efficiency and wear in an engine. The method comprising adding to an engine, an engine oil lubricant composition having a sulfated ash content of about 0.8 wt% and an HTHS of about 2.9 cP at 150°C. The lubricant composition comprises a zinc dialkyl dithio phosphate, a polymeric viscosity modifier and a mixture of alkaline earth metal detergents.

[0008] Other objects and advantages of the present invention will become apparent from the detailed description that follows.

DETAILED DESCRIPTION

[0009] It has now been found that an engine oil lubricant composition comprising a major amount of base oil and an effective amount of a zinc dialkyl dithio phosphate, a polymeric viscosity index improver and a mixture of alkaline earth metal detergents provides improved fuel efficiency while providing excellent wear in an engine. The engine oil lubricant composition has a sulfated ash content of less than about 0.8 wt% and an HTHS of less than about 2.9 cP at 150°C.

[0010] A wide range of lubricating base oils is known in the art. Lubricating base oils that are useful in the present invention 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.

[0011] Groups I, II, III, IV and V are broad categories of base oil stocks 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 generally 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 generally 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 generally 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.

<u>Base Oil Properties</u>			
	<u>Saturates</u>	<u>Sulfur</u>	<u>Viscosity Index</u>
Group I	< 90 &/or	> 0.03% &	≥ 80 & < 120
Group II	≥ 90 &	≤ 0.03% &	≥ 80 & < 120
Group III	≥ 90 &	≤ 0.03% &	≥ 120
Group IV	Includes polyalphaolefins (PAO)		
Group V	All other base oil stocks not included in Groups I, II, III, or IV		

[0012] 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, hydrotreated, or solvent extracted.

[0013] 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.

[0014] Synthetic oils include hydrocarbon oil. Hydrocarbon oils include oils such as polymerized and interpolymers of 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. Patents 4,956,122; 4,827,064; and 4,827,073.

[0015] 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, C_2 to about C_{32} alphaolefins with the C_8 to about 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.

[0016] 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 4,149,178 or U.S. Patent 3,382,291

may be conveniently used herein. Other descriptions of PAO synthesis are found in the following U.S. Patents 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 C₁₄ to C₁₈ olefins are described in U.S. Patent 4,218,330.

[0017] 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.

[0018] 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.

[0019] 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.

[0020] 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).

[0021] 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.

[0022] 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.

[0023] The base oil constitutes the major component of the engine oil lubricant composition of the present invention and typically is present in an amount ranging from about 50 to about 99 wt%, e.g., from about 85 to about 95 wt%, 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.

[0024] The engine oil lubricant composition of the present invention has an sulfated ash content of less than about 0.8 wt% and an HTHS of less than about 2.9 cP at 150°C, preferably about 2.7cP at 150°C.

[0025] While there are many different types of antiwear additives, for several decades the principal antiwear additive for internal combustion engine crankcase oils is a metal alkylthiophosphate and more particularly a metal dialkyldithiophosphate in which the metal constituent is zinc, or zinc dialkyldithiophosphate (ZDDP). ZDDP can be primary, secondary or mixtures thereof. ZDDP compounds generally are of the formula $\text{Zn}[\text{SP}(\text{S})(\text{OR}^1)(\text{OR}^2)]_2$ 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. The ZDDP is typically used in amounts of from about 0.4 to 1.4 wt% of the total lubricant oil composition, although more or less can often be used advantageously. Preferably, the ZDDP is a secondary ZDDP and present in an amount of from about 0.6 to 1.0 wt% of the total lubricant composition.

[0026] 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".

[0027] During engine operation, oil-insoluble oxidation byproducts are produced. Dispersants help keep these byproducts in solution, thus diminishing their deposition on metal surfaces. Dispersants 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.

[0028] 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.

[0029] 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 substituted alkenyl succinic compound, usually a substituted succinic anhydride, with a polyhydroxy or polyamino compound. The long chain 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 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. Patents 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.

[0030] Hydrocarbyl-substituted succinic acid compounds are popular 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.

