METHOD FOR LUBRICATING HEAVY DUTY GEARED APPARATUS

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PROCÉDÉ POUR LUBRIFIER UN APPAREIL À ENGRENAGE RENFORCÉ

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BACKGROUND OF THE INTENTION

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.

RELATED ART

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).

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.

In USP 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 halogen-substituted hydrocarbon oils such as oligomerized, polymericized and interpolymerized olefins (e.g., polybutenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polyacetylenes, 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 oxidepolymers, interpolymerops, copolymers and derivatives thereof, diesters which are the esters of diacrylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkylidene succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, adipic acid, linoleic acid dimers, malonic acid, alkyl malonic acids, alkyl 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, diolyl sebacate, disuccinyl azelate, disodicyl azelate, dioctyl phthalate, dicetyl 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 C30 monocarboxylic acids with polyols and/or polyolester, such as neopentyl glycol, trimethylol propane, pentaerythritol, etc.

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.

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In USP 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 1 to 10 mm²/s, and from 1 to 49 wt% of a high viscosity polyalphaolefin having a kinematic viscosity at 100°C of from 40 to 500 mm²/s.

In USP 5,089,156 is directed to lubricating oil compositions comprising a major amount of a polyalphaolefin fluid having a kinematic viscosity at 100°C of 2 to 10 mm²/s, and minor amounts of a polyalphaolefin fluid having a kinematic viscosity @ 100°C of 40 to 120 mm²/s and antwear/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.

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.

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The formulation can also contain synthetic esters such as mixed C8 and C11 dialkyl phthalates, trimethylpropane trioleate, di-isotridecyl-adipate, pentaerythritol tetraheptanoate and the like. The Examples utilize mixtures of PAO 6, PAO 8, PAO 110 and disononyl adipate, dioctyl sebacate, dibutyl phthalate or di (tridecyl) phthalate along with performance additives.
DESCRIPTION OF THE INVENTION

[0011] USP 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 2 to 10 mm²/s, and 30 to 1 wt% of polyol ester fluid having a kinematic viscosity at 100°C of 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, diocetyl sebacate, dibutylyl phthalate, dioctyl sebacate, Emery 2935, Emery 2939.

[0012] USP 6,713,438 is directed to high performance engine oil and other liquid lubricants comprising 50 to 90 wt% of base oil selected from mineral oil, polyalpha olefin, hydrosisomerized Fischer-Tropsch wax and having a KV at 100°C of form 1.5 to 12 mm²/s, 0.1 to 20 wt% of a first polymer and 0.1 to 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 furmarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didicyclopentane, dilicosyl sebacate, etc.

[0013] 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 C₉-C₃₀ acids. Examples of such polyol esters are Mobil P-41 and Mobil P-51 esters (Mobil Chemical Company).

[0014] Published Patent Application US 2003/0195128 directed to a VI improving lubricant additive and lubricating oil composition. The additive comprises an olefin oligomer of 2,000 to 20,000 number average molecular weight and a viscosity of 75 to 3,000 mm²/s at 100°C and a hydrocarbyl aromatic which contains at least 5% of its weight from aromatic moieties and has a viscosity of 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 150 mm²/s and is used 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.

[0015] Published Patent Application US 2003/0207775 is directed to a lubricating fluid for automotive gears. The finished fluid has a viscosity index equal to or greater than 175.

[0016] The fluid comprises a high viscosity fluid, preferably polyalpha olefin blended with a lower viscosity fluid comprising a synthetic hydrocarbon which can also be polyol ester fluid. 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 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 (Estex™M11) Supersyn™2150 (PAO 150); additives, PAO-25 (SHF™23), Estex™M11, SHF™1003 (PAO-100) (high viscosity hydrocarbon fluid) and Supersyn™2300 (PAO 300). Estex™M11 is a commercially available ester which has a kinematic viscosity at 100°C in the range of 1.25 to 1.45 mm²/s.

[0017] 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 21,000 cP or less and a CCS @ -25°C of 3800 cP or less.

