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(54) **METHOD FOR LUBRICATING HEAVY DUTY
GEARED APPARATUS**

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(57) **ABSTRACT**

A method for improving the oil drain interval, fuel and energy efficiency of heavy duty geared machinery by lubricating said apparatus using a lubricating oil composition comprising as base oil about 20 to 75 wt % PAO 2 to 10, about 5 to 40 wt % PAO 150-1000, about 10 to 40 wt % PAO 20-100, about 5 to 20 wt % of one or more polyol ester or dibasic acid ester having a kinematic viscosity of between about 2 to 5 mm²/s at 100° C. mm²/s and further containing an effective amount of at least one gear oil additive, said lubricating oil composition having a kinematic viscosity at 100° C. between 9 and 12.5 mm²/s, and exhibiting a traction coefficient value (100°C./30 SSR value) of 0.0197 or less, a Brookfield viscosity at -40° C. of about 26,000 cP or less a CCS viscosity at -25° C. of 4200 cP or less, a flash point of 220° C. or higher and a NOACK volatility of 15% or less.

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Related U.S. Application Data

(60) Provisional application No. 60/832,692, filed on Jul. 21, 2006.

METHOD FOR LUBRICATING HEAVY DUTY GEARED APPARATUS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Application No. 60/832,692 filed Jul. 21, 2006.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] This invention relates to power transmitting fluids or gear oils and to a method for improving the energy efficiency of heavy duty geared machinery/apparatus by using lubricating oils of enhanced performance efficiency.

[0004] 2. Related Art

[0005] Heavy duty geared machinery such as manual transmissions, automatic transmissions, differentials, gear boxes, etc., operated at high temperature and high load over extended or prolonged periods of time are not adequately lubricated using current lubricating oil formulations which do not provide adequate film thickness leading to metal-to-metal contact (boundary lubrication).

[0006] Similarly geared equipment manufacturers are stipulating that the lubricating oil used to lubricate the newer designs of equipment meet more stringent low temperature performance requirements in terms of Brookfield viscosity and cold cranking simulation (CCS) viscosity.

[0007] U.S. Pat. No. 5,858,935 is directed to automotive transmission fluids comprising no less than 50 wt % of a natural mineral oil having a kinematic viscosity at 100° C. of from 1 to 10 mm²/s, up to 49 wt % of a synthetic lubricating oil having a kinematic viscosity @ 100° C. of from 1 to 10 mm²/s and from 1 to 25 wt % of a high viscosity polyalphaolefin having a kinematic viscosity at 100° C. of from 40 to 500 mm²/s.

[0008] In U.S. Pat. No. 5,858,935 it is recited that the synthetic lubricating oil having a kinematic viscosity @ 100° C. of from 1 to 10 mm²/s can be selected from hydrocarbon oils and halo-substituted hydrocarbon oils such as oligomerized, polymerized and interpolymerized olefins (e.g., polybutenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polyactenes, poly(1-hexenes) poly(1-octenes), poly(1-decenes), etc., and mixtures thereof, alkyl benzenes, polyphenyls, alkylated diphenyl ethers, alkylated diphenyl sulfides, preferably polyalphaolefins. Additional synthetic lubricating oils include alkylene oxide polymers, interpolymers, copolymers and derivatives thereof, diesters which are the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimers, malonic acid, alkyl malonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol, monoethers, propylene glycol, etc.), in particular dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, 2-ethylhexyl diester of linoleic acid dimer, preferably the adipates of C₄-C₁₂ alcohols. Other useful synthetic lubricating oils include those made from C₅ to C₁₂ monocarboxylic acids with polyols and/or polyolester, such as neopentyl glycol, trimethylol propane, pentaerythritol, etc.

[0009] It is generally stated that preferred synthetic oils are polyalphaolefins, diesters and polyol esters, having kinematic viscosities at 100° C. of from 2 to 8 mm²/s, preferably 3 to 5 mm²/s.

[0010] U.S. Pat. No. 6,713,439 is directed to energy conserving power transmission fluids comprising from 1 to 49 wt % of a polyalpha olefin base stock having a kinematic viscosity at 100° C. of from 40 to 500 mm²/s, from 1 to 95 wt % of a lubricant base stock having a kinematic viscosity at 100° C. of from 2 to 10 mm²/s, from 1 to 49 wt % of a polyol ester of a C₅ to C₃₀ aliphatic mono-carboxylic acid and a polyol of the formula R(OH)_n where n is at least 2 and an effective amount of a performance additive package, the power transmission fluid composition having a kinematic viscosity at 100° C. of at least 4 mm²/s.

[0011] The lubricant base stock can be mineral oil, or synthetic lubricating oils, preferably polyalphaolefin or mineral oil. No viscosity range is given for the polyol ester, but the only one exemplified is Priolube 3999 from Uniquema, Gouda, Netherlands, having a kinematic viscosity at 100° C. of 13.19 mm²/s.

[0012] U.S. Pat. No. 5,089,156 is directed to lubricating oil compositions comprising a major amount of a polyalphaolefin fluid having a kinematic viscosity @ 100° C. of about 2 to 10 mm²/s, and minor amounts of a polyalphaolefin fluid having a kinematic viscosity @ 100° C. of about 40 to 120 mm²/s and antiwear/extreme pressure agent selected from phospho-dispersant and phosphorus- and boron-containing ashless dispersant, the composition being devoid of metal containing components and characterized as having a kinematic viscosity at 100° C. of at least 5.5 mm²/s, a Brookfield viscosity at -40° C. of less than 20,000 cP or a kinematic viscosity at 100° C. of at least 6.8 mm²/s and a Brookfield viscosity at -40° C. of less than 50,000 cP.

[0013] The formulation can also contain synthetic esters such as mixed C₉ and C₁₁, dialkyl phthalates, trimethylol propane trioleate, di-isotridecyl-adipate, pentaerythritol tetraheptanoate and the like. The Examples utilizes mixtures of PAO 6, PAO 8, PAO 110 and diisononyl adipate, dioctyl sebacate, dibutyl phthalate or di (tridecyl) phthalate along with performance additives.

[0014] U.S. Pat. No. 5,360,562 is directed to an automatic transmission fluid comprising a base oil composed entirely of 70 to 99% polyalpha olefin having a kinematic viscosity at 100° C. of about 2 to 10 mm²/s, and 30 to 1 wt % of polyalphaolefin having a kinematic viscosity at 100° C. of about 40 to 120 mm²/s and further containing 1 to 15 wt % antiwear/extreme pressure additive, other performance additives and no more than 10 wt % viscosity index improver, and essentially devoid of metal containing components, said fluid having a KV @ 100° C. of at least 5.5 mm²/s and a Brookfield viscosity at -40° C. of less than 20,000 cP or a KV at 100° C. of at least 6.8 mm²/s, and a Brookfield viscosity at -40° C. of less than 50,000 cP. The fluid can also contain synthetic esters such as mixed C₉ and C₁₁ dialkylphthalates, trimethylol propane trioleate, di (isotridecyl) adipate, pentaerythritol tetraheptanoate, and the like. The Examples used mixtures of PAO 6 and/or PAO 8 plus PAO 110, along with diisononyl adipate, di(tridecyl) adipate, synthetic esters identified at Hatcol 2923, Hatcol 2920, Hatcol 2915, Hatcol 2970, dioctyl sebacate, dibutyl phthalate, dioctyl sebacate, Emery 2935, Emery 2939.