[0031] Succinimides are formed by the condensation reaction between alkenyl succinic anhydrides and amines. Molar ratios can vary depending on the polyamine. For example, the molar ratio of alkenyl succinic anhydride to TEPA

can vary from about 1:1 to about 5:1. Representative examples are shown in U.S. Patents 3,087,936; 3,172,892; 3,219,666; 3,272,746; 3,322,670; and 3,652,616, 3,948,800; and Canada Pat. No. 1,094,044.

[0032] Succinate esters are formed by the condensation reaction between alkenyl succinic anhydrides and alcohols or polyols. Molar ratios can vary depending on the alcohol or polyol used. For example, the condensation product of an alkenyl succinic anhydride and pentaerythritol is a useful dispersant.

[0033] Succinate ester amides are formed by condensation reaction between alkenyl 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 4,426,305.

[0034] The molecular weight of the alkenyl 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, and boron compounds such as borate esters or highly borated dispersants. The dispersants can be borated with from about 0.1 to about 5 moles of boron per mole of dispersant reaction product.

[0035] Mannich base dispersants are made from the reaction of alkylphenols, formaldehyde, and amines. See U.S. Patent 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. Patents 3,697,574; 3,703,536; 3,704,308; 3,751,365; 3,756,953; 3,798,165; and 3,803,039.

[0036] Typical high molecular weight aliphatic acid modified Mannich condensation products useful in this invention can be prepared from high molecular weight alkyl-substituted hydroxyaromatics or HN(R)_2 group-containing reactants.

[0037] Hydrocarbyl substituted amine ashless dispersant additives are well known to one skilled in the art; see, for example, U.S. Patents 3,275,554; 3,438,757; 3,565,804; 3,755,433, 3,822,209, and 5,084,197.

[0038] 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 wt%, preferably about 0.5 to 8 wt%.

[0039] Viscosity index improvers (also known as VI improvers, viscosity modifiers, and viscosity improvers) provide lubricants with high and low temperature operability. These additives impart shear stability at elevated temperatures and acceptable viscosity at low temperatures.

[0040] 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 1,000,000, more typically about 20,000 to 500,000, and even more typically between about 50,000 and 200,000.

[0041] 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.

[0042] 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".

[0043] Viscosity index improvers may be used in an amount of about 0.01 to 4 wt%, preferably about 0.01 to 2 wt%, on a solid polymer basis.

[0044] Detergents are commonly used in lubricating compositions. 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.

[0045] 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, mildly overbased, or highly overbased.

[0046] 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 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 can be used in the present invention.

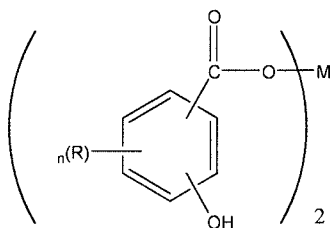
[0047] Preferred detergents include the alkali or alkaline earth metal salts of sulfonates, phenates, carboxylates, phosphates, and salicylates.

[0048] 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.

[0049] Klamann in "Lubricants and Related Products", op cit discloses a number of overbased metal salts of various sulfonic acids which are useful as detergents and dispersants in lubricants. The book entitled "Lubricant Additives", C.V. Smallheer and R.K. Smith, published by the Lezius-Hiles Co. of Cleveland, Ohio (1967), similarly discloses a number of overbased sulfonates that are useful as dispersants/detergents.

[0050] Alkaline earth phenates are another useful class of detergent. These detergents can be made by reacting alkaline earth metal hydroxide or oxide (CaO , $\text{Ca}(\text{OH})_2$, BaO , $\text{Ba}(\text{OH})_2$, MgO , $\text{Mg}(\text{OH})_2$, 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.

[0051] 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. Preferred R groups are alkyl chains of at least C₁₁, preferably C₁₃ 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.

[0052] Hydrocarbyl-substituted salicylic acids may be prepared from phenols by the Kolbe reaction (see U.S. Patent 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.

[0053] Alkaline earth metal phosphates are also used as detergents.

[0054] 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 6,034,039, for example.

[0055] Preferred detergents include calcium phenates, calcium sulfonates, calcium salicylates, magnesium phenates, magnesium sulfonates, magnesium salicylates and other related components (including borated detergents). Typically, the total detergent concentration is about 0.01 to about 6.0 wt%, preferably, about 0.1 to 3.5 wt%.

