METHOD FOR IMPROVING THE FUEL EFFICIENCY OF ENGINE OIL COMPOSITIONS FOR LARGE LOW, MEDIUM AND HIGH SPEED ENGINES BY REDUCING THE TRACTION COEFFICIENT

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

[0001] The present invention relates to the operation of large low, medium and high speed engines using additized lubricating oil formulations.

DESCRIPTION OF THE RELATED ART

[0002] Diesel engines designed for marine and stationary power applications can be either 2-stroke or 4-stroke cycle having up to 20 cylinders and are typically classified as low-speed, medium-speed or high-speed diesel engines. These engines burn a wide variety of fuels ranging from residual or heavy fuel oils to natural gas (diesel compression or spark-ignited) and are most commonly used for marine propulsion, marine auxiliary (vessel electricity generation), distributed power generation and combined heating and power (CHP). Lubrication of such engines can be all-loss (i.e., lubricant fed directly to the cylinder by cylinder oil) or recirculation involving oil sumps. Lubrication of critical engine parts includes piston rings, cylinder liners, bearings, piston cooling, fuel pump, engine control hydraulics, etc. Fuel is typically the major cost of operating these engines and a typical 12 cylinder, 90 cm bore low-speed diesel engine used in marine vessel container service will burn up to approximately $33M of heavy fuel per year at today's price of $480/MT. Therefore, a fuel efficiency gain of as little as 1% would result in approximately up to $330k annual savings to the ship operator. In addition, governmental organizations, such as the International Marine Organization, U.S.

Environmental Protection Agency and the California Air Resources Board are legislating emissions requirements for these engines. Improving fuel efficiency will reduce emissions (CO_2, SO_x, No_x and Particulate Matter) commensurately which should result in some emissions credit trading value.

[0003] In addition to providing adequate oil film thickness to prevent metal-to-metal contact, lubricants for these engines are designed to cope with a variety of other stresses, including neutralizing acids formed by the combustion of fuels containing sulfur to minimize corrosive wear of the piston rings and cylinder liner, minimizing engine deposits formed by fuel combustion and by contamination of the lubricant with raw or partially burned fuel, resisting thermal/oxidation degradation of the lubricant due to the extreme heat in these engines, transferring heat away from the engine, etc.

[0004] A long term requirement is that the lubricant must maintain cleanliness within the high temperature environment of the engine, especially for critical components such as the piston and piston rings. Contamination of the engine oil in the engine by the accumulation in it of raw and partially burned fuel combustion products, water, soot as well as the thermal/oxidation degradation of the oil itself can degrade the engine cleanliness performance of the engine oil. Therefore, it is desirable for engine oils to be formulated to have good cleanliness qualities and to resist degradation of those qualities due to contamination and thermal/oxidative degradation.

[0005] U.S. Patent 6,339,051 is directed to a diesel engine cylinder oil of improved cleanliness and load carrying ability and reduced port deposit characteristics for use in marine and stationary slow speed diesel engines comprising a medium heavy Group I or Group II neutral base oil, typically 300 to 500-600 SUS (KV at 100°C of about 12 mm^2/s and less) in combination with a liquid, oil miscible polyisobutylene (PIB) and an additive package comprising

a detergent, preferably one or more of an overbased phenate, phenylate, salicylate or sulfonate, an anti-oxidant, an anti-wear agent and a dispersant. The finished lubricant has a KV at 100°C in the range 15 to 25 mm^2/s and a total base number in the range 40 to 100 mg KOH/g.

[0006] Gas engine oil of enhanced life as evidenced by an increase in the resistance of the oil to oxidation, nitration and deposit formation is the subject of U.S. Patent No. 5,726,133. The gas engine oil of that patent is a low ash gas engine oil comprising a major amount of a base oil of lubricating viscosity and a minor amount of an additive mixture comprising a mixture of detergents comprising at least one alkali or alkaline earth metal salt having a Total Base Number (TBN) of about 250 and less and a second alkali or alkaline earth metal salt having a TBN lower than the aforesaid component. The TBN of this second alkali or alkaline earth metal salt will typically be about half or less that of the aforesaid component.

[0007] U.S. Patent 6,191,081 is directed to a lubricating oil composition for natural gas engines comprising a major amount of a base oil of lubricating viscosity and a minor amount of a mixture of one or more metal salicylate detergents and one or more metal phenate(s) and/or metal sulfonate detergents.

[0008] The lubricating oil base stock is any natural or synthetic lubricating base oil stock fraction typically having a kinematic viscosity at 100°C of about 5 to 20 cSt, more preferably about 7 to 16 cSt, most preferably about 9 to 13 cSt. In a preferred embodiment, the use of the viscosity index improver permits the omission of oil of viscosity about 20 cSt or more at 100°C from the lube base oil fraction used to make the present formulation. Therefore, a preferred base oil is one which contains little, if any, heavy fraction; e.g., little, if any, lube oil fraction of viscosity 20 cSt or higher at 100°C.

[0009] The lubricating oil base stock can be derived from natural lubricating oils, synthetic lubricating oils or mixtures thereof. Suitable lubricating oil base stocks include base stocks obtained by isomerization of synthetic wax and slack wax, as well as hydrocrackate base stocks produced by hydrocracking (rather than solvent extracting) the aromatic and polar components of the crude. Suitable base stocks include those in API categories I, II and III, where saturates level and Viscosity Index are:

Group I – less than 90% and 80-120, respectively;

Group II – greater than 90% and 80-120, respectively; and

Group III – greater than 90% and greater than 120, respectively.