[0015] U.S. Pat. No. 6,713,438 is directed to high performance engine oil and other liquid lubricants comprising

about 50 to 90 wt % of base oil selected from mineral oil, polyalpha olefin, hydroisomerized Fischer-Tropsch wax and having a KV at 100° C. of from 1.5 to 12 mm²/s, about 0.1 to about 20 wt % of a first polymer and about 0.1 to about 5 wt % of a second polymers, the first polymer being of lower molecular weight than the second, and being a polyalpha olefin having a viscosity from 20 to 3000 mm²/s, the second polymer having a molecular weight of at least 100,000 and having viscosity thickening properties. In the Examples various mixtures of PAO, 1.7 mm²/s at 100° C., PAO, 4 mm²/s at 100° C., PAO 5.6 mm²/s at 100° C. and PAO 150 mm²/s at 100° C. are prepared and formulated with an unidentified "ester". The low viscosity component can also include esters generally identified as having kinematic viscosity at 100° C. in the range 1.5 to 12 mm²/s. The esters are derived from dibasic acids reacted with mono alcohols and the polyol ester of monocarboxylic acids. Useful esters include 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 various alcohols such as butyl, hexyl, dodecyl, 2-ethylhexyl alcohol. Specific esters include dibutyl adipate, di (2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecylphthalate, dilicosyl sebacate, etc.

[0016] Useful polyol esters include those made by reacting one or more polyhydric alcohols, preferably the hindered polyols such as the neopentyl polyols, e.g., neopentyl glycol, trimethylol ethane, trimethylol propane, 2-methyl-2-propyl-1,3-propane diol, pentaerythritol and dipentaerythritol with alkanolic acids containing at least 4 carbon atoms, usually C₅-C₃₀ acids. Examples of such polyol esters are Mobil P-41 and Mobil P-51 esters (Mobil Chemical Company).

[0017] Published Patent Application U.S. 2003/0195128 directed to a VI improving lubricant additive and lubricating oil composition. The additive comprises an olefin oligomer of about 2,000 to 20,000 number average molecular weight and a viscosity of about 75 to 3,000 mm²/s at 100° C. and a hydrocarbyl aromatic which contains at least about 5% of its weight from aromatic moieties and has a viscosity of about 3 to 50 mm²/s at 100° C. Lubricating oils are described containing this additive. Such lubricating oils comprise base oils which can be mineral oil, synthetic oil or mixtures thereof, synthetic oils include PAO and esters as well as other possible synthetic materials. In the Examples the olefin oligomer is a polymer of decene-1 having a viscosity at 100° C. of about 150 mm²/s and it is employed in formulations containing PAO 4, mineral oil and an unidentified ester which has a KV at 100° C. of 5.5 mm²/s, VI 131, see Examples 4.2, 4.4 and 4.6.

[0018] Published Patent Application U.S. 2003/0207775 is directed to a lubricating fluid for automotive gears. The finished fluid has a viscosity index equal to or greater than 175.

[0019] The fluid comprises a high viscosity fluid, preferably polyalpha olefin blended with a lower viscosity fluid comprising a synthetic hydrocarbon which can also be polyalphaolefin. The high viscosity fluid has a KV @ 100° C. between 40 and 3000 mm²/s, while the lower viscosity fluid has a KV @ 100° C. 5 of 40 mm²/s or less. The formulation can also contain esters and mineral oil as well as one or more performance additives. Examples are presented of formulations comprising mixtures of additives, lower viscosity

hydrocarbon fluid PAO-2 (SHF™ 23), lower viscosity ester (Esterex™ M11) Supersyn™ 2150 (PAO 150);

[0020] additives, PAO-25 (SHF_v 23), Esterex™ M11, SHF™ 1003 (PAO-100) (high viscosity hydrocarbon fluid) and Supersyn™ 2300 (PAO 300). Esterex™ M11 is a commercially available ester which has a kinematic viscosity at 100° C. in the range of about 1.25 to 1.45 mm²/s.

[0021] It would be advantageous to enhance the drain interval, fuel and energy efficiency of heavy duty geared machinery by identifying a lubricating oil formulation useful for such heavy duty geared machinery that exhibits during use an improvement in traction coefficient, a Brookfield viscosity at -40° C. of about 21,000 cP or less and a CCS @ -25° C. of about 3800 cP or less.

DESCRIPTION OF THE INVENTION

[0022] A method has been discovered for improving the fuel and energy efficiency of heavy duty geared machinery under high load conditions by lubricating the heavy duty geared machinery using a lubricating oil composition 25 comprising from about 20 to 75 wt %, preferably about 30 to about 60 wt %, more preferably about 45 to 55 wt % of a polyalpha olefin fluid having a kinematic viscosity at 100° C. (ASTM D-445-5) of between about 2 to 10 mm²/s, preferably between about 3.5 to 8 mm²/s, most preferably 3.5 to 6 mm²/s, about 5 to 40 wt %, preferably about 5 to 20 wt %, more preferably about 8 to 12 wt % of a 30 polyalpha olefin fluid having a kinematic viscosity at 100° C. (ASTM D-445-5) between about 150 to 3000 mm²/s, preferably between about 150 to 1500 mm²/s, more preferably between about 150 to 1000 mm²/s, still more preferably between about 150 to 500 mm²/s, most preferably between about 150 to 300 mm²/s, about 10 to 40 wt %, preferably about 15 to 30 wt %, more preferably about 18 to 22 wt % of a polyalphaolefin fluid having a kinematic viscosity at 100° C. (ASTM D-445-5) between about 20 to 100 mm²/s, preferably between about 20 to 80 mm²/s, more preferably between about 20 to 60 mm²/s, most preferably between about 40 to 60 mm²/s, about 5 to 20 wt %, preferably about 5 to 15 wt %, more preferably about 8 to 12 wt % of an ester of a polybasic acid with a mono-alkanol or mixture of mono alkanol and poly alkanol, or a polyol ester, preferably a non-polyol ester, more preferably esters of dibasic acids with mono alkanols, most preferably esters of adipic acid, having a kinematic viscosity at 100° C. of between about 2 to 5 mm²/s, preferably about 2 to 4.5 mm²/s, more preferably about 2.5 to 4.5 mm²/s, and a pour point of at least -25° C., preferably at least -25° C., more preferably at least -45° C., and further containing at least one gear oil additive, said lubricating oil composition having a KV at 100° C. of between 9 and 12.5 mm²/s, preferably between 10 and 12 mm²/s exhibiting a traction coefficient value (measured as the 100° C./30 SSR value) of about 0.0197 or less, preferably about 0.0191 or less, a Brookfield viscosity at -40° C. of about 26,000 cP or less, preferably about 21,000 cP or less and a CCS viscosity at -25° C. of about 4200 cP or less, preferably about 3,600 cP or less, more preferably about 3400 cP or less, all weight percent based on the total weight of the lubricating oil composition.