[0056] 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. Patents 4,798,684 and 5,084,197, for example.

[0057] 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 invention. 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).

[0058] 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.

[0059] 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 invention include: p,p'-dioctyldiphenylamine; t-octylphenyl-alpha-naphthylamine; phenyl-alphanaphthylamine; and p-octylphenyl-alpha-naphthylamine.

[0060] Sulfurized alkyl phenols and alkali or alkaline earth metal salts thereof also are useful antioxidants.

[0061] 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 wt%, preferably

about 0.01 to 1.5 wt%, more preferably zero to less than 1.5 wt%, most preferably zero.

[0062] Conventional pour point depressants (also known as lube oil flow improvers) may be added to the compositions of the present invention if desired. These pour point depressant may be added to lubricating compositions of the present invention 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 wt%, preferably about 0.01 to 1.5 wt%.

[0063] 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 wt%, preferably about 0.01 to 2 wt%.

[0064] 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 percent and often less than 0.1 percent.

[0065] 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 invention if desired. Friction modifiers that lower the coefficient of friction are particularly advantageous in combination with the base oils and lube compositions of this invention. 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 metal-ligand 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. Patents 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; and WO 99/66013; WO 99/47629; WO 98/26030.

[0066] Ashless friction modifiers may have 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.

[0067] Useful concentrations of friction modifiers may range from about 0.01 wt% to 10-15 wt% or more, often with a preferred range of about 0.1 wt% to 5 wt%. 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 invention. Often mixtures of two or more friction modifiers, or mixtures of friction modifier(s) with alternate surface active material(s), are also desirable.

[0068] 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 invention are shown in Table A below.

[0069] Note that many of the additives are shipped from the manufacturer and used with a certain amount of base oil diluent in the formulation. 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 wt% indicated below are based on the total weight of the lubricating oil composition.

TABLE 1
Typical Amounts of Various Lubricant Oil Components

Compound	Approximate wt% (Useful)	Approximate wt% (Preferred)
Detergent	0.01-6	0.01-4
Dispersant	0.1-20	0.1-8
Friction Modifier	0.01-5	0.01-1.5
Viscosity Index Improver (solid polymer basis)	0.0-4	0.01-4, more preferably 0.01-2, most preferably
Antioxidant	0.1-5	0.1-1.5
Anti-wear Additive	0.01-6	0.01-4
Pour Point Depressant (PPD)	0.0-5	0.01-1.5
Anti-foam Agent	0.001-3	0.001-0.15
Base stock or base oil	Balance	Balance

[0070] 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.

[0071] The following non-limiting examples are provided to illustrate the invention.

[0072] Lubricating oil compositions according to the invention were prepared using a blend of PAO, ester and Group III base oils.

[0073] In addition to a metal detergent, viscosity index improver, and ZDDP, the composition included borated and non-borated ashless dispersant, phenolic and aminic antioxidants, defoamant, pour point depressant, friction modifier and seal swelling agent.

[0074] Representative formulations are given in Table 2.

TABLE 2

Formulation	<u>Invention</u> <u>Ex. 1</u>	<u>Invention</u> <u>Ex. 2</u>	<u>Comp.</u> <u>Ex. 3</u>	<u>Comp.</u> <u>Ex. 4</u>	<u>Comp.</u> <u>Ex. 5</u>	<u>Comp.</u> <u>Ex. 6</u>	<u>Comp.</u> <u>Ex. 7</u>
Viscosity Grade	0W-20	0W-20	0W-30	0W-20	5W-30	5W-30	5W-30
Component, wt%							
Salicylate and/or Sulfonate Detergent	2.20	1.80	2.25	1.50	3.52	3.52	1.50
Friction Modifier	0.15	0.15	0.15	0.48	0.73	0.77	0.40
Viscosity Index Improver (solid polymer content)	0.57	0.57	0.37	0.56	0.71	0.66	0.86
ZDDP	0.80	0.91	0.80	0.74	0.75	0.85	0.86
Dispersant (Borated/Non-Borated)	7.97	7.10	8.20	4.55	4.25	6.10	4.55
Other Additives (antioxidant, defoamant, PPD, seal swell agent)	2.12	1.87	2.12	1.90	1.90	1.90	1.90
Base oil	balance	balance	balance	balance	balance	balance	balance
Formulated Oil KV@100C, cSt	8.6	8.8	12.1	8.5	11.0	11.1	10.8
Sulfated Ash	0.6	0.6	0.6	0.9	1.0	1.0	0.9
Sulfur	0.2	0.2	0.2	0.2	0.2	0.2	0.2