DESCRIPTION OF THE INVENTION

[0018] The present invention relates to an improved lubricating oil composition and its use for improving the fuel economy and energy efficiency of heavy duty geared machinery under high load conditions. The lubricating oil composition comprising from 20 to 75 wt%, preferably 30 to 60 wt%, more preferably 45 to 55 wt% of a polyalpha olefin fluid having a kinematic viscosity at 100°C (ASTM D-445-5) of between 2 to 10 mm²/s, preferably between 3.5 to 8 mm²/s, most preferably 3.5 to 6 mm²/s, 5 to 40 wt%, preferably 5 to 20 wt%, more preferably 8 to 12 wt% of a polyalpha olefin fluid...
having a kinematic viscosity at 100°C (ASTM D-445-5) between 150 to 3000 mm²/s, preferably between 150 to 1500 mm²/s, more preferably between 150 to 1000 mm²/s, still more preferably between 150 to 500 mm²/s, most preferably between 150 to 300 mm²/s, 10 to 40 wt%, preferably 15 to 30 wt%, more preferably 18 to 22 wt% of a polyalphaolefin fluid having a kinematic viscosity at 100°C (ASTM D-445-5) between 20 to 100 mm²/s, preferably between 20 to 80 mm²/s, more preferably between 20 to 60 mm²/s, most preferably between 20 to 40 mm²/s, 5 to 20 wt%, preferably 5 to 15 wt%, more preferably 8 to 12 wt% of one or more esters of dibasic acids with mono alkanols, most preferably esters of adipic acid, having a kinematic viscosity at 100°C of between 2 to 5 mm²/s, preferably 2 to 4.5 mm²/s, more preferably 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 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 0.0197 or less, preferably 0.0191 or less, a Brookfield viscosity at -40°C of 26,000 cP or less, preferably 21,000 cP or less and a CCS viscosity at -25°C of 4200 cP or less, preferably 3,600 cP or less, more preferably 3400 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 all weight percent based on the total weight of the lubricating oil composition.

0019 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 characteristics.

0020 Polyalphaolefins (PAOs) are a hydrocarbon base stock oil well known in the lubricating oil trade. PAOs are derived by the polymerization or copolymerization of alphaolefins having from 2 to 32 carbons, more typically C6, C10, C12, C14 olefins or mixtures thereof are utilized.

0021 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, Albemarl Corporation and others, typically vary from 250 to 3,000 or higher and may have viscosities at 100°C in the range from 2 to 3000 mm²/s or higher.

0022 The PAOs are typically comprised of relatively low molecular weight hydrogenated polymers or oligomers of alphaolefins which include, but are not limited to, C2 to C32 alphaolefins with C8 to C18 alphaolefins, such as 1-octene, 1-decene, 1-dodecene and the like, being preferred. The preferred polyalphaolefins are poly-1-octene, poly-1-decene and poly-1-dodecene and mixtures thereof and mixed olefin-derived polyolefins. However, the dimers of higher olefins in the range of C14 to C18 may be used to provide low viscosity 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.

0023 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 USP 4,149,178 or USP 3,822,291 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. 4,218,330.

0024 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 USP 4,827,073 (Wu); USP 4,827,064 (Wu); USP 4,967,032 (Ho et al); USP 4,926,004 (Pelrine et al); and, USP 4,794,254 (Pelrine). The dimers of the C14 to C18 olefins are described in USP 4,218,330. Commercially available high viscosity PAOs include SuperSyn™ 2150, SuperSyn™ 2300, SuperSyn™ 21000, SuperSyn™ 23000 (ExxonMobil Chemical Company).

0025 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.

0026 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/100C/30 SSR.

0027 The present formulations are further preferably distinguished by the absence of viscosity index improvers, the presence of which is detrimental to traction coefficient.

0028 Esters of 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, or dieicosyl sebacate.

0029 The gear oil formulation contains at least one of a gear oil performance addition in an effective amount. By
Esters of glycerol may be used as antiwear agents. For example, mono-, di, and tri-oleates, mono-palmitates is to produce low SAP formulations. Alkyl (alkyl) are also useful antiwear agents. The use or addition of such materials should be kept to a minimum if the object where each of R3-R6 are independently hydrogen or a hydrocarbon radical. Preferred hydrocarbon radicals are alkyl or alkenyl radicals. Any two of R3-R6 may be connected so as to form a cyclic ring. Additional information concerning sulfurized olefins and their preparation can be found in USP 4,941,984.

Antiwear and EP Additives

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. 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 dialkyldithio phosphate in which the primary metal constituent is zinc, or zinc dialkyldithiophosphate (ZDDP). ZDDP compounds generally are of the formula \( \text{Zn(SP(S)(OR1)(OR2))}_2 \) where R1 and R2 are C1-C18 alkyl groups, preferably C2-C12 alkyl groups. These alkyl groups may be straight chain or branched. The ZDDP is typically used in amounts of from 0.4 to 6 wt%, preferably 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 420-1500 ppm P and 450 to 1600 ppm Zn.

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, alylaliphatic or alicyclic olefinic hydrocarbons containing from 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

\[ R^3R^4C=CR^5R^6 \]

where each of R3-R6 are independently hydrogen or a hydrocarbon radical. Preferred hydrocarbon radicals are alkyl or alkenyl radicals. Any two of R3-R6 may be connected so as to form a cyclic ring. Additional information concerning sulfurized olefins and their preparation can be found in USP 4,941,984.