[0010] The mixture of detergents comprises a first metal salt or group of metal salts selected from the group consisting of one or more metal sulfonates(s), salicylate(s), phenate(s) and mixtures thereof having a high TBN of greater than about 150 to 300 or higher, preferably about 160 to 300, used in an amount in combination with the other metal salts or groups of metal salts (recited below) sufficient to achieve a lubricating oil of at least 0.65 wt% sulfated ash content, a second metal salt or group of metal salts selected from the group consisting of one or more metal salicylate(s), metal sulfonate(s), metal phenate(s) and mixtures thereof having a medium TBN of greater than about 50 to 150, preferably about 60 to 120, and a third metal salt or group of metal salts selected from the group consisting of one or more metal sulfonate(s), metal salicylate(s) and mixtures thereof identified as neutral or low TBN, having a TBN of about 10 to 50, preferably about 20 to 40, the total amount of medium plus neutral/low TBN detergent being about 0.7 vol% or higher (active ingredient), preferably about 0.9 vol% or higher (active ingredient), most preferably about 1 vol% or higher (active ingredient), wherein at least one of the medium or low/neutral TBN detergent(s) is metal salicylate, preferably at least

one of the medium TBN detergent(s) is a metal salicylate. The total amount of high TBN detergents is about 0.3 vol% or higher (active ingredient), preferably about 0.4 vol% or higher (active ingredient), most preferably about 0.5 vol% or higher (active ingredient). The mixture contains salts of at least two different types, with medium or neutral salicylate being an essential component. The volume ratio (based on active ingredient) of the high TBN detergent to medium plus neutral/low TBN detergent is in the range of about 0.15 to 3.5, preferably 0.2 to 2, most preferably about 0.25 to 1.

[0011] The mixture of detergents is added to the lubricating oil formulation in an amount up to about 10 vol% based on active ingredient in the detergent mixture, preferably in an amount up to about 8 vol% based on active ingredient, more preferably 6 vol% based on active ingredient in the detergent mixture, most preferably between about 1.5 to 5.0 vol%, based on active ingredient in the detergent mixture. Preferably, the total amount of metal salicylate(s) used of all TBNs is in the range of between 0.5 vol% to 4.5 vol%, based on active ingredient of metal salicylate.

[0012] U.S. Published Application US2005/0059563 is directed to a lubricating oil composition, automotive gear lubricating composition and fluids useful in the preparation of finished automotive gear lubricants and gear oil comprising a blend of a PAO having a viscosity of between about 40 cSt (mm^2/s) @ 100°C, and an ester having a viscosity of less than or equal to about 2.0 cSt (mm^2/s) @ 100°C wherein the blend of PAO and ester has a viscosity index greater than or equal to the viscosity index of the PAO. The composition may further contain thickeners, anti-oxidants, inhibitor packages, anti-rust additives, dispersants, detergents, friction modifiers, traction improving additives, demulsifiers, defoamants, dyes and haze inhibitors.

[0013] U.S. Published Application US2003/0191032 is directed to a detergent additive for lubricating oil compositions comprising at least two of low, medium and high TBN detergents, preferably a calcium salicylate. The detergent is in a lubricating oil composition comprising at least one of Group II base stock, Group III base stock or wax isomerate base stock and mixtures thereof, and an optional minor quantity of a co-base stock(s). Co-base stocks include polyalpha olefin oligomeric low and medium and high viscosity oil, di-basic acid esters, polyol esters, other hydrocarbon oils, supplementary hydrocarbyl aromatics and the like.

[0014] US Published Application 2006/0276355 is directed to a lubricant blend for enhanced micropitting properties wherein the lubricant comprises at least two base stocks with a viscosity difference between the first and second base stock of greater than 96 (mm^2/s) @ 100°C. At least one base stock is a polyalpha olefin with a viscosity of less than 6 mm^2/s but greater than 2 mm^2/s, and the second base stock is a synthetic oil with a viscosity greater than 100 mm^2/s but less than 300 mm^2/s @ 100°C. The second base stock can be a high viscosity polyalpha olefin.

[0015] U.S. Published Application 2007/0289897 is directed to a lubricating oil blend comprising at least two base stocks with a viscosity difference between the first and second base stock of greater than 96 cSt (mm^2/s) @ 100°C, the lubricant exhibiting improved air release. The blend contains at least one synthetic PAO having a viscosity of less than 10 cSt (mm^2/s) but greater than 2 cSt (mm^2/s) @ 100°C and a second synthetic oil having a viscosity greater than 100 cSt (mm^2/s) but less than 300 mm^2/s @ 100°C. The lubricant can contain anti-wear, anti-oxidant, defoamant, demulsifier, detergent, dispersant, metal passivator, friction reducer, rust inhibitor additive and mixtures thereof.

[0016] U.S. Published Application 2007/0298990 is directed to a lubricating oil comprising at least two base stocks, the first base stock has a viscosity greater than 40 cSt (mm^2/s) @ 100°C and a molecular weight distribution (MWD) as a function of viscosity at least 10% less than algorithm:

$$MWD = 0.2223 + 1.0232 * \log (Kv \text{ at } 100°C \text{ in cSt})$$

and a second base stock with a viscosity less than 10 cSt (mm^2/s) @ 100°C. Preferably the difference in viscosity between the first and second stocks is greater than 30 cSt (mm^2/s) @ 100°C. Preferably the first stock is a metallocene catalyzed PAO base stock. The second stock can be selected from GTL lubricants, wax-derived lubricants, PAO, brightstock, brightstock with PIB, Group I base stocks, Group II base stocks, Group III base stocks and mixtures thereof. The lubricant can contain additives including detergents. Preferably the first stock has a viscosity of greater than 300 cSt (mm^2/s) @ 100°C, the second stock has a viscosity of between 1.5 cSt mm^2/s to 6 cSt (mm^2/s) @ 100°C. Preferably the difference in viscosity between the first and second stocks is greater than 96 cSt (mm^2/s) @ 100°C.

[0017] U.S. Published Application US2008/0207475 is directed to a lubricating oil comprising at least two base stocks, the first base stock having a viscosity of at least 300 cSt (mm^2/s) @ 100°C and a molecular weight distribution (MSD) as a function of viscosity at least 10% less than algorithm:

$$MWD = 0.2223 + 1.0232 * \log (KV @ 100°C \text{ in cSt})$$

and the second stock has a viscosity of less than 100 cSt (mm^2/s) @ 100°C. Preferably the difference in viscosity between the first and second stocks is greater than 250 cSt (mm^2/s) @ 100°C. Preferably the first stock is a metallocene catalyzed PAO base stock. The second stock can be chosen from GTL base stock, wax-derived base stock, PAO, brightstock, brightstock with

PIB, Group I base stock, Group II base stock, Group III base stock, Group V base stock, Group VI base stock and mixtures thereof. The lubricant can contain additives including detergents.