[0023] In the present invention the base oil comprises a particular combination of polyalphaolefin base oils in combination with one or more of the recited esters to produce a formulation exhibiting unexpectedly enhanced performance characteristic.

[0024] Polyalphaolefins (PAOs) are a hydrocarbon base stock oil well known in the lubricating oil trade. PAOs are derived by the polymerization or copolymerization of alpha-olefins having from 2 to 32 carbons, more typically C₈, C₁₀, C₁₂, C₁₄ olefins or mixtures thereof are utilized.

[0025] The number average molecular weight of PAOs, which are known materials and are generally available on a commercial scale from suppliers such as ExxonMobil Chemical Company, Chevron-Phillips, BP-Amoco, Albemarle Corporation and others, typically vary from about 250 to about 3,000 or higher and may have viscosities at 100° C. in the range from about 2 to about 3000 mm²/s or higher.

[0026] The PAOs are typically comprised of relatively low molecular weight hydrogenated polymers or oligomers of alphaolefins which include, but are not limited to, about C₂ to about C₃₂ alphaolefins with about 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 about C₁₄ to C₁₈ may be used to provide low viscosity base stocks 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.

[0027] 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. Pat. No. 4,149,178 or U.S. Pat. No. 3,382,291 may be conveniently used herein. Other descriptions of PAO synthesis are found in the following U.S. Pat. Nos. 3,742,082; 3,769,363; 3,876,720; 4,239,930; 4,367,352; 4,413,156; 4,434,408; 4,827,064; 4,827,073; 4,910,355; 4,956,122; and 5,068,487. The dimers of the C₁₄ to C₁₈ olefins are described in U.S. Pat. No. 4,218,330.

[0028] High viscosity PAOs suitable for the present invention may be prepared by the action of a reduced chromium catalyst with the alphaolefin, such PAOs are described in U.S. Pat. No. 4,827,073 (Wu); U.S. Pat. No. 4,827,064 (Wu); U.S. Pat. No. 4,967,032 (Ho et al); U.S. Pat. No. 4,926,004 (Peltine et al); and, U.S. Pat. No. 4,914,254 (Peltine). The dimers of the C₁₄ to C₁₈ olefins are described in U.S. Pat. No. 4,218,330. Commercially available high viscosity PAOs include SuperSyn™ 2150, SuperSyn™ 2300, SuperSyn™ 21000, SuperSyn™ 23000 (ExxonMobil Chemical Company).

[0029] In the present invention the lubricating oil comprises a base oil consisting of a specific mixture of PAOs of different viscosities, and further containing an ester, and at least one performance additive.

[0030] The lubricating oil formulation comprises:

[0031] (a) from about 20 to 75 wt %, preferably about 30 to about 60 wt %, more preferably about 45 to 55 wt % of a PAO having a kinematic viscosity at 100° C. of between about 2 to 10 mm²/s, preferably between about 3.5 to 8 mm²/s, most preferably between about 3.5 to 6 mm²/s;

[0032] (b) from about 5 to 40 wt %, preferably about 5 to about 20 wt %, more preferably about 8 to 12 wt % of a PAO having a kinematic viscosity at 100° C. of between about 150 to 3,000 mm²/s, preferably between about 150

to 1500 mm²/s, more preferably between about 150 to 1000 mm²/s, still more preferably between about 150 to 500 mm²/s, most preferably between about 150 to 300 mm²/s;

[0033] (c) from about 10 to 40 wt %, preferably about 15 to 30 wt %, more preferably about 18 to 22 wt % of a PAO having a kinematic viscosity at 100° C. between about 20 to 100 mm²/s, preferably between about 20 to 80 mm²/s, more preferably between about 20 to 60 mm²/s, most preferably between about 40 to 60 mm²/s.

[0034] (d) about 5 to 20 wt %, preferably about 5 to 15 wt %, more preferably about 8 to 12 wt % of one or more ester(s) selected from polyol esters, esters of mono basic or polybasic acids with monoalkanols, or mixtures of monoalkanols and polyalkanols, preferably a non-polyol ester, more preferably esters of dibasic acids with monoalkanols, most preferably esters of adipic acid, having a kinematic viscosity at 100° C. of between about 2 to 5 mm²/s, preferably about 2 to 4.5 mm²/s, more preferably about 2.5 to 4.5 mm²/s; and

[0035] (e) further containing at least one gear oil performance additive, said lubricant oil composition having a KV at 100° C. of between 9 and 12.5 mm²/s, preferably between 10 and 12 mm²/s, and exhibiting a traction coefficient value (measured as the 100° C./30 SSR value) of about 0.0197 or less, preferably about 0.0195 or less, a Brookfield viscosity at -40° C. of about 26,000 cP or less, preferably about 21,000 cP or less and a CCS viscosity at -25° C. of about 4200 cP or less, preferably about 3,600 cP or less, more preferably about 3,400 cP or less, a NOACK volatility of 15% or less, preferably 13% or less, and a flash point of 220° C. or higher, preferably 230° C. or higher all weight percentages being based on the total lubricant composition.

[0036] In this text and the appended claims Kinematic Viscosity is determined by ASTM D-445-5 test method, Brookfield viscosity @ -40° C. by ASTM D-2983-31, cold cranking simulation (CCS) viscosity at -25° C. by ASTM D-5293-5, NOACK volatility by ASTM D-5800, flash point by ASTM D-97 and traction coefficient by 16N/100° C./30SSR.

[0037] The present formulations are further distinguished by the absence of viscosity index improvers, the presence of which is deleterious to traction coefficient.

[0038] Esters of mono-basic and polybasic, especially dibasic acids with monoalkanols are exemplified by 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., or mixtures thereof with polyalkanols. Specific examples of these types of esters include nonyl heptanoate, dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, etc.

[0039] Other 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 alkanolic 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).

[0040] Suitable synthetic ester components include the esters of trimethylol propane, trimethylol butane, trimethylol ethane, pentaerythritol and/or dipenta-erythritol with one or more monocarboxylic acids containing from about 5 to about 10 carbon atoms.

[0041] The preferred esters are the esters of dibasic acids with monoalkanols.

[0042] The gear oil formulation contains at least one of a gear oil performance addition in an effective amount. By effective amount is meant a minor amount, based on the total weight of the formulated lubricant, sufficient for the additive to produce the desired performance modification effect. Effective amount is usually about 20 wt % or less, preferably about 3 to 12 wt %, more preferably about 4 to 7 wt % in total of at least one (i.e., one or more) performance additive(s).

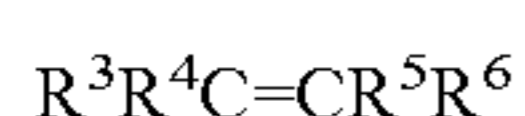
[0043] Performance additives suitable for use in the present gear oil to achieve the desired lubricating oil performance are antioxidant, antiwear additives, metal corrosion inhibitors, friction modifiers, ashless dispersants, detergents, anti-foamants, seal swellant. Notably absent in the present gear oil formulations are viscosity modifiers and viscosity index improvers.