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 USP 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 USP 4,501,678. USP 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 USP 5,693,598. Thiocarbamate/molybdenum complexes such as moly-sulfur alkyl dithiocarbamate trimer complex (R=C8-C18 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.

Esters of glycerol may be used as antiwear agents. For example, mono-, di, and tri-oleates, mono-palmitates and mono-myristates may be used. ZDDP can be combined with other compositions that provide antiwear properties. USP 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. USP 5,034,142 discloses that use of a metal alkoyxalkylxanthate (nickel ethoxyethylxanthate, for example) and a dixanthogen (diethoxyethyl dixanthogen, for example) in combination with ZDDP improves antiwear properties. Preferred antiwear additives include phosphorus and sulfur compounds such as zithiophosphates and/or sulfur, nitrogen, boron, molybdenum phosphorodithioates, molybdenum dithiocarbamates and various organo-molybdenum derivatives including heterocyclics, for example dimercaptodithiazoles, mercaptobenzothiazoles, triazines, and the like, alicyclics, amines, alcohols, esters, diols, triols, fatty amines and the like can also be used. Such additives may be used in an amount of 0.01 to 6 wt%, preferably 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

[0038] 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, Klamm in Lubricants and Related Products, op cit, and U.S. Patents 4,798,684 and 5,084,197, for example.

[0039] 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 C3+ 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-alkylphenolic proprionic ester derivatives. Bis-phenolic antioxidants may also be advantageous-

ly 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).

[0040] 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 R1R2R3R4N where R1 is an aliphatic, aromatic or substituted aromatic group, R2 is an aromatic or a substituted aromatic group, and R3 is a is H, alkyl, aryl or R1S(O)xR12 where R3 is an alkylene, alkenylene, or aralkylene group, R12 is a higher alkyl group, or an alkyl, aryl, or alkenyl group, and x is 0, 1 or 2. The aliphatic group R3 may contain from 1 to 20 carbon atoms, and preferably contains from 6 to 12 carbon atoms. The aliphatic group is a saturated aliphatic group. Preferably, both R5 and R6 are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring aromatic group such as naphthyl. Aromatic groups R5 and R6 may be joined together with other groups such as S.

[0041] Typical aromatic amines antioxidants have alkyl substituent groups of at least 6 carbon atoms. Examples of aliphatic groups include hexyl, heptyl, octyl, nonyl, and decyl. Generally, the aliphatic groups will not contain more than 14 carbon atoms. The general types of amine antioxidants useful in the present compositions include diphenylamines, phenyl naphthylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more aromatic amines are also useful. Polymeric amine antioxidants can also be used. 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’-dioctyldiphenylamine; t-octylphenyl-alphanaphthylamine; phenyl-alphanaphthylamine; and p-octylphenyl-alphanaphthylamine.

[0042] Sulphurized 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 phosphates such as the dialkyl dithiocarbamates and mixtures thereof are also useful antioxidants.

[0043] 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 dihydrocarbonyl thio- or dithio-phosphates and copper salts of carboxylic acid (naturally occurring or synthet). Other suitable copper salts include copper dithiacarbamates, sulphonates, phenates, and acetylaconates. 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.

[0044] Preferred antioxidants include hindered phenols, arylamines. These antioxidants may be used individually by type or in combination with one another. Such additives may be used in an amount of 0.01 to 5 wt%, preferably 0.01 to 1.5 wt%.

Detergents

[0045] 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.

[0046] Salts that contain a substantially stochiometric amount of the metal are described as neutral salts and have a total base number (TBN, as measured by ASTM D2896) of from 0 to 80. Many compositions are overbased, containing large amounts of a metal base that is achieved by reacting an excess of a metal compound (a metal hydroxide or oxide,
for example) with an acidic gas (such as carbon dioxide). Useful detergents can be neutral, mildly overbased, or highly overbased.

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

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

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

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.

Alkaline earth phenates are another useful class of detergent. These detergents can be made by reacting alkaline earth metal hydroxide or oxide (CaO, Ca(OH)$_2$, BaO, Ba(OH)$_2$, MgO, Mg(OH)$_2$, for example) with an alkyl phenol or sulfurized alkylphenol. Useful alkyl groups include straight chain or branched C$_1$-C$_{30}$ alkyl groups, preferably, C$_4$-C$_{20}$. Examples of suitable phenols include isobutylphenol, 2-ethylhexylphenol, nonylphenol, dodecyl phenol, and the like. It should be noted that starting alkylphenols may contain more than one alkyl substituent that are each independently straight chain or branched. When a non-sulfurized alkylphenol is used, the sulfurized product may be obtained by methods well known in the art. These methods include heating a mixture of alkylphenol and sulfurizing agent (including elemental sulfur, sulfur halides such as sulfur dichloride, and the like) and then reacting the sulfurized phenol with an alkaline earth metal base.