[0075] Among the features of the composition of the invention is that they have demonstrated both unexpected combination of wear and fuel efficiency performance. For instance, fuel economy is improved by at least 3.2% as measured in the M111FE engine test and while the wear performance is improved relative to the comparison oils. Additionally, the composition of the invention is a low sulfated ash, low sulfur composition.

[0076] Performance evaluation of the formulations is given in Table 3-6. The following engine tests were performed to measure wear and fuel economy of the engine oil lubricant composition of the present invention: TU3M, Sequence IIIG (ASTM D7320), OM646LA and M111FE, all of which are incorporated herein by reference.

TABLE 3

Description		<u>Invention</u> <u>Ex. 1</u>	<u>Invention</u> <u>Ex. 2</u>	<u>Comp.</u> <u>Ex. 3</u>	<u>Comp.</u> <u>Ex. 4</u>	<u>Comp.</u> <u>Ex. 5</u>	<u>Comp.</u> <u>Ex. 6</u>	<u>Comp.</u> <u>Ex. 7</u>
HTHS, cP at 150°C		2.7	2.8	3.5	2.6	3.0	3.0	3.0
Viscosity Grade		0W-20	0W-20	0W-30	0W-20	5W-30	5W-30	5W-30
<u>Engine</u> <u>Test</u>	<u>Parameter</u>							
TU3M	<u>Valve Train</u> <u>Scuffing Wear</u>							
CEC L- 038-94	Average cam wear, μm	1.9	3.8	2	3.4	3.6	7	2.9
	Maximum cam wear, μm	3.2	4.5	2.6	5.5	5.5	8	5.0

TABLE 4

Description		<u>Invention</u> <u>Ex. 1</u>	<u>Invention</u> <u>Ex. 2</u>	<u>Comp.</u> <u>Ex. 3</u>	<u>Comp.</u> <u>Ex. 4</u>	<u>Comp.</u> <u>Ex. 5</u>	<u>Comp.</u> <u>Ex. 6</u>	<u>Comp.</u> <u>Ex. 7</u>
HTHS, cP at 150°C		2.7	2.8	3.5	2.6	3.0	3.0	3.0
Viscosity Grade		0W-20	0W-20	0W-30	0W-20	5W-30	5W-30	5W-30
Engine Test	Parameter							
Sequence IIG ASTM D7320	Wear and Oil Thickening							
	Average cam and lifter wear, μm	14	20	34	15	46	41	12

TABLE 5

Description		<u>Invention</u> <u>Ex. 1</u>	<u>Invention</u> <u>Ex. 2</u>	<u>Comp.</u> <u>Ex. 3</u>	<u>Comp.</u> <u>Ex. 4</u>	<u>Comp.</u> <u>Ex. 5</u>	<u>Comp.</u> <u>Ex. 6</u>	<u>Comp.</u> <u>Ex. 7</u>
HTHS, cP at 150°C		2.7	2.8	3.5	2.6	3.0	3.0	3.0
Viscosity Grade		0W-20	0W-20	0W-30	0W-20	5W-30	5W-30	5W-30
Engine Test	Parameter							
OM646LA	Wear							
CEC L-099-08	Main bearing wear, μm	0.0	0.2	0.4	0.2	NA	0.7	0.7
	Conrod bearing wear, μm	0.0	0.1	0.2	0.2	NA	0.3	0.5
	Cam wear outlet (avg. max wear 8 cams), μm	55.0	27.9	67.3	89.7	NA	63.2	118.6
	Cam wear inlet (avg. max wear 8 cams), μm	39.9	41.8	58.1	71.4	NA	58.8	79.3