Antiwear and EP Additives

[0044] Many lubricating oils require the presence of antiwear and/or extreme pressure (EP) additives in order to provide adequate antiwear protection. Increasingly specifications for, e.g., engine oil performance have exhibited a trend for improved antiwear properties of the oil. Antiwear and extreme EP additives perform this role by reducing friction and wear of metal parts, yellow metal protection, thermal stability wear, scuffing, surface fatigue.

[0045] 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 primary metal constituent is zinc, or zinc dialkyldithio-phosphate (ZDDP). 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. The ZDDP is typically used in amounts of from about 0.4 to 6 wt %, preferably about 0.8 to 4.0 wt % of the total lube oil composition, although more or less can often be used advantageously the amount of phosphorus and zinc attributable to the ZDDP being about 420-1500 ppm P and 450 to 1600 ppm Zn.

[0046] A variety of non-phosphorous additives are also used as antiwear additives. Sulfurized olefins are useful as antiwear and EP additives. Sulfur-containing olefins can be prepared by sulfurization or various organic materials including aliphatic, arylaliphatic or alicyclic olefinic hydrocarbons containing from about 3 to 30 carbon atoms, preferably 3-20 carbon atoms. The olefinic compounds contain at least one non-aromatic double bond. Such compounds are defined by the formula



[0047] where each of R^3 - R^6 are independently hydrogen or a hydrocarbon radical. Preferred hydrocarbon radicals are alkyl or alkenyl radicals. Any two of R^3 - R^6 may be connected

so as to form a cyclic ring. Additional information concerning sulfurized olefins and their preparation can be found in U.S. Pat. No. 4,941,984.

[0048] The use of polysulfides of thiophosphorus acids and thiophosphorus acid esters as lubricant additives is disclosed in U.S. Pat. Nos. 2,443,264; 2,471,115; 2,526,497; and 2,591,577. Addition of phosphorothionyl disulfides as an antiwear, antioxidant, and EP additive is disclosed in U.S. Pat. No. 3,770,854. Use of alkylthiocarbamoyl compounds (bis(dibutyl)thiocarbamoyl, for example) in combination with a molybdenum compound (oxymolybdenum diisopropylphosphorodithioate sulfide, for example) and a phosphorous ester (dibutyl hydrogen phosphite, for example) as antiwear additives in lubricants is disclosed in U.S. Pat. No. 4,501,678. U.S. Pat. No. 4,758,362 discloses use of a carbamate additive to provide improved antiwear and extreme pressure properties. The use of thiocarbamate as an antiwear additive is disclosed in U.S. Pat. No. 5,693,598. Thiocarbamate/molybdenum complexes such as moly-sulfur alkyl dithio-carbamate trimer complex ($R=C_8$ - C_{18} alkyl) are also useful antiwear agents. The use or addition of such materials should be kept to a minimum if the object is to produce low SAP formulations.

[0049] Esters of glycerol may be used as antiwear agents. For example, mono-, di, and tri-oleates, mono-palmitates and mono-myristates may be used.

[0050] ZDDP can be combined with other compositions that provide antiwear properties. U.S. Pat. No. 5,034,141 discloses that a combination of a thiodixanthogen compound (octylthiodixanthogen, for example) and a metal thiophosphate (ZDDP, for example) can improve antiwear properties. U.S. Pat. No. 5,034,142 discloses that use of a metal alkoxyalkylxanthate (nickel ethoxyethylxanthate, for example) and a dixanthogen (diethoxyethyl dixanthogen, for example) in combination with ZDDP improves antiwear properties.

[0051] Preferred antiwear additives include phosphorus and sulfur compounds such as zinc dithiophosphates and/or sulfur, nitrogen, boron, molybdenum phosphorodithioates, molybdenum dithiocarbamates and various organo-molybdenum derivatives including heterocyclics, for example dimercaptiothia-diazoles, mercaptobenzothiadiazoles, triazines, and the like, alicyclics, amines, alcohols, esters, diols, triols, fatty amides and the like can also be used. Such additives may be used in an amount of about 0.01 to 6 wt %, preferably about 0.01 to 4 wt %. ZDDP-like compounds provide limited hydroperoxide decomposition capability, significantly below that exhibited by compounds disclosed and claimed in this patent and can therefore be eliminated from the formulation or, if retained, kept at a minimal concentration to facilitate production of low SAP formulations.

Antioxidants

[0052] 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. Pat. Nos. 4,798,684 and 5,084,197, for example.

[0053] Useful antioxidants include hindered phenols. These phenolic anti-oxidants 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).

[0054] 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 R⁸R⁹R¹⁰N where R⁸ is an aliphatic, aromatic or substituted aromatic group, R⁹ is an aromatic or a substituted aromatic group, and R¹⁰ is H, alkyl, aryl or R¹¹S(O)_xR¹² where R¹¹ is an alkylene, alkenylene, or aralkylene group, R¹² is a higher alkyl group, or an alkenyl, aryl, or alkaryl group, and x is 0, 1 or 2. The aliphatic group R⁸ 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 R⁸ and R⁹ are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring aromatic group such as naphthyl. Aromatic groups R⁸ and R⁹ may be joined together with other groups such as S.

[0055] 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 naphthyl-amines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more aromatic amines are also useful. Polymeric amine antioxidants can also be used. Polymeric aromatic amine antioxidants include polymeric diphenyl amine antioxidants, polymeric phenyl naphthylene amine antioxidants and polymeric diphenyl amine/phenyl naphthalene amine antioxidants. Particular examples of aromatic amine antioxidants useful in the present invention include: p,p'-dioctyl-diphenylamine; t-octylphenyl-alpha-naphthylamine; phenyl-alphanaphthylamine; and p-octylphenyl-alpha-naphthylamine.

[0056] Sulfurized alkyl phenols, alkali or alkaline earth metal salts thereof, alkyl aromatic sulfides, phosphorus compounds such as the phosphites and phosphonic acid esters and the sulfur-phosphorus compounds such as the dithiophosphates and other types such as the dialkyl dithiocarbamates and mixtures thereof also are useful antioxidants.

[0057] Another class of antioxidant used in lubricating oil compositions is oil-soluble copper compounds. Any oil-

soluble suitable copper compound may be blended into the lubricating oil. Examples of suitable copper antioxidants include copper dihydrocarbyl thio- or dithio-phosphates and copper salts of carboxylic acid (naturally occurring or synthetic). Other suitable copper salts include copper dithiocarbamates, sulphonates, phenates, and acetylacetonates. Basic, neutral, or acidic copper Cu(I) and or Cu(II) salts derived from alkenyl succinic acids or anhydrides are known to be particularly useful.

[0058] 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 %.

Detergents

[0059] 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.

[0060] 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.

[0061] 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.

[0062] Preferred detergents include the alkali or alkaline earth metal salts of sulfonates, phenates, carboxylates, phosphates, and salicylates.