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

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

Hydrocarbyl-substituted salicylic acids may be prepared from phenols by the Kolbe reaction. See USP 3,595,791, 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.

Alkaline earth metal phosphates are also used as detergents.

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 USP 6,034,039 for example.

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 0.01 to 6.0 wt%, preferably, 0.1 to 0.4 wt%.
Supplementary Dispersant

[0057] 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 non-borated dispersants can be used in amount of 0.1 to < 20 wt% preferably 0.1 to 8 wt% on an as received basis.

Pour Point Depressants

[0058] 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 dialkyulfumimates, vinyl esters of fatty acids and alkyld 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 0.01 to 5 wt%, preferably 0.01 to 1.5 wt%.

Corrosion Inhibitors/Metal Deactivators

[0059] 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 tetrapropenyl succinic mono esters, and imidazoline succinic anhydride derivatives. See, for example, USP Nos. 2,719,125; 2,719,126; and 3,087,932. Such additives may be used in an amount of 0.01 to 5 wt%, preferably 0.01 to 1.5 wt%.

Seal Compatibility Additives

[0060] 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 0.01 to 3 wt%, preferably 0.01 to 2 wt%.

Anti-Foam Agents

[0061] 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.

Inhibitors and Antirust Additives

[0062] Antitrust 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.

[0063] One type of antitrust additive is a polar compound that wets the metal surface preferentially, protecting it with a film of oil. Another type of antitrust 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 antitrust 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 0.01 to 5 wt%, preferably 0.01 to 1.5 wt%.

Friction Modifiers

[0064] 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, glycerals, partial ester glycerols, thiol, carboxylates, carboxamides, thiocarboxamides, dithiocarbonates, phosphates, thiophosphates, dithiophosphates, amides, imides, amines, thiaizoles, 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 USP 5,824,627; USP 6,232,276; USP 6,153,564; USP 6,143,701; USP 6,110,878; USP 5,837,657; USP 6,010,987; USP 5,906,968; USP 6,734,150; USP 6,730,638; USP 6,689,725; USP 6,569,820; WO 99/66013; WO 99/47629; WO 98/26030. [0065] Ashless friction modifiers may have also include lubricant materials that contain effective amounts of polar groups, for example, hydroxyl-containing hydrocarbyl base oils, glycerals, partial glycerals, 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. [0066] Useful concentrations of friction modifiers may range from 0.01 wt% to 10-15 wt% or more, often with a preferred range of 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 10 ppm to 3000 ppm or more, and often with a preferred range of 20-2000 ppm, and in some instances a more preferred range of 30-1000 ppm. Friction modifiers of all types may be used alone or in mixtures with the materials of this 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

[0067] 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. [0068] 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. [0069] Chemically, many dispersants may be characterized as phenates, sulfonates, sulfurized phenates, salicylates, naphthenates, stearates, carboxamides, thiocarboxamides, 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 constitutes the oleophoric 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; 3,2145,707; 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. 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. [0070] 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.
[0071] 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 1:1 to 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.

[0072] 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.

[0073] 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 hexamethylene-diamine. Representative examples are shown in USP 4,426,305.

[0074] 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.

[0075] Mannich base dispersants are made from the reaction of alkylphenols, formaldehyde, and amines (See USP 4,767,551). 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.

[0076] 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.

[0077] Examples of high molecular weight alkyl-substituted hydroxyaromatic compounds are polypropylphenol, polybutylene, and other polyalkylphenols. These polyalkylphenols can be obtained by the alkylation, in the presence of an alkylating catalyst, such as BF3, of phenol with high molecular weight polypropylene, polybutylene, and other polyalkylene compounds to give alkyl substituents on the benzene ring of phenol having an average 600-100,000 molecular weight.

[0078] Other representative organic compounds containing at least one HN(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., ethyleneamine and diethanolamine; aromatic diamines, e.g., benzidine diamine, diamino naphthalenes; heterocyclic amines, e.g., morpholine, pyrrole, pyrrolidine, imidazole, imidazolidine, and piperidine; melamine and their substituted analogs.

[0079] Examples of alkylene polyamide reactants include ethylenediamine, diethylene triamine, triethylene tetraamine, tetraethylene pentaamine, pentaethylene hexamine, hexaethylene heptaamine, heptaethylene octamine, octaethylene nonamine, nonaethylene decamine, and decaethylene undecamine and mixture of such amines having nitrogen contents corresponding to the alkylene polyamines, in the formula H2N-(Z-NH)ₙ-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 polyamines are usually obtained by the reaction of ammonia and dihalo alkanes, such as dichloroalkanes. 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.

[0080] 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.

[0081] Hydrocarbon 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.

[0082] Borated dispersants can be used. Any dispersant containing either or both of nitrogen and/or oxygen atoms can be borated.