[0018] U.S. Patent 6,140,281 is directed to long life gas engine lubricating oils containing detergents. The lubricating oil comprises a major amount of a base oil of lubricating viscosity and a minor amount of a mixture of one or more metal sulfonate(s) and/or phenate(s) and one or more metal salicylate(s) detergents, all detergents in the mixture having the same or substantially the same Total Base Number (TBN).

[0019] The lubricating oil base stock is any natural or synthetic lubricating base stock fraction typically having a kinematic viscosity at 100°C of about 5 to 20 cSt (mm^2/s), more preferably about 7 to 16 cSt, (mm^2/s), most preferably about 9 to 13 cSt (mm^2/s). In a preferred embodiment, the use of the viscosity index improver permits the omission of oil of viscosity 20 cSt (mm^2/s) or more at 100°C from the lube base oil fraction used to make the present formulation. Therefore, a preferred base oil is one which contains little, if any, heavy fractions; e.g., little, if any, lube oil fraction of viscosity 20 cSt (mm^2/s) or higher at 100°C.

[0020] The lubricating oil base stock can be derived from natural lubricating oils, synthetic lubricating oils or mixtures thereof. Suitable lubricating oil base stocks include base stocks obtained by isomerization of synthetic wax and slack wax, as well as hydrocrackate base stocks produced by hydrocracking (rather than solvent extracting) the aromatic and polar components of the crude. Suitable base stocks include those in API categories I, II and III, where saturates level and Viscosity Index are:

Group I – less than 90% and 80-120, respectively;

Group II – greater than 90% and 80-120, respectively; and

Group III – greater than 90% and greater than 120, respectively.

[0021] The detergent is a mixture of one or more metal sulfonate(s) and/or metal phenate(s) with one or more metal salicylate(s). The metals are any alkali or alkaline earth metals; e.g., calcium, barium, sodium, lithium, potassium, magnesium, more preferably calcium, barium and magnesium. It is a feature of the present lubricating oil that each of the metal salts used in the mixture has the same or substantially the same TBN as the other metal salts in the mixture; thus, the mixture can comprise one or more metal sulfonate(s) and/or metal phenate combined with one or more metal salicylate(s) wherein each of the one or more metal salts is a low TBN detergent, or each is a medium TBN detergent or each is a high TBN detergent. Preferably each are low TBN detergent, each metal detergent having the same or substantially the same similar TBN below about 100. For the purposes of the specification and the claims, for the metal salts, by low TBN is meant a TBN of less than 100; by medium TBN is meant a TBN between 100 to less than 250; and by high TBN is meant a TBN of about 250 and greater. By the same or substantially similar TBN is meant that even as within a given TBN category; e.g., low, medium and high, the TBNs of the salts do not simply fall within the same TBN category but are close to each other in absolute terms. Thus, a mixture of sulfonate and/or phenate with salicylate of low TBN would not only be made up of salts of TBN less than 100, but each salt would have a TBN substantially the same as that of the other salts in the mixture; e.g., a sulfonate of TBN 60 paired with a salicylate of TBN 64, or a phenate of TBN 65 paired with a salicylate of TBN 64. Thus, the individual salts would not have TBNs at the extreme opposite end of the applicable TBN category, or varying substantially from each other.

[0022] The TBNs of the salts will differ by no more than about 15%, preferably no more than about 12%, more preferably no more than about 10% or less.

[0023] The one or more metal sulfonate(s) and/or metal phenate(s), and the one or more metal salicylate(s) are utilized in the detergent as a mixture, for example, in a ratio by parts of 5:95 to 95:5, preferably 10:90 to 90:10, more preferably 20:80 to 80:20.

[0024] The mixture of detergents is added to the lubricating oil formulation in an amount up to about 10 vol% based on active ingredient in the detergent mixture, preferably in an amount up to about 8 vol% based on active ingredient, more preferably up to about 6 vol% based on active ingredient in the detergent mixture, most preferably between about 0.3 vol% to 3 vol% based on active ingredient in the detergent mixture.

[0025] U.S. Patent 6,645,922 is directed to a lubricating oil for two-stroke cross-head marine diesel engines comprising a base oil and an oil-soluble overbased detergent additive in the form of a complex wherein the basic material of the detergent is stabilized by more than one surfactant. The more than one surfactants can be mixtures of: (1) surfulrized and/or non-sulfurized phenols and one other surfactant which is not a phenol surfactant; (2) sulfurized and/or non-sulfurized salicylic acid and one other surfactant which is not a salicylic surfactant; or (3) at least three surfactants which are sulfurized or non-sulfurized phenol, sulfurized or non-sulfurized salicylic acid and one other surfactant which is not a phenol or salicylic surfactant; or (4) at least three surfactants which are sulfurized or non-sulfurized phenol, sulfurized or non-sulfurized salicylic acid and at least one sulfuric acid surfactant.

[0026] The base stock is an oil of lubricating viscosity and may be any oil suitable for the system lubrication of a cross-head engine. The lubricating oil may suitably be an animal, vegetable or a mineral oil. Suitably the lubricating oil is a petroleum-derived lubricating oil, such as naphthenic base, paraffinic base or mixed base oil. Alternatively, the lubricating oil may be a synthetic

lubricating oil. Suitable synthetic lubricating oils include synthetic ester lubricating oils, which oils include diesters such as di-octyl adipate, di-octyl sebacate and tri-decyl adipate, or polymeric hydrocarbon lubricating oils, for example, liquid polyisobutene and polyalpha olefins. Commonly, a mineral oil is employed. The lubricating oil may generally comprise greater than 60, typically greater than 70 % by mass of the lubricating oil composition and typically have a kinematic viscosity at 100°C of from 2 to 40, for example, from 3 to 15 mm^2/s, and a viscosity index from 80 to 100, for example, from 90 to 95.