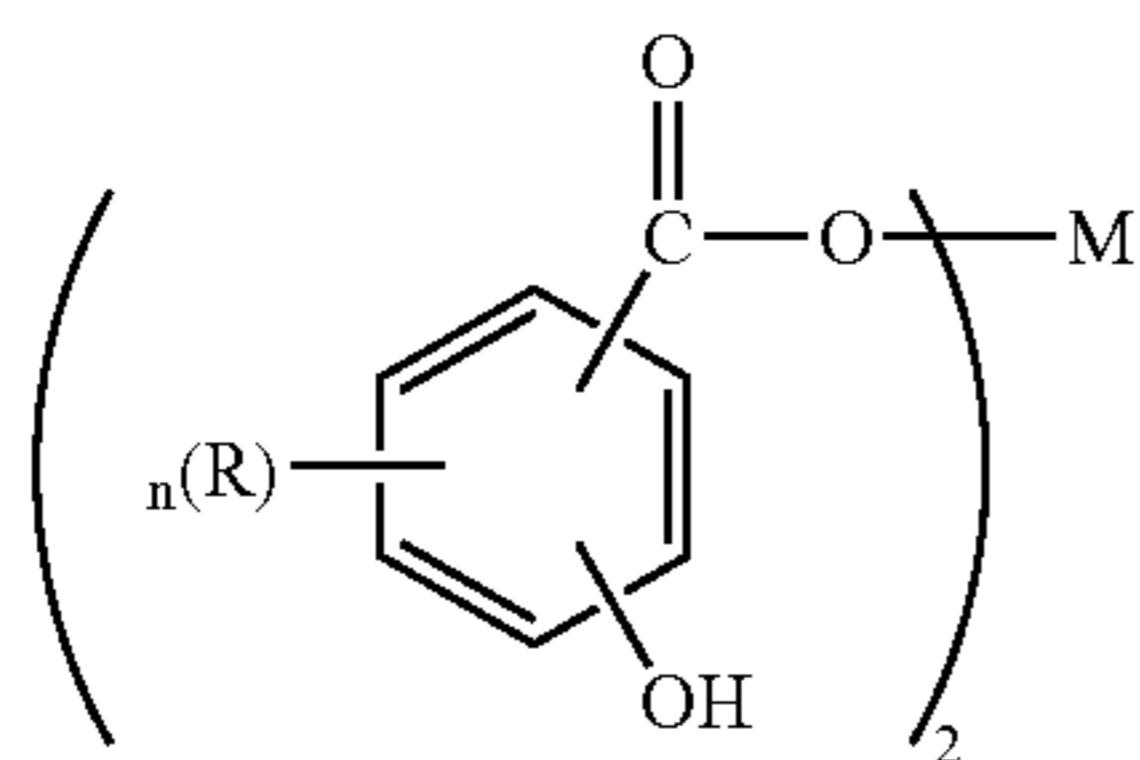
[0063] Sulfonates may be prepared from sulfonic acids that are typically obtained by sulfonation of alkyl substituted aromatic hydrocarbons. Hydrocarbon examples include those obtained by alkylating benzene, toluene, xylene, naphthalene, biphenyl and their halogenated derivatives (chlorobenzene, chlorotoluene, 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.

[0064] 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.

[0065] 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 C₁-C₃₀ alkyl groups, preferably, C₄-C₂₀. 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.

[0066] 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.

[0067] Hydrocarbyl-substituted salicylic acids may be prepared from phenols by the Kolbe reaction. See U.S. Pat. No. 3,595,791, which is incorporated herein by reference in its entirety, for additional information on synthesis of these compounds. 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.

[0068] Alkaline earth metal phosphates are also used as detergents.

[0069] 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. Pat. No. 6,034,039 for example.

[0070] Preferred detergents include calcium phenates, calcium sulfonates, calcium salicylates, magnesium phenates, magnesium sulfonates, magnesium salicylates and other related components (including borated detergents). Typi-

cally, the total detergent concentration is about 0.01 to about 6.0 wt %, preferably, about 0.1 to 0.4 wt %.

Supplementary Dispersant

[0071] 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. As supplementary dispersants use may be made of the unborated version of any of the dispersant types previously recited. Such supplementary do non-borated dispersants can be used in amount of about 0.1 to <20 wt % preferably about 0.1 to 8 wt % on an as received basis.

Pour Point Depressants

[0072] 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. Pat. Nos. 1,815,022; 2,015,748; 2,191,498; 2,387,501; 2,655, 479; 2,666,746; 2,721,877; 2,721,878; and 3,250,715 describe useful pour point depressants and/or the preparation thereof. Such additives may be used in an amount of about 0.01 to 5 wt %, preferably about 0.01 to 1.5 wt %.

Corrosion Inhibitors/Metal Deactivators

[0073] Corrosion inhibitors are used to reduce the degradation of metallic parts that are in contact with the lubricating oil composition. Suitable corrosion inhibitors include triazoles and thiadiazoles, succinimide derivatives such as the higher alkyl substituted amides of dodecylene succinic acid, such as the tetra-propenyl succinic mono esters, and imidazoline succinic anhydride derivatives. See, for example, U.S. Pat. Nos. 2,719,125; 2,719,126; and 3,087,932. Such additives may be used in an amount of about 0.01 to 5 wt %, preferably about 0.01 to 1.5 wt %.

Seal Compatibility Additives

[0074] 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, 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 %.

Anti-Foam Agents

[0075] 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. Antifoam 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.

Inhibitors and Antirust Additives

[0076] Antirust 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; they are referred to in Klamann in *Lubricants and Related Products*, op cit.

[0077] One type of antirust additive is a polar compound that wets the metal surface preferentially, protecting it with a film of oil. Another type of antirust 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 antirust 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 wt %, preferably about 0.01 to 1.5 wt %.

Friction Modifiers

[0078] 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. Pat. No. 5,824,627; U.S. Pat. No. 6,232,276; U.S. Pat. No. 6,153,564; U.S. Pat. No. 6,143,701; U.S. Pat. No. 6,110,878; U.S. Pat. No. 5,837,657; U.S. Pat. No. 6,010,987; U.S. Pat. No. 5,906,968; U.S. Pat. No. 6,734,150; U.S. Pat. No. 6,730,638; U.S. Pat. No. 6,689,725; U.S. Pat. No. 6,569,820; WO 99/66013; WO 99/47629; WO 98/26030.

[0079] 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.

[0080] 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.

Dispersant

[0081] During machinery 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.

[0082] 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.

[0083] 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 U.S. Pat. Nos. 3,172,892; 3,2145,707; 3,219,666; 3,316,177; 3,341,542; 3,444,170; 3,454,607; 3,541,012; 3,630,904; 3,632,511; 3,787,374 and 4,234,435. Other types of dispersant are described in U.S. Pat. Nos. 3,036,003; 3,200,107; 3,254,025; 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,413,347; 3,697,574; 3,725,277; 3,725,480; 3,726,882; 4,454,059; 3,329,658; 3,449,250;

3,519,565; 3,666,730; 3,687,849; 3,702,300; 4,100,082; 5,705,458. A further description of dispersants may be found, for example, in European Patent Application No. 471 071, to which reference is made for this purpose.