[0083] 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 hydrocarbonyl succinimide is derived from a hydrocarbonyl group such as polyisobutylene having a Mn of from 500 to 5000 or a mixture of such hydrocarbonyl groups. Other preferred dispersants include succinic acid-esters and amides, alkylphenol-polyamine-coupled Mannich adducts, their capped derivatives, and other related components. Such additives may be used in an amount of 0.1 to 20 wt%, preferably 0.1 to 8 wt%.

Typical Additive Amounts

[0084] 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.

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Approximate Wt% (Useful)</th>
<th>Approximate Wt% (Preferred)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detergent</td>
<td>0.01-6</td>
<td>0.01-4</td>
</tr>
<tr>
<td>Dispersant</td>
<td>0.1-20</td>
<td>0.1-8</td>
</tr>
<tr>
<td>Friction Reducer</td>
<td>0.01-5</td>
<td>0.01-1.5</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>0.0-5</td>
<td>0.0-1.5</td>
</tr>
<tr>
<td>Corrosion Inhibitor</td>
<td>0.01-5</td>
<td>0.01-1.5</td>
</tr>
<tr>
<td>Anti-wear Additive</td>
<td>0.01-6</td>
<td>0.01-4</td>
</tr>
<tr>
<td>Pour Point Depressant</td>
<td>0.0-5</td>
<td>0.01-1.5</td>
</tr>
<tr>
<td>Anti-foam Agent</td>
<td>0.001-3</td>
<td>0.001-0.15</td>
</tr>
<tr>
<td>Base Oil</td>
<td>Balance</td>
<td>Balance</td>
</tr>
</tbody>
</table>

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

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

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

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.

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

In both instances the 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 viscometrics 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.

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™ M11 (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).

[0093] 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 standpoint 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>
<thead>
<tr>
<th></th>
<th>Comparative Example 1</th>
<th>Comparative Example 2</th>
<th>Comparative Example 3</th>
<th>Comparative Example 4</th>
<th>Comparative Example 5</th>
<th>Comparative Example 6</th>
<th>Comparative Example 7</th>
<th>Example 1 (ref.)</th>
<th>Example 2</th>
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<tbody>
<tr>
<td><strong>Commercial adpack (wt%) (as received)</strong></td>
<td>10</td>
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<td></td>
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<tr>
<td><strong>Custom adpack (wt%) (as received)</strong></td>
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<td><strong>Ditridecyl adipate, 5.1-55 mm²/s</strong></td>
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<td><strong>TMP ester of C₈-C₁₀ acid, 4.2-4.5 mm²/s</strong></td>
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<td><strong>Emoline 2958, 2.8-2.9 mm²/s</strong></td>
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<td><strong>KV 100 (D445-5)</strong></td>
<td>11.23, 11.3</td>
<td>11.56, 11.62</td>
<td>11.87, 11.95</td>
<td>9.74</td>
<td>18.25, 18.89</td>
<td>10.36</td>
<td>9.447</td>
<td>11.01, 11.07</td>
<td>10.36, 10.39</td>
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<tr>
<td><strong>KV 40 (D445-3)</strong></td>
<td>68.75, 68.2</td>
<td>71.62, 71.3</td>
<td>74.65, 74.28</td>
<td>55.97</td>
<td>127.07, 130.63</td>
<td>58.83</td>
<td>51.11</td>
<td>66.41, 66.06</td>
<td>56.69, 59.31</td>
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<tr>
<td><strong>Viscosity index</strong></td>
<td>156</td>
<td>156</td>
<td>154</td>
<td>160</td>
<td>161</td>
<td>166</td>
<td>171</td>
<td>158</td>
<td>174</td>
</tr>
<tr>
<td>Example 1 (ref.)</td>
<td>Comparative Example 2</td>
<td>Comparative Example 3</td>
<td>Comparative Example 4</td>
<td>Comparative Example 5</td>
<td>Comparative Example 6</td>
<td>Comparative Example 7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------</td>
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<td>-----------------------</td>
<td>-----------------------</td>
<td>-----------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BF viscosity @ -40°C (D2983-31)</td>
<td>30,094</td>
<td>35,892</td>
<td>44,787</td>
<td>17,896</td>
<td>13,640; 14,000; 15,460</td>
<td>76,384</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>CCS viscosity @ -25°C (D5293-5)</td>
<td>4,510</td>
<td>5,176</td>
<td>6,380</td>
<td>3,260</td>
<td>3,260</td>
<td>2,550</td>
<td></td>
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<tr>
<td>Traction coefficient (16N/100°C/30 SSR)*</td>
<td>0.02161</td>
<td>0.02228</td>
<td>0.02382</td>
<td>0.02025</td>
<td>0.009751</td>
<td>0.009873</td>
<td></td>
<td></td>
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<tr>
<td>ASTM D5800 (% evaporation)</td>
<td>8.9</td>
<td>9.0</td>
<td>12.5</td>
<td>18.6</td>
<td>10.894</td>
<td>14,118</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASTM D97 (flash point, °C)</td>
<td>234</td>
<td>206</td>
<td>242.0</td>
<td>234</td>
<td>10,894</td>
<td>3,260</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDSC (onset temperature)</td>
<td>265.6</td>
<td>264.6</td>
<td>267.1</td>
<td>267.8</td>
<td>265.6</td>
<td>264.6</td>
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</tr>
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</table>