TABLE 6

Description		<u>Invention</u> Ex. 1	<u>Invention</u> Ex. 2	<u>Comp.</u> Ex. 3	<u>Comp.</u> Ex. 4	<u>Comp.</u> Ex. 5	<u>Comp.</u> Ex. 6	<u>Comp.</u> Ex. 7
HTHS, cP at 150°C		2.7	2.8	3.5	2.6	3.0	3.0	3.0
Viscosity Grade		0W-20	0W-20	0W-30	0W-20	5W-30	5W-30	5W-30
Engine Test	Parameter							
M111FE	Fuel Economy							
CEC L-054-96	Fuel Economy Improvement, %	3.5	3.4	2.6	NA	3.1	NA	2.9

[0077] As can be seen from the foregoing Tables, the composition of the invention provided improved antiwear properties while providing a substantial improvement in fuel economy when compared to the other oils identified.

[0078] It will thus be seen that the objects set forth above, among those apparent in the preceding description, are efficiently attained and, since certain changes may be made in carrying out the present invention without departing from the spirit and scope of the invention, it is intended that all matter contained in the above description and shown in the accompanying drawing be interpreted as illustrative and not in a limiting sense.

[0079] It is also understood that the following claims are intended to cover all of the generic and specific features of the invention herein described and all statements of the scope of the invention, which as a matter of language, might be said to fall therebetween.

CLAIMS:

1. An engine oil lubricant composition comprising a major amount of base oil and an effective amount of a zinc dialkyl dithio phosphate, a polymeric viscosity index improver and a mixture of alkaline earth metal detergents, wherein said engine oil lubricant composition has having a sulfated ash content of less than about 0.8 wt% and an HTHS of less than about 2.9 cP at 150°C.
2. The lubricant composition of claim 1, wherein the alkaline earth metal detergents are selected from metallic salicylates and sulfonates.
3. The lubricant composition of claim 2, wherein the metallic salicylates and sulfonates are selected from calcium and magnesium.
4. The lubricant composition of claim 1, wherein the polymeric viscosity index improver has a weight average molecular weight greater than about 500,000.
5. The lubricant composition of claim 4, wherein the polymeric viscosity index improver has a number average molecular weight greater than about 300,000.
6. The lubricant composition of claim 1, wherein the polymeric viscosity index improver is selected from a hydrogenated star polyisoprene, styrene-isoprene block co-polymer and ethylene-propylene copolymer.
7. The lubricant composition of claim 1, wherein the ZDDP is a secondary dialkyl dithiophosphate.
8. The lubricant composition of claim 1, further comprising a mixture of at least two dispersants wherein at least one dispersant is a borated succinimide.

9. A engine oil lubricant composition comprising a major amount of base oil and an effective amount of a zinc dialkyl dithio phosphate, a polymeric viscosity modifier present in an amount of less than about 1.0 wt% solid polymer content and a mixture of detergents selected from salicylates and sulfonates, wherein said engine oil lubricant composition has having a sulfated ash content of less than about 0.8 wt%.

10. A method for improving fuel efficiency and wear in an engine, said method comprising

- i) adding to said engine an engine oil lubricant composition having a sulfated ash content of about 0.8 wt% and an HTHS of about 2.9 cP at 150°C, said lubricant composition comprising a zinc dialkyl dithio phosphate, a polymeric viscosity modifier and a mixture of alkaline earth metal detergents.

11. The method of claim 10, wherein the alkaline earth metal detergents are selected from metallic salicylates and sulfonates.

12. The method of claim 11, wherein the metallic salicylates and sulfonates are selected from calcium and magnesium.

13. The method of claim 10, wherein the polymeric viscosity index improver has a weight average molecular weight greater than about 500,000.

14. The method of claim 13, wherein the polymeric viscosity index improver has a number average molecular weight greater than about 300,000.

15. The method of claim 10, wherein the polymeric viscosity index improver is selected from a hydrogenated star polyisoprene, styrene-isoprene block co-polymer and ethylene-propylene copolymer.

16. The method of claim 1, wherein the ZDDP is a secondary dialkyl dithiophosphate.