[0027] Another class of lubricating oil is hydrocracked oils, where the re fining process further breaks down the middle and heavy distillate fractions in the presence of hydrogen at high temperatures and moderate pressures. Hydrocracked oils typically have kinematic viscosity at 100°C of from 2 to 40, for example, from 3 to 15 mm^2/s, and a viscosity index typically in the range of from 100 to 110, for example, from 105 to 108.

[0028] Brightstock refers to base oils which are solvent-extracted, de-asphalted products from vacuum residuum generally having a kinematic viscosity at 100°C from 28 to 36 mm^2/s, and are typically used in a proportion of less than 30, preferably less than 20, more preferably less than 15, most preferably less than 10, such as less than 5 mass%, based on the mass of the lubricating oil composition.

[0029] U.S. Patent 6,613,724 is directed to gas fueled engine lubricating oil comprising an oil of lubricating viscosity, a detergent including at least one calcium salicylate having a TBN in the range 70 to 45, 0 to 0.2 mass% of nitrogen, based on the mass of the oil composition, of a dispersant and minor amounts of one or more co-additive. The base oil can be any animal, vegetable or mineral oil or synthetic oil. The base oil is used in a proportion of greater than 60 mass% of the composition. The oil typically has a viscosity at 100°C of

from 2 to 40, for example 3 to 15 mm^2/s and a viscosity index of from 80 to 100. Hydrocracked oils can also be used which have viscosities of 2 to 40 mm^2/s at 100°C and viscosity indices of 100 to 110. Brightstock having a viscosity at 100°C of from 28 to 36 mm^2/s can also be used, typically in a proportion less than 30, preferably less than 20, most preferably less than 5 mass%.

[0030] U.S. Patent 7,101,830 is directed to a gas engine oil having a boron content of more than 95 ppm comprising a major amount of a lubricating oil having a viscosity index of 80 to 120, at least 90 mass% saturates, 0.03 mass% or less sulfur and at least one detergent. Metal salicylate is a preferred detergent.

[0031] U.S. Patent 4,956,122 is directed to a lubricating oil composition containing a high viscosity synthetic hydrocarbon such as high viscosity PAO, liquid hydrogenated polyisoprenes, or ethylene-alpha olefin copolymers having a viscosity of 40-1000 cSt (mm^2/s) at 100°C, a low viscosity synthetic hydrocarbon having a viscosity of between 1 and 10 cSt (mm^2/s) at 100°C, optionally a low viscosity ester having a viscosity of between 1 and 10 cSt (mm^2/s) at 100°C and optionally up to 25 wt% of an additive package.

DESCRIPTION OF THE FIGURES

[0032] Figure 1 presents the effect on traction coefficient versus speed (mm/s) of formulations based on Group III (6.5 mm^2/s) base oil and Group IV base oil (PAO 150) and Group III (6.5 mm^2/s) base oil and Group IV base oil (PAO 300), all utilizing the same detergent package comprising a mixture of phenate and sulfonate, all formulations containing detergents having a formulation BN of 70, the blends differing in kinematic viscosity versus Reference Oil A.

[0033] Figure 2 presents the effect on traction coefficient versus speed (mm/s) of formulations based on Group III (6.5 mm^2/s) base oil and Group IV

base oil (PAO 150) blended to KV at 100°C of 20 mm^2/s utilizing different detergents versus Reference Oil A (Ref. A) and Reference Oil B (Ref. B) which is a blend containing just the mixture of base oils, oil formulations containing detergents having a formulation BN of 70.

[0034] Figure 3A presents the effect on traction coefficient versus speed (mm/s) of formulations based on Group III (6.5 mm^2/s) base oil and two different Group IV base oils (PAO 150 and PAO 300) blended to different kinematic viscosities utilizing mixtures of phenate and salicylate detergents versus Reference Oil A (Ref. A), all formulations containing detergents having a formulation BN of 70.

[0035] Figure 3B presents the effect on traction coefficient versus speed (mm/s) of formulations based on Group III (6.5 mm^2/s) base oil and two different Group IV base oils (PAO 40 and PAO 150) blended to different blend kinematic viscosities and utilizing mixtures of phenate and salicylate detergents (blended to different formulation Base Numbers of 40 and 70) versus Reference Oil A (Ref. A) (containing phenate/sulfonate detergents) and Reference Oil B (Ref. B) which is a blend only of Group III (6.5 mm^2/s) base oil and Group IV (PAO 150) base oil.

[0036] Figure 4 presents the effect on traction coefficient versus speed (mm/s) of a formulation based on blends of Group I base oils of different kinematic viscosities utilizing a mixture of phenate and salicylate detergents and formulations based on blends of Group IV base oils of different kinematic viscosities (PAO 8 and PAO 40) blended to different blend kinematic viscosities and containing mixtures of phenate and salicylate detergents versus Reference Oil A (Ref. A) and Reference Oil B (Ref. B) which is a blend only of Group III (6.5 mm^2/s) and Group IV (PAO 150) base oils, the formulations containing detergents having a formulation BN of 70.

[0037] Figure 5 presents the effect on traction coefficient versus speed (mm/s) of a formulation based on a Group I (12 mm^2/s) base oil and a Group IV base oil (PAO 150) containing a mixture of phenate and salicylate detergents and formulations based on different kinematic viscosity Group II (3 mm^2/s and 12 mm^2/s) base oils mixed with Group IV (PAO 40 and PAO 150) base oils containing mixtures of phenate and salicylate detergents versus Reference Oil A (Ref. A) and Reference Oil B (Ref. B) which is a blend only of Group III (6.5 mm^2/s) and Group IV (PAO 150) base oils, all formulations containing detergents having a formulation BN of 70.

[0038] Figure 6A presents the effect on traction coefficient versus speed (mm/s) of formulations based on Group III (6.5 mm^2/s) base oil and Group IV (PAO 150) base oil blended to a blend KV at 100°C of 20 mm^2/s utilizing mixtures of different detergents, phenate/salicylate or phenate/sulfonate, versus Reference Oil A (Ref. A.), all formulations containing detergent having a formulation BN of 70.