* Determined using Mini Traction Machine
1. A lubricating oil composition comprising from 20 to 75 wt% of a polyalphaolefin fluid having a kinematic viscosity at 100°C of between 2 to 10 mm²/s, 5 to 40 wt% of a polyalphaolefin fluid having a kinematic viscosity at 100°C of between 150 to 3,000 mm²/s, 10 to 40 wt% of a polyalphaolefin fluid having a kinematic viscosity at 100°C of between 20 to 100 mm²/s, 5 to 20 wt% of one or more esters of dibasic acids with mono alkanols having a kinematic viscosity at 100°C of between 2 to 5 mm²/s and a pour point of at least -25°C, all wt% being based on the total lubricant composition, the lubricating oil composition further containing at least one gear oil performance additive and being characterized by having a kinematic viscosity at 100°C by ASTM D-445-5 of between 9 and 12.5 mm²/s and exhibiting a traction coefficient value, measured as the 16N/100°C/30 SSR value by the mini traction machine, of 0.0197 or less, a Brookfield viscosity at -40°C by ASTM D-2983-31 of 26,000 cP or less, and a CCS viscosity at -25°C by ASTM D-5293-5 of 4200 cP or less, a flash point by ASTM D-97 of 220°C or higher and a NOACK volatility by ASTM D-5800 of 15% or less.

2. The lubricating oil composition of claim 1, wherein the lubricating oil composition comprises 30 to 60 wt% of a PAO fluid having a kinematic viscosity at 100°C of between 3.5 to 8 mm²/s, 5 to 20 wt% of a PAO fluid having a kinematic viscosity of between 150 to 1500 mm²/s, 15 to 30 wt% of a PAO fluid having a kinematic viscosity at 100°C of between 20 to 80 mm²/s, 5 to 15 wt% of an ester having a kinematic viscosity at 100°C of between 2 to 4.5 mm²/s and further containing at least one gear oil performance additive.

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

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

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

6. The lubricating oil composition of claim 1, comprising from 5 to 15 wt% of one or more diesters having a kinematic viscosity at 100°C of between 2 to 4.5 mm²/s.

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

8. The lubricating oil composition of any of claims 1 to 6, characterized by a traction coefficient value measured as the 16N/100°C/30 SSR value of 0.0191 or less.

9. The lubricating oil composition of any of claims 1 to 6, characterized by a Brookfield viscosity at -40°C of 21,000 cP or less, a flash point of 230°C or higher and a NOACK volatility of 15% or less.

10. The lubricating oil composition of any of claims 1 to 6, characterized by a CCS viscosity at -25°C of 3,600 cP or less.

11. The lubricating oil composition of any of claims 1 to 6, characterized by a CCS viscosity at -25°C of 3400 cP or less.

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

13. The lubricating oil composition of claim 1 to 6, characterized by the absence of viscosity index improvers.

14. Use of the lubricating oil according to any of claims 1 to 13 for improving the fuel economy and energy efficiency of heavy duty geared machinery operated under high load conditions.
Patentansprüche

1. Schmierölzusammensetzung, die 20 bis 75 Gew.-% Poly-α-olefin-Fluid mit einer kinematischen Viskosität bei 100°C von 2 bis 10 mm²/s, 5 bis 40 Gew.-% Poly-α-olefin-Fluid mit einer kinematischen Viskosität bei 100°C von 150 bis 3000 mm²/s, 10 bis 40 Gew.-% Poly-α-olefin-Fluid mit einer kinematischen Viskosität bei 100°C von 20 bis 100 mm²/s, 5 bis 20 Gew.-% eines oder mehrerer Ester von zweibasigen Säuren mit Monoalkoholen mit einer kinematischen Viskosität bei 100°C von 2 bis 5 mm²/s und einem Fließpunkt von mindestens -25°C, wobei alle Gew.-% auf die gesamte Schmierzusammensetzung bezogen sind, wobei die Schmierölzusammensetzung ferner mindestens ein Getriebölleistungsadditiv enthält und dadurch gekennzeichnet ist, dass sie eine kinematische Viskosität bei 100°C gemäß ASTM D-445-5 von 9 bis 12,5 mm²/s aufweist und einen Traktionskoeffizientwert, gemessen als 16N/100°C/30 SSR-Wert durch das Minitraktionsgerät, von 0,0197 oder niedriger, eine Brookfield-Viskosität bei -40°C gemäß ASTM D-2983-31 von 26.000 cP oder niedriger und eine CCS-Viskosität bei -25°C gemäß ASTM D-5293-5 von 4200 cP oder niedriger, einen Flammkugeltest gemäß ASTM D-97 von 220°C oder höher und eine NOACK-Flüchtigkeit gemäß ASTM D-5800 von 15% oder niedriger aufweist.