[0084] 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.

[0085] 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. Pat. 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 Pat. No. 1,094,044.

[0086] 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.

[0087] 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. Pat. No. 4,426,305.

[0088] 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.

[0089] Mannich base dispersants are made from the reaction of alkylphenols, formaldehyde, and amines. See U.S. Pat. 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. Pat. Nos. 3,697,574; 3,703,536; 3,704,308; 3,751,365; 3,756,953; 3,798,165; and 3,803,039.

[0090] 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 $\text{HN}(\text{R})_2$ group-containing reactants.

[0091] Examples of high molecular weight alkyl-substituted hydroxyaromatic compounds are polypropylphenol, polybutylphenol, and other polyalkylphenols. These polyalkylphenols can be obtained by the alkylation, in the presence of an alkylating catalyst, such as BF_3 , of phenol with high molecular weight poly-propylene, polybutylene, and other polyalkylene compounds to give alkyl substituents on the benzene ring of phenol having an average 600-100,000 molecular weight.

[0092] Examples of $\text{HN}(\text{R})_2$ group-containing reactants are alkylene polyamines, principally polyethylene polyamines. Other representative organic compounds containing at least one $\text{HN}(\text{R})_2$ group suitable for use in the preparation of Mannich condensation products are well known and include the mono- and di-amino alkanes and their substituted analogs, e.g., ethylamine and diethanol amine; aromatic diamines, e.g., phenylene diamine, diamino naphthalenes; heterocyclic amines, e.g., morpholine, pyrrole, pyrrolidine, imidazole, imidazolidine, and piperidine; melamine and their substituted analogs.

[0093] Examples of alkylene polyamide reactants include ethylenediamine, diethylene triamine, triethylene tetraamine, tetraethylene pentaamine, pentaethylene hexamine, hexaethylene heptaamine, heptaethylene octaamine, octaethylene nonaamine, nonaethylene decamine, and decaethylene undecamine and mixture of such amines having nitrogen contents corresponding to the alkylene polyamines, in the formula $\text{H}_2\text{N}-(\text{Z}-\text{NH}-)_n\text{H}$, mentioned before, Z is a divalent ethylene and n is 1 to 10 of the foregoing formula. Corresponding propylene polyamines such as propylene diamine and di-, tri-, tetra-, pentapropylene tri-, tetra-, penta- and hexaamines are also suitable reactants. The alkylene poly-amines are usually obtained by the reaction of ammonia and dihalo alkanes, such as dichloro alkanes. Thus the alkylene polyamines obtained from the reaction of 2 to 11 moles of ammonia with 1 to 10 moles of dichloroalkanes having 2 to 6 carbon atoms and the chlorines on different carbons are suitable alkylene polyamine reactants.

[0094] Aldehyde reactants useful in the preparation of the high molecular products useful in this invention include the aliphatic aldehydes such as formaldehyde (also as paraformaldehyde and formalin), acetaldehyde and aldol (β -hydroxybutyraldehyde). Formaldehyde or a formaldehyde-yielding reactant is preferred.

[0095] Hydrocarbyl substituted amine ashless dispersant additives are well known to one skilled in the art; see, for example, U.S. Pat. Nos. 3,275,554; 3,438,757; 3,565,804; 3,755,433, 3,822,209, and 5,084,197, which are incorporated herein in their entirety by reference.

[0096] Borated dispersants can be used. Any dispersant containing either or both of nitrogen and/or oxygen atoms can be borated.

[0097] 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 0.1 to 8 wt %.

Typical Additive Amounts

[0098] 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 1 below.

[0099] Note that many of the additives are shipped from the manufacturer and used with a certain amount of base oil solvent in the formulation. Accordingly, the weight amounts in the table below, as well as other amounts mentioned in this patent unless otherwise indicated, are directed to the amount of active ingredient (that is the non-solvent 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 Reducer	0.01-5	0.01-1.5
Antioxidant	0.0-5	0.0-1.5
Corrosion Inhibitor	0.01-5	0.01-1.5
Anti-wear Additive	0.01-6	0.01-4
Pour Point Depressant	0.0-5	0.01-1.5
Anti-foam Agent	0.001-3	0.001-0.15
Base Oil	Balance	Balance

[0100] The present invention is demonstrated by the following nonlimiting Examples and Comparative Examples.

[0101] The following Examples and Comparative Examples are gear oils meeting a nominal 30 grade viscosity target unless otherwise indicated.

[0102] Traction coefficient is determined using the Mini Traction Machine which is a computer controlled, precision traction measurement system. A small sample of fluid is placed in the test cell and the machine automatically runs through a range of speeds, slide/roll ratios, temperatures and loads to produce a comprehensive traction map for the test fluid without any operator intervention. The MTM can be used with different specimen configuration but the standard test specimens used herein are a polished 19.05 mm (3/4 inch) ball and a 50.0 mm diameter disc manufactured from AISI 52100 bearing steel. The specimens are designed to be single use, throw away items. The specimens are independently driven by DC servo motors and drives to allow high precision speed control, particularly at low slide/roll ratios. Each specimen is end mounted on shafts in a small stainless steel test fluid bath. The vertical shaft and drive system, which supports the 50 mm diameter test specimen, is fixed. However, the shaft and drive system which supports the 19.05 mm diameter test specimen is supported by a gimbal arrangement such that it can rotate around two orthogonal axes. One axis is normal to the load application direction, the other to the traction force direction. Application of the load and restraint of the traction force is made through high stiffness force transducers appropriately mounted in the gimbal arrangement to minimize the overall support system deflections. The output from these force transducers is monitored directly by a personal com-

puter (PC). The test conditions used herein are: 16 newton load, 100° C. temperature, and 30% slide to roll ratio (16N/100° C./30 SSR).

[0103] Comparative Examples 1, 2 and 3 use of an adipate ester of KV @ 100° C. of between 5.1 to 5.5 mm²/s, while Comparative Example 4 differed in using a different additive package while still employing the adipate ester of KV @ 100° C. of between 5.1 to 5.5 mm²/s.

[0104] The inventive formulations of Examples 1 and 2, while utilizing the same base stock combination of PAO and additive package as Comparative Examples 1, 2, 3, 6 and 7 differed in the nature of the esters used, Example 1 using a polyolester of KV @ 100° C. of 4.2 to 4.5 mm²/s, pour point below -45° C. and Example 2 using an adipate (a di ester) of KV @ 100° C. of 2.7 mm²/s, pour point below -45° C.

[0105] In both instances the Inventive oils of Examples 1 and 2 demonstrate an unexpected improvement in all low temperature viscometries properties and traction coefficient. Brookfield viscosities @ -40° C. of Examples 1 and 2 are 25,747 cP and 20,546 cP respectively, CCS viscosities at -25° C. are 4118 cP and 3,357 cP respectively, traction coefficients are 0.01969 and 0.01945 respectively. Flash points of 242 and 234° C. respectively while NOACK volatility was 9.0 and 12.7% respectively. Such improvements in low temperature viscometries and traction coefficients while retaining acceptable NOACK volatility and flash point could not be expected from such minor changes in the viscosity of the ester used in combination with the mixed PAO base stock.