[0039] Figure 6B presents the effect on traction coefficient versus speed (mm/s) of two formulations based on Group III (6.5 mm^2/s) base oil and Group IV (PAO 150) base oil employing mixtures either of phenate and carboxylate detergents or of phenate and salicylate detergents versus Reference Oil A (Ref. A) and Reference Oil B (Ref. B) which is a mixture only of Group III (6.5 mm^2/s) base oil and Group IV (PAO 150) base oil, the formulations containing detergents having a formulation BN of 70.

[0040] Figure 7 presents the effect on traction coefficient versus speed (mm/s) of formulations based on Group III (6.5 mm^2/s) base oil and Group IV base oil (PAO 150) blended to a blend KV at 100°C of 20 mm^2/s utilizing only phenate detergent or only salicylate detergent or mixtures of salicylate and phenate detergent or mixtures of phenate, sulfonate and salicylate detergent in

different ratios, all formulations having a BN of 70, versus Reference Oil A (Ref. A).

[0041] Figure 8 presents the effect on traction coefficient versus speed (mm/s) of formulations based on Group III (6.5 mm^2/s) base oil and Group IV base oil (PAO 150) blended to a blend KV at 100°C of 20 mm^2/s utilizing only phenate detergent, only salicylate detergent or mixtures of phenate and salicylate detergents in different ratios, all formulations having a BN of 70 versus Reference Oil A (Ref. A).

[0042] Figure 9 presents the effect on traction coefficient versus speed (mm/s) of formulations based on Group III (6.5 mm^2/s) base oil and Group IV base oil (PAO 150) employing either just phenate detergent or mixtures of phenate and sulfonate detergents in different ratios, all blended to a KV at 100°C of 20 mm^2/s and a BN of 70 versus Reference Oil A (Ref. A).

DESCRIPTION OF THE INVENTION

[0043] The present invention is directed to a method for improving the fuel economy of a large low, medium and high speed engines lubricated using a lubricating oil in which the interfacing surface speeds reach at least about 3 mm/s, preferably at least about 10 mm/s by reducing the traction coefficient of the engine oil by lubricating said engine. This is achieved by using as the engine oil a lubricating oil having a kinematic viscosity at 100°C of 13 to 30 mm^2/s, preferably 16 to 30 mm^2/s, more preferably 18 to 25 mm^2/s, most preferably 20 to 25 mm^2/s, and a base number (BN) of at least 5 mg KOH/g, preferably 40 to 100 mg KOH/g, more preferably 40 to 70 mg KOH/g, containing a base oil comprising a bimodal blend of two different base oils, the first base oil being one or more oils selected from the group consisting of Group II base oils, Group III base oils and Group IV base oils, preferably Group III and Group IV base

oils, more preferably Group III base oils, having a kinematic viscosity at 100°C of from 2 to 16 mm^2/s, preferably 2 to 12 mm^2/s, and a second base oil selected from one or more oils selected from Group IV base oils having a kinematic viscosity at 100°C of at least 38 mm^2/s, preferably 38 to 1200 mm^2/s, more preferably 38 to 600 mm^2/s, still more preferably 38 to less than 300 mm^2/s, most preferably 38 to 150 mm^2/s, and a detergent selected from alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium salicylates, phenates, carboxylates, sulfonates, mixtures of salicylate and phenate or mixtures of phenate and carboxylate, preferably phenates, salicylates and carboxylates or mixtures of phenates and carboxylates or of phenates and salicylates at a total treat level of greater than 6 to 40 wt%, preferably 8 to 40 wt%, more preferably 10 to 30 wt%, of the lubricant (based on active ingredient), wherein the improvement in fuel economy is evidenced by the traction coefficient of the engine oil employing the bimodal blend being lower as compared to the traction coefficient of engine oils which are not bimodal or which are based on only Group I and/or Group II base stocks or which contain no Group IV base stocks having a KV at 100°C of at least 38 mm^2/s or which contain different detergents or detergent mixtures.

[0044] By "surface speed" is meant the velocity at which interfacing surfaces in the engine, e.g. cylinder wall and piston or interfacing surfaces of bearings move past each other as the engine operates. This surface speed is a primary factor in influencing whether the lubrication regime for the interfacing surfaces is boundary, hydrodynamic or mixed (boundary/hydrodynamic).

[0045] For engines that reach surface speeds of at least about 30 mm/s, preferably at least 60 mm/s, more preferably at least 75 mm/s, most preferably at least 100 mm/s, the first base oil is one or more of Group II, Group III and Group IV base stock, preferably Group III and Group IV base stock having a kinematic viscosity at 100°C of 2 to 16 mm^2/s, preferably 2 to 12 mm^2/s, and the

second base oil is one or more of Group IV base oil having a kinematic viscosity of at least 38 mm^2/s, preferably 38 to 1200 mm^2/s, more preferably 38 to 600 mm^2/s, still more preferably 38 to 300 mm^2/s, and the detergent can be any alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, salicylate, phenate, sulfonate, carboxylate and mixtures thereof, the total amount of detergent employed being in the range of greater than 6 to 40 wt%, preferably 8 to 40 wt%, more preferably 10 to 30 wt%, most preferably 12 to 25 wt%, of the lubricant (based on active ingredient), the lubricating oil having a TBN of at least 5 mg KOH/g, preferably 40 to 100 mg KOH/g, more preferably 40 to 70 mg KOH/g and a kinematic viscosity at 100°C of 6 to 30 mm^2/s, preferably 8 to 25 mm^2/s, more preferably 12 to 20 mm^2/s.

[0046] In another embodiment for engines that reach surface speeds of at least 3 mm/s, the first base oil is one or more Group II, Group III and Group IV base stock, preferably Group III and Group IV base stock, having a KV @ 100°C of 2 to 16 mm^2/s, preferably 2 to 12 mm^2/s, and the second base oil is one or more Group IV base oil having a KV at 100°C of 38 to <300 mm^2/s, preferably 38 to 150 $mm^2/$, and the detergent is an alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, sulfonate detergent or a mixture of alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, phenates and sulfonates, the total amount of detergent being in the range greater than 6 to 40 wt%, preferably 8 to 40 wt%, more preferably 10 to 30 wt%, still more preferably 12 to 25 wt%, of the lubricant (based on active ingredient), wherein the phenate is present in an amount in the range 5 to 30 wt%, preferably 8 to 30 wt%, more preferably 10 to 30 wt%, and sulfonate is present in an amount in the range 1 to 10 wt%, preferably 2 to 10 wt%, more preferably 3 to 10 wt%, based on the total weight of the lubricant, the lubricating oil having a BN of at least 5 mg KOH/g, preferably 40 to 100 mg

KOH/g, more preferably 40 to 70 mg KOH/g, and a kinematic viscosity at 100°C of 13 to 30 mm^2/s, preferably 16 to 30 mm^2/s, more preferably 18 to 25 mm^2/s.

[0047] In another embodiment the invention is directed to a method for improving the fuel economy of large low, medium and high speed engines that reach surface speeds of at least about 3 mm/s, preferably at least about 30 mm/s, and are lubricated by an engine oil by reducing the traction coefficient of the engine oil used to lubricate the engine, by employing as the engine oil a lubricating oil having a kinematic viscosity at 100°C of 6 to 30 mm^2/s, preferably 13 to 30 mm^2/s, and a base number of at least 5 mg KOH/g comprising a first base oil selected from the group consisting of a Group II base oil, Group III base oil and Group IV base oil having a kinematic viscosity at 100°C of from 2 to 16 mm^2/s and a second base oil selected from Group IV base oils having a kinematic viscosity at 100°C of at least 38 mm^2/s, the difference in kinematic viscosity between the first and second base oils being at least 30 mm^2/s, and a detergent selected from alkali and/or alkaline earth metal salicylates, phenates, carboxylates, sulfonates, mixtures of phenates and salicylates or mixtures of phenates and carboxylates at a total treat level in an amount of greater than 6 to 40 wt% (active ingredient), based on the total weight of the lubricating oil, wherein the improvement in fuel economy is evidenced by the engine oil having a traction coefficient which is lower than the traction coefficient of an engine oil of the same kinematic viscosity at 100°C comprising a single base oil component of a Group II base oil, Group III base oil or Group IV base oil, or a blend of comparable base oils having a difference in kinematic viscosity between a first and second base oil of less than 30 mm^2/s or which are based only on Group I and/or Group II base oils or which contain no Group IV base oils having a kinematic viscosity at 100°C of at least 38 mm^2/s.

[0048] The method of the present invention utilizes a bimodal mixture of base stocks. By bimodal in the present specification is meant a mixture of at least two

base stocks each having a different kinematic viscosity at 100°C wherein the difference in kinematic viscosity at 100°C between the at least two base stocks in the bimodal blend is at least 30 mm^2/s. The mixture of at least two base stocks comprises one or more low kinematic viscosity base stock(s) having a kinematic viscosity at 100°C of from 2 to 16 mm^2/s, preferably 2 to 12 mm^2/s, which base stock is selected from the group consisting of Group II, Group III and Group IV base stocks using the API classification in combination with one or more high kinematic viscosity Group IV base stocks having a KV at 100°C of at least 38 mm^2/s.

[0049] As employed herein and in the appended claims, the terms "base stock" and "base oil" are used synonymously and interchangeably.

[0050] Group II base stocks are classified by the American Petroleum Institute as oils containing greater than or equal to 90% saturates, less than or equal to 0.03 wt% sulfur and a viscosity index greater than or equal to 80 and less than 120.

[0051] Group III base stocks are classified by the American Petroleum Institute as oils containing greater than or equal to 90% saturates, less than or equal to 0.03% sulfur and a viscosity index of greater than or equal to 120. Group III base stocks are usually produced using a three-stage process involving hydrocracking an oil feed stock, such as vacuum gas oil, to remove impurities and to saturate all aromatics which might be present to produce highly paraffinic lube oil stock of very high viscosity index, subjecting the hydrocracked stock to selective catalytic hydrodewaxing which converts normal paraffins into branched paraffins by isomerization followed by hydrofinishing to remove any residual aromatics, sulfur, nitrogen or oxygenates.

[0052] Group III stocks also embrace non-conventional or unconventional base stocks and/or base oils which include one or a mixture of base stock(s)

and/or base oil(s) derived from: (1) one or more Gas-to-Liquids (GTL) materials; as well as (2) hydrodewaxed, or hydroisomerized/cat (and/or solvent) dewaxed base stock(s) and/or base oil(s) derived from synthetic wax, natural wax or waxy feeds, waxy feeds including mineral and/or non-mineral oil waxy feed stocks such as gas oils, slack waxes (derived from the solvent dewaxing of natural oils, mineral oils or synthetic; e.g., Fischer-Tropsch feed stocks) and waxy stocks such as waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, foots oil or other mineral, mineral oil, or even non-petroleum oil derived waxy materials such as waxy materials recovered from coal liquefaction or shale oil, linear or branched hydrocarbyl compounds with carbon number of about 20 or greater, preferably about 30 or greater and mixtures of such base stocks and/or base oils.

[0053] GTL materials are materials that are derived via one or more synthesis, combination, transformation, rearrangement, and/or degradation/deconstructive processes from gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks such as hydrogen, carbon dioxide, carbon monoxide, water, methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane, butylenes and butynes. GTL base stocks and/or base oils are GTL materials of lubricating viscosity that are generally derived from hydrocarbons; for example, waxy synthesized hydrocarbons, that are themselves derived from simpler gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks. GTL base stock(s) and/or base oil(s) include oils boiling in the lube oil boiling range (1) separated/ fractionated from synthesized GTL materials such as, for example, by distillation and subsequently subjected to a final wax processing step which involves either or both of a catalytic dewaxing process, or a solvent dewaxing process, to produce lube oils of reduced/low pour point; (2) synthesized wax isomerates, comprising, for example, hydrodewaxed or

hydroisomerized cat and/or solvent dewaxed synthesized wax or waxy hydrocarbons; (3) hydrodewaxed or hydroisomerized cat and/or solvent dewaxed Fischer-Tropsch (F-T) material (i.e., hydrocarbons, waxy hydrocarbons, waxes and possible analogous oxygenates); preferably hydrodewaxed or hydroisomerized/followed by cat and/or solvent dewaxing dewaxed F-T waxy hydrocarbons, or hydrodewaxed or hydroisomerized/followed by cat (and/or solvent) dewaxing dewaxed, F-T waxes, or mixtures thereof.

[0054] GTL base stock(s) and/or base oil(s) derived from GTL materials, especially, hydrodewaxed or hydroisomerized/followed by cat and/or solvent dewaxed wax or waxy feed, preferably F-T material derived base stock(s) and/or base oil(s), are characterized typically as having kinematic viscosities at 100°C of from about 2 mm^2/s to about 50 mm^2/s (ASTM D445). They are further characterized typically as having pour points of -5°C to about -40°C or lower (ASTM D97). They are also characterized typically as having viscosity indices of about 80 to about 140 or greater (ASTM D2270).

[0055] In addition, the GTL base stock(s) and/or base oil(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stock(s) and/or base oil(s) typically have very low sulfur and nitrogen content, generally containing less than about 10 ppm, and more typically less than about 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock(s) and/or base oil(s) obtained from F-T material, especially F-T wax, is essentially nil. In addition, the absence of phosphorous and aromatics make this material especially suitable for the formulation of low SAP products.

[0056] The term GTL base stock and/or base oil and/or wax isomerate base stock and/or base oil is to be understood as embracing individual fractions of such materials of wide viscosity range as recovered in the production process, mixtures of two or more of such fractions, as well as mixtures of one or two or more low viscosity fractions with one, two or more higher viscosity fractions to produce a blend wherein the blend exhibits a target kinematic viscosity.

[0057] The GTL material, from which the GTL base stock(s) and/or base oil(s) is/are derived is preferably an F-T material (i.e., hydrocarbons, waxy hydrocarbons, wax).

[0058] In a preferred embodiment, the GTL material, from which the GTL base stock(s) and/or base oil(s) is/are derived is an F-T material (i.e., hydrocarbons, waxy hydrocarbons, wax). A slurry F-T synthesis process may be beneficially used for synthesizing the feed from CO and hydrogen and particularly one employing an F-T catalyst comprising a catalytic cobalt component to provide a high Schultz-Flory kinetic alpha for producing the more desirable higher molecular weight paraffins. This process is also well known to those skilled in the art.

[0059] Useful compositions of GTL base stock(s) and/or base oil(s), hydrodewaxed or hydroisomerized/cat (and/or solvent) dewaxed F-T material derived base stock(s), and wax-derived hydrodewaxed, or hydroisomerized/cat (and/or solvent) dewaxed base stock(s), such as wax isomerates or hydrodewaxates, are recited in U.S. Patent Nos. 6,080,301; 6,090,989, and 6,165,949, for example.

[0060] Base stock(s) and/or base oil(s) derived from waxy feeds, which are also suitable for use as the Group III stocks in this invention, are paraffinic fluids of lubricating viscosity derived from hydrodewaxed, or hydroisomerized/cat (and/or solvent) dewaxed waxy feed stocks of mineral oil, non-mineral oil, non-

petroleum, or natural source origin, e.g. feed stocks such as one or more of gas oils, slack wax, waxy fuels hydrocracker bottoms, hydrocarbon raffinates, natural waxes, hydrocrackates, thermal crackates, foots oil, wax from coal liquefaction or from shale oil, or other suitable mineral oil, non-mineral oil, non-petroleum, or natural source derived waxy materials, linear or branched hydrocarbyl compounds with carbon number of about 20 or greater, preferably about 30 or greater, and mixtures of such isomerate/isodewaxate base stock(s) and/or base oil(s).

[0061] Slack wax is the wax recovered from any waxy hydrocarbon oil including synthetic oil such as F-T waxy oil or petroleum oils by solvent or auto-refrigerative dewaxing. Solvent dewaxing employs chilled solvent such as methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), mixtures of MEK/MIBK, mixtures of MEK and toluene, while auto-refrigerative dewaxing employs pressurized, liquefied low boiling hydrocarbons such as propane or butane.

[0062] Slack waxes secured from synthetic waxy oils such as F-T waxy oil will usually have zero or nil sulfur and/or nitrogen containing compound content. Slack wax(es) secured from petroleum oils, may contain sulfur and nitrogen-containing compounds. Such heteroatom compounds must be removed by hydrotreating (and not hydrocracking), as for example by hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) so as to avoid subsequent poisoning/ deactivation of the hydroisomerization catalyst.

[0063] The process of making the lubricant oil base stocks from waxy stocks, e.g. slack wax, F-T wax or waxy feed, may be characterized as an isomerization process. If slack waxes are used as the feed, they may need to be subjected to a preliminary hydrotreating step under conditions already well known to those skilled in the art to reduce (to levels that would effectively avoid catalyst

poisoning or deactivation) or to remove sulfur- and nitrogen-containing compounds which would otherwise deactivate the hydroisomerization or hydrodewaxing catalyst used in subsequent steps. If F-T waxes are used, such preliminary treatment is not required because such waxes have only trace amounts (less than about 10 ppm, or more typically less than about 5 ppm to nil) of sulfur or nitrogen compound content. However, some hydrodewaxing catalyst fed F-T waxes may benefit from prehydrotreatment for the removal of oxygenates while others may benefit from oxygenates treatment. The hydroisomerization or hydrodewaxing process may be conducted over a combination of catalysts, or over a single catalyst.

[0064] Following any needed hydrodenitrogenation or hydrosulfurization, the hydroprocessing used for the production of base stocks from such waxy feeds may use an amorphous hydrocracking/hydroisomerization catalyst, such as a lube hydrocracking (LHDC) catalysts, for example catalysts containing Co, Mo, Ni, W, Mo, etc., on oxide supports, e.g., alumina, silica, silica/alumina, or a crystalline hydrocracking/hydroisomerization catalyst, preferably a zeolitic catalyst.

[0065] Hydrocarbon conversion catalysts useful in the conversion of the n-paraffin waxy feedstocks disclosed herein to form the isoparaffinic hydrocarbon base oil are zeolite catalysts, such as ZSM-5, ZSM-11, ZSM-23, ZSM-35, ZSM-12, ZSM-38, ZSM-48, Offretite, ferrierite, zeolite beta, zeolite theta, and zeolite alpha, as disclosed in U.S. Patent 4,906,350. These catalysts are used in combination with Group VIII metals, in particular palladium or platinum. The Group VIII metals may be incorporated into the zeolite catalysts by conventional techniques, such as ion exchange.

[0066] In one embodiment, conversion of the waxy feed stock may be conducted over a combination of Pt/zeolite beta and Pt/ZSM-23 catalysts or over

such catalysts used in series in the presence of hydrogen. In another embodiment, the process of producing the lubricant oil base stocks comprises hydroisomerization and dewaxing over a single catalyst, such as Pt/ZSM-35. In yet another embodiment, the waxy feed can be fed over a catalyst comprising Group VIII metal loaded ZSM-48, preferably Group VIII noble metal loaded ZSM-48, more preferably Pt/ZSM-48 in either one stage or two stages. In any case, useful hydrocarbon base oil products may be obtained. Catalyst ZSM-48 is described in U.S. Patent 5,075,269.

[0067] A dewaxing step, when needed, may be accomplished using one or more of solvent dewaxing, catalytic dewaxing or hydrodewaxing processes or combinations of such processes in any sequence.

[0068] In solvent dewaxing, the hydroisomerate may be contacted with chilled solvents such as acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), mixtures of ME/MIBK, or mixtures of MEK/toluene and the like, and further chilled to precipitate out the higher pour point material as a waxy solid which is then separated from the solvent-containing lube oil fraction which is the raffinate. The raffinate is typically further chilled in scraped surface chillers to remove more wax solids. Auto-refrigerative dewaxing using low molecular weight hydrocarbons, such as propane, can also be used in which the hydroisomerate is mixed with, e.g., liquid propane, at least a portion of which is flashed off to chill down the hydroisomerate to precipitate out the wax. The wax is separated from the raffinate by filtration, membrane separation or centrifugation. The solvent is then stripped out of the raffinate, which is then fractionated to produce the preferred base stocks useful in the present invention.

[0069] In catalytic dewaxing the hydroisomerate is reacted with hydrogen in the presence of a suitable dewaxing catalyst at conditions effective to lower the pour point of the hydroisomerate. Catalytic dewaxing also converts a portion of

the hydroisomerate to lower boiling materials which are separated from the heavier base stock fraction. This base stock fraction can then be fractionated into two or more base stocks. Separation of the lower boiling material may be accomplished either prior to or during fractionation of the heavy base stock fraction material into the desired base stocks.

[0070] Any dewaxing catalyst which will reduce the pour point of the hydroisomerate and preferably those which provide a large yield of lube oil base stock from the hydroisomerate may be used. These include shape selective molecular sieves which, when combined with at least one catalytic metal component, have been demonstrated as useful for dewaxing petroleum oil fractions and include, for example, ferrierite, mordenite, ZSM-5, ZSM-11, ZSM-23, ZSM-35, ZSM-22 also known as theta one or RON, and the silicoaluminophosphates known as SAPOs. A dewaxing catalyst which has been found to be unexpectedly particularly effective comprises a noble metal, preferably Pt, composited with H-mordenite. The dewaxing may be accomplished with the catalyst in a fixed, fluid or slurry bed. Typical dewaxing conditions include a temperature in the range of from about 400 to 600°F, a pressure of 500 to 900 psig, H_2 treat rate of 1500 to 3500 SCF/B for flow-through reactors and LHSV of 0.1 to 10, preferably 0.2 to 2.0. The dewaxing is typically conducted to convert no more than 40 wt% and preferably no more than 30 wt% of the hydroisomerate having an initial boiling point in the range of 650 to 750°F to material boiling below its initial boiling point.

[0071] The first base stock of the bimodal mixture can also be a Group IV base stock which for the purposes of this specification and the appended claims are identified as polyalpha olefins.

[0072] The polyalpha olefins (PAOs) in general are typically comprised of relatively low molecular weight hydrogenated polymers or oligomers of

polyalphaolefins which include, but are not limited to, C_2 to about C_{32} alphaolefins with the C_8 to about C_{16} alphaolefins, such as 1-octene, 1-decene, 1-dodecene and the like, being preferred. The preferred polyalphaolefins are poly-1-octene, poly-1-decene and poly-1-dodecene and mixtures thereof and mixed olefin-derived polyolefins.

[0073] The PAO fluids may be conveniently made by the polymerization of an alphaolefin in the presence of a polymerization catalyst such as the Friedel-Crafts catalyst 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 proprionate. For example, the methods disclosed by U.S. Patent 4,149,178 or U.S. Patent 3,382,291 may be conveniently used herein. Other descriptions of PAO synthesis are found in the following U.S. Patents: 3,742,082; 3,769,363; 3,876,720; 4,239,930; 4,367,352; 4,413,156; 4,434,408; 4,910,355; 4,956,122; and 5,068,487. The dimers of the C_{14} to C_{18} olefins are described in U.S. Patent 4,218,330.

[0074] The PAOs useful in the present invention can also be made by metallocene catalysis. The metallocene-catalyzed PAO (mPAO) can be a copolymer made from at least two alphaolefins or more, or a homo-polymer made from a single alphaolefin feed by a metallocene catalyst system.

[0075] The metallocene catalyst can be simple metallocenes, substituted metallocenes or bridged metallocene catalysts activated or promoted by, for instance, methylaluminoxane (MAO) or a non-coordinating anion, such as N,N-dimethylanilinium tetrakis(perfluorophenyl)borate or other equivalent non-coordinating anion. mPAO and methods for producing mPAO employing metallocene catalysis are described in WO 2009/123800, WO 2007/011832 and U.S. Published Application 2009/0036725.

[0076] The copolymer mPAO composition is made from at least two alphaolefins of C_3 to C_{30} range and having monomers randomly distributed in the polymers. It is preferred that the average carbon number is at least 4.1. advantageously, ethylene and propylene, if present in the feed, are present in the amount of less than 50 wt% individually or preferably less than 50 wt% combined. The copolymers of the invention can be isotactic, atactic, syndiotactic polymers or any other form of appropriate taciticity.

[0077] mPAO can also