2. Schmierölzusammensetzung nach Anspruch 1, bei der die Schmierölzusammensetzung 30 bis 60 Gew.-% PAO-Fluid mit einer kinematischen Viskosität bei 100°C von 3,5 bis 8 mm²/s, 5 bis 20 Gew.-% PAO-Fluid mit einer kinematischen Viskosität von 150 bis 1500 mm²/s, 15 bis 30 Gew.-% PAO-Fluid mit einer kinematischen Viskosität bei 100°C von 20 bis 80 mm²/s, 5 bis 15 Gew.-% Ester mit einer kinematischen Viskosität bei 100°C von 2 bis 4,5 mm²/s umfasst und ferner mindestens ein Getriebölleistungsadditiv enthält.

3. Schmierölzusammensetzung nach Anspruch 1, bei der die Schmierölzusammensetzung 30 bis 60 Gew.-% PAO-Fluid mit einer kinematischen Viskosität bei 100°C von 2 bis 10 mm²/s umfasst.

4. Schmierölzusammensetzung nach Anspruch 1, bei der die Schmierölzusammensetzung 5 bis 20 Gew.-% PAO-Fluid mit einer kinematischen Viskosität bei 100°C von 150 bis 3000 mm²/s umfasst.

5. Schmierölzusammensetzung nach Anspruch 1, bei der die Schmierölzusammensetzung 15 bis 30 Gew.-% PAO-Fluid mit einer kinematischen Viskosität bei 100°C von 20 bis 100 mm²/s umfasst.

6. Schmierölzusammensetzung nach Anspruch 1, die 5 bis 15 Gew.-% eines oder mehrerer Diester mit einer kinematischen Viskosität bei 100°C von 2 bis 4,5 mm²/s umfasst.

7. Schmierölzusammensetzung nach einem der Ansprüche 1 bis 6, bei der die Schmierölzusammensetzung 45 bis 55 Gew.-% PAO-Fluid mit einer kinematischen Viskosität bei 100°C von 3,5 bis 6 mm²/s, 8 bis 12 Gew.-% PAO-Fluid mit einer kinematischen Viskosität bei 100°C von 150 bis 500 mm²/s, 18 bis 22 Gew.-% PAO-Fluid mit einer kinematischen Viskosität von 20 bis 60 mm²/s umfasst.

8. Schmierölzusammensetzung nach einem der Ansprüche 1 bis 6, gekennzeichnet durch einen Traktionskoeffizientwert, gemessen als 16N/100°C/30 SSR-Wert, von 0,0191 oder niedriger.


10. Schmierölzusammensetzung nach einem der Ansprüche 1 bis 6, gekennzeichnet durch eine CCS-Viskosität bei -25°C von 3600 cP oder niedriger.

11. Schmierölzusammensetzung nach einem der Ansprüche 1 bis 6, gekennzeichnet durch eine CCS-Viskosität bei -25°C von 3400 cP oder niedriger.


13. Schmierölzusammensetzung nach einem der Ansprüche 1 bis 6, gekennzeichnet durch die Abwesenheit von Viskositätsindexverbesserern.
14. Verwendung der Schmierölzusammensetzung gemäß einem der Ansprüche 1 bis 13 zur Verbesserung der Brennstoffwirtschaftlichkeit und Energieeffizienz von Schwerlastgetriebegeräten, die unter Hochlastbedingungen betrieben werden.

Revendications

1. Composition d’huile lubrifiante comprenant 20 à 75 % en poids d’une polyalphaoléfine liquide ayant une viscosité cinématique à 100 °C comprise entre 2 et 10 mm²/s, 5 à 40 % en poids d’une polyalphaoléfine liquide ayant une viscosité cinématique à 100 °C comprise entre 150 et 3000 mm²/s, 10 à 40 % en poids d’une polyalphaoléfine liquide ayant une viscosité cinématique à 100 °C comprise entre 20 et 100 mm²/s, 5 à 20 % en poids d’un ou plusieurs esters d’acides dibasiques avec des monoalcools ayant une viscosité cinématique à 100 °C comprise entre 2 et 5 mm²/s et un point d’écoulement d’au moins -25 °C, tous les % en poids étant basés sur la composition totale de lubrifiant, la composition d’huile lubrifiante contenant en outre au moins un additif de performance pour huile pour engrenages et étant caractérisée en ce qu’elle a une viscosité cinématique à 100 °C selon l’ASTM D-445-5 comprise entre 9 et 12,5 mm²/s et présente une valeur de coefficient de traction, mesurée comme la valeur 16 N/100 °C/30 SSR par la machine de minitraction, de 0,0197 ou moins, une viscosité Brookfield à -40 °C selon l’ASTM D-2983-31 de 26 000 cP ou moins, et une viscosité CCS à -25 °C selon l’ASTM D-5293-5 de 4200 cP ou moins, un point d’éclair selon l’ASTM D-97 de 220 °C ou plus et une volatilité NOACK selon l’ASTM D-5800 de 15 % ou moins.

2. Composition d’huile lubrifiante selon la revendication 1, la composition d’huile lubrifiante comprenant 30 à 60 % en poids d’une PAO liquide ayant une viscosité cinématique à 100 °C comprise entre 3,5 et 8 mm²/s, 5 à 20 % en poids d’une PAO liquide ayant une viscosité cinématique comprise entre 150 et 1500 mm²/s, 15 à 30 % en poids d’une PAO liquide ayant une viscosité cinématique à 100 °C comprise entre 20 et 80 mm²/s, 5 à 15 % en poids d’un ester ayant une viscosité cinématique à 100 °C comprise entre 2 et 4,5 mm²/s, et contenant en outre au moins un additif de performance pour huile pour engrenages.

3. Composition d’huile lubrifiante selon la revendication 1, la composition d’huile lubrifiante comprenant 30 à 60 % en poids d’une PAO liquide ayant une viscosité cinématique à 100 °C comprise entre 2 et 10 mm²/s.

4. Composition d’huile lubrifiante selon la revendication 1, la composition d’huile lubrifiante comprenant 5 à 20 % en poids d’une PAO liquide ayant une viscosité cinématique à 100 °C comprise entre 150 et 3000 mm²/s.

5. Composition d’huile lubrifiante selon la revendication 1, la composition d’huile lubrifiante comprenant 15 à 30 % en poids d’une PAO liquide ayant une viscosité cinématique à 100 °C comprise entre 20 et 100 mm²/s.

6. Composition d’huile lubrifiante selon la revendication 1, comprenant 5 à 15 % en poids d’un ou plusieurs diesters ayant une viscosité cinématique à 100 °C comprise entre 2 et 4,5 mm²/s.

7. Composition d’huile lubrifiante selon l’une quelconque des revendications 1 à 6, la composition d’huile lubrifiante comprenant 45-55 % en poids d’une PAO liquide ayant une viscosité cinématique à 100 °C comprise entre 3,5 et 6 mm²/s, 8 à 12 % en poids d’une PAO liquide ayant une viscosité cinématique à 100 °C comprise entre 150 et 500 mm²/s, 18 à 22 % en poids d’une PAO liquide ayant une viscosité cinématique comprise entre 20 et 60 mm²/s.

8. Composition d’huile lubrifiante selon l’une quelconque des revendications 1 à 6, caractérisée par une valeur de coefficient de traction mesurée comme la valeur 16 N/100 °C/30 SSR de 0,0191 ou moins.

9. Composition d’huile lubrifiante selon l’une quelconque des revendications 1 à 6, caractérisée par une viscosité Brookfield à -40 °C de 21 000 cP ou moins, un point d’éclair de 230 °C ou plus et une volatilité NOACK de 15 % ou moins.

10. Composition d’huile lubrifiante selon l’une quelconque des revendications 1 à 6, caractérisée par une viscosité CCS à -25 °C de 3600 cP ou moins.

11. Composition d’huile lubrifiante selon l’une quelconque des revendications 1 à 6, caractérisée par une viscosité CCS à -25 °C de 3400 cP ou moins.
12. Composition d’huile lubrifiante selon la revendication 7, caractérisée par une valeur de coefficient de traction mesurée comme la valeur 16 N/100 °C/30 SSR de 0,0191 ou moins, une viscosité Brookfield à -40 °C de 21 000 cP ou moins et une viscosité CCS à -25 °C de 3600 cP ou moins, un point d’éclair de 230 °C ou plus et une volatilité NOACK de 13 % ou moins.

13. Composition d’huile lubrifiante selon l’une quelconque des revendications 1 à 6, caractérisée par l’absence d’agents améliorant l’indice de viscosité.

14. Utilisation de l’huile lubrifiante selon l’une quelconque des revendications 1 à 13 pour améliorer l’économie de carburant et le rendement énergétique d’une machinerie à engrenages renforcés fonctionnant dans des conditions de forte charge.
REFERENCES CITED IN THE DESCRIPTION

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