[0106] Comparative Example 5 was similar to Comparative Example 4 but substituted Emoline 2958 (believed to be a di-2-hexyl adipate) which has a reported of KV @ 100° C. of 2.8-2.9 mm²/s pour point below -45° C. for the 5.1-5.5 mm²/s adipate. Comparative Examples 6 and 7 were similar to Comparative Examples 1, 2, 3 but substituted Esterex™ M31 (ethyl hexyl polmitate a mono ester, KV @ 100° C. of 2.7 mm²/s pour point 3° C.) and Esterer™ M 11 (nonyl heptanoate a mono ester literature value KV @ 100° C. of 1.25-1.45 mm²/s pour point, below -45° C.) respectively for the 5.1-5.5 mm²/s adipate (di ester).

[0107] While the formulation of Comparative Examples 6 and 7 exhibited CCS viscosities and traction coefficients, and in the case of Comparative Example 7 a Brookfield viscosity meeting the specification targets of the present invention, they would prove to be undesirable and insufficient from a practical stand point if employed in an actual working environment. The formulation of Comparative Example 6 exhibited a totally unsatisfactory high Brookfield viscosity while the formulation of Comparative Example 7 exhibited unsatisfactory flash point and NOACK volatility. Comparative Example 5 demonstrates that even when a diester of desirable KV is employed, if the combination of PAO base stocks does not correspond to that recited in the present application, the resulting formulated oil having a KV outside the target of between 9 to 12.5 mm²/s exhibits an unacceptable Brookfield viscosity, an unacceptable CCS viscosity and does not achieve the desired traction coefficient.

TABLE 2

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Example 1	Example 2
Commercial adpack (wt %) (as received)				10	10				
Custom adpack (wt %) (as received)	11.7	11.7	11.7			11.7	11.7	11.7	11.7

TABLE 2-continued

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Example 1	Example 2
Ditridecyl adipate, 5.1-55 mm ² /s	10	20	30	10					
TMP ester of C ₈ -C ₁₀ acid, 4.2-4.5 mm ² /s								10	
Diisooctyl adipate, 2.7 mm ² /s									10
Emoline 2958, 2.8-2.9 mm ² /s					10				
Esterex M31, 2.7 mm ² /s						10			
Esterex M11, 1.25-1.45 mm ² /s							10		
PAO 40	19.3	19.3	19.3	19.3		19.3	19.3	19.3	19.3
Supersyn 2150, 150 mm ² /s PAO	10	10	10	10		10	10	10	10
PAO 100					38.7				
PAO 6					41.3				
PAO 4	49	39	29	50.7		49	49	49	49
KV 100 (D445-5)	11.23, 11.3	11.56, 11.62	11.87, 11.95	9.74	18.25, 18.89	10.36	9.447	11.01, 11.07	10.36, 10.39
KV 40 (D445-3)	68.75, 68.2	71.62, 71.3	74.65, 74.28	55.97	127.07, 130.63	58.83	51.11	66.41, 66.06	56.69, 59.31
Viscosity index	156	156	154	160	161	166	171	158	174
BF viscosity @ -40° C. (D2983-31)	30,094	35,892	44,341	17,896	76,384	1,000,000; 609,870	13,640; 14,397	25,747	20,546
CCS viscosity @ -25° C. (D5293-5)	4,510	5,176	5,986	3,187	10,894	3,260	2,550	4,118	3,357
Traction coefficient (16N/100° C./30 SSR)*	0.02161	0.02228	0.02382	0.02025	0.02097	0.009751	0.009873	0.01969	0.01945
ASTM D5800 (% evaporation)	8.9						18.6	9.0	12.5
ASTM D97 (flash point, ° C.)	234						206	242.0	234
PDSC (onset temp) ramping @ 10° C./min	265.6	267.1	279.7		266.4	262	264.6	267.1	267.8

*Determined using Mini Traction Machine

What is claimed is:

1. A method for improving the fuel economy and energy efficiency of heavy duty geared machinery operated under high load conditions comprising running the heavy duty geared machinery under high load conditions while lubricating said machinery by using a lubricating oil composition comprising from about 20 to 75 wt % of a polyalphaolefin fluid having a kinematic viscosity at 100° C. of between about 2 to 10 mm²/s, about 5 to 40 wt % of a polyalpha-olefin fluid having a kinematic viscosity at 100° C. of between about 150 to 3,000 mm²/s, about 10 to 40 wt % of a polyalphaolefin fluid having a kinematic viscosity at 100° C. of between about 20 to 100 mm²/s, about 5 to 20 wt % of one or more polyesters or diesters having a kinematic viscosity at 100° C. of between about 2 to 5 mm²/s and a pour point of at least -25° C., and further containing at least one gear oil performance additive, said lubricating oil composition being characterized by having a kinematic viscosity at 100° C. of between 9 and 12.5 mm²/s and exhibiting a traction coefficient value, measured as the 16N/100° C./30 SSR value, of about 0.0197 or less, a Brookfield viscosity at -40° C. of about 26,000 cP or less, and a CCS viscosity at -25° C. of about 4200 cP or less, a flash point of 220° C. or higher and a NOACK volatility of 15% or less.

2. The method of claim 1 wherein the lubricating oil composition comprises about 30 to 60 wt % of a PAO fluid having a kinematic viscosity at 100° C. of between about 3.5 to 8 mm²/s, about 5 to 20 wt % of a PAO fluid having a kinematic

viscosity of between about 150 to 1500 mm²/s, about 15 to 30 wt % of a PAO fluid having a kinematic at 100° C. of between about 20 to 80 mm²/s, about 5 to 15 wt % of an ester having a kinematic viscosity at 100° C. of between about 2 to 4.5 mm²/s and further containing at least one gear oil performance additive.

3. The method of claim 1 wherein the lubricating oil composition comprises about 30 to 60 wt % of a PAO fluid having a kinematic viscosity at 100° C. of between about 2 to 10 mm²/s.

4. The method of claim 1 wherein the lubricating oil composition comprises about 5 to 20 wt % of a PAO fluid having a kinematic viscosity at 100° C. of between about 150 to 3000 mm²/s.

5. The method of claim 1 wherein the lubricating oil composition comprises about 15 to 30 wt % of a PAO fluid having a kinematic viscosity at 100° C. of between about 20 to 100 mm²/s.

6. The method of claim 1 wherein the ester comprises about 5 to 15 wt % of the lubricating oil and has a kinematic viscosity at 100° C. of between about 2 to 4.5 mm²/s.

7. The method of claim 1, 2, 3, 4, 5 or 6 wherein the lubricating oil composition comprises about 45-55 wt % of a PAO fluid having a kinematic viscosity at 100° C. of between about 3.5 to 6 mm²/s, about 8 to 12 wt % of a PAO fluid having a kinematic viscosity at 100° C. of between about 150 to 500 mm²/s, about 18 to 22 wt % of a PAO fluid having a kinematic viscosity between about 20 to 60 mm²/s.

8. The method of claim 7 wherein the ester is a non-polyol ester.

9. The method of claim 8 wherein the non-polyol ester comprises about 5 to 15 wt % of the lubricating oil and has a kinematic viscosity at 100° C. of between about 2.5 to 4.5 mm²/s.

10. The method of claim 1, 2, 3, 4, 5 or 6 wherein the lubricating oil composition is characterized by exhibiting a traction coefficient value measured as the 16N/100° C./30 SSR value of about 0.0191 or less.

11. The method of claim 1, 2, 3, 4, 5 or 6 wherein the lubricating oil composition is characterized by exhibiting a Brookfield viscosity at -40° C. of about 21,000 cP or less, a flash point of 230° C. or higher and a NOACK volatility of 15% or less.

12. The method claim 1, 2, 3, 4, 5 or 6 wherein the lubricating oil composition is characterized by exhibiting a CCS viscosity at -25° C. of about 3,600 cP or less.

13. The method of claim 1, 2, 3, 4, 5 or 6 wherein the lubricating oil composition is characterized by exhibiting a CCS viscosity at -25° C. of about 3400 cP or less.

14. The method of claim 7 wherein the lubricating oil composition is characterized by exhibiting a traction coefficient value measured as the 16N/100° C./30 SSR value of about 0.0191 or less, a Brookfield viscosity at -40° C. of about 21,000 cP or less and a CCS viscosity at -25° C. of about 3600 cP or less, a flash point of 230° C. or less and a NOACK volatility of 13% or less.

15. The method of claim 14 wherein the ester comprises about 5 to 15 wt % of the lubricating oil and has a kinematic viscosity at 100° C. of between about 2.5 to 4.5 mm²/s.

16. The method of claim 9 wherein the ester comprises about 8 to 12 wt % of the lubricating oil and has a kinematic viscosity at 100° C. of between about 2.5 to 4.5 mm²/s.

17. The method of claim 1, 2, 3, 4, 5 or 6 wherein the lubricating oil composition is characterized by the absence of viscosity index improvers.

18. A lubricating oil composition comprising from about 20 to 75 wt % of a polyalphaolefin fluid having a kinematic viscosity at 100° C. of between about 2 to 10 mm²/s, about 5 to 40 wt % of a polyalphaolefin fluid having a kinematic viscosity at 100° C. of between about 150 to 3,000 mm²/s, about 10 to 40 wt % of a polyalphaolefin fluid having a kinematic viscosity at 100° C. of between about 20 to 100 mm²/s, about 5 to 20 wt % of one or more polyolesters or diesters having a kinematic viscosity at 100° C. of between about 2 to 5 mm²/s and a pour point of at least -25° C., and further containing at least one gear oil performance additive, said lubricating oil composition being characterized by having a kinematic viscosity at 100° C. of between 9 and 12.5 mm²/s and exhibiting a traction coefficient value, measured as the 16N/100° C./30 SSR value, of about 0.0197 or less, a Brookfield viscosity at -40° C. of about 26,000 cP or less, and a CCS viscosity at -25° C. of about 4200 cP or less, a flash point of 220° C. or higher and a NOACK volatility of 15% or less.

19. The lubricating oil composition of claim 18 wherein the lubricating oil composition comprises about 30 to 60 wt % of a PAO fluid having a kinematic viscosity at 100° C. of between about 3.5 to 8 mm²/s, about 5 to 20 wt % of a PAO fluid having a kinematic viscosity of between about 150 to 1500 mm²/s, about 15 to 30 wt % of a PAO fluid having a kinematic at 100° C. of between about 20 to 80 mm²/s, about 5 to 15 wt % of an ester having a kinematic viscosity at 100°

C. of between about 2 to 4.5 mm²/s and further containing at least one gear oil performance additive.

20. The lubricating oil composition of claim 18 wherein the lubricating oil composition comprises about 30 to 60 wt % of a PAO fluid having a kinematic viscosity at 100° C. of between about 2 to 10 mm²/s.

21. The lubricating oil composition of claim 18 wherein the lubricating oil composition comprises about 5 to 20 wt % of a PAO fluid having a kinematic viscosity at 100° C. of between about 150 to 3000 mm²/s.

22. The lubricating oil composition of claim 18 wherein the lubricating oil composition comprises about 15 to 30 wt % of a PAO fluid having a kinematic viscosity at 100° C. of between about 20 to 100 mm²/s.

23. The lubricating oil composition of claim 18 wherein the ester comprises about 5 to 15 wt % of the lubricating oil and has a kinematic viscosity at 100° C. of between about 2 to 4.5 mm²/s.

24. The lubricating oil composition of claim 18, 19, 20, 21, 22 or 23 wherein the lubricating oil composition comprises about 45-55 wt % of a PAO fluid having a kinematic viscosity at 100° C. of between about 3.5 to 6 mm²/s, about 8 to 12 wt % of a PAO fluid having a kinematic viscosity at 100° C. of between about 150 to 500 mm²/s, about 18 to 22 wt % of a PAO fluid having a kinematic viscosity between about 20 to 60 mm²/s.

25. The lubricating oil composition of claim 24 wherein the ester is a non-polyol ester.

26. The lubricating oil composition of claim 25 wherein the non-polyol ester comprises about 5 to 15 wt % of the lubricating oil composition and has a kinematic viscosity at 100° C. of between about 2.5 to 4.5 mm²/s.

27. The lubricating oil composition of claim 18, 19, 20, 21, 22 or 23 characterized by a traction coefficient value measured as the 16N/100° C./30 SSR value of about 0.0191 or less.

28. The lubricating oil composition of claim 18, 19, 20, 21, 22 or 23 characterized by a Brookfield viscosity at -40° C. of about 21,000 cP or less, a flash point of 230° C. or higher and a NOACK volatility of 15% or less.

29. The lubricating oil composition of claim 18, 19, 20, 21, 22 or 23 characterized by a CCS viscosity at -25° C. of about 3,600 cP or less.

30. The lubricating oil composition of claim 18, 19, 20, 21, 22 or 23 characterized by a CCS viscosity at -25° C. of about 3400 cP or less.

31. The lubricating oil composition of claim 24 characterized by a traction coefficient value measured as the 16N/100° C./30 SSR value of about 0.0191 or less, a Brookfield viscosity at -40° C. of about 21,000 cP or less and a CCS viscosity at -25° C. of about 3600 cP or less, a flash point of 230° C. or less and a NOACK volatility of 13% or less.

32. The lubricating oil composition of claim 31 wherein the ester comprises about 5 to 15 wt % of the lubricating oil and has a kinematic viscosity at 100° C. of between about 2.5 to 4.5 mm²/s.

33. The lubricating oil composition of claim 26 wherein the ester comprises about 8 to 12 wt % of the lubricating oil and has a kinematic viscosity at 100° C. of between about 2.5 to 4.5 mm²/s.

34. The lubricating oil composition of claim 18, 19, 20, 21, 22 or 23 characterized by the absence of viscosity index improvers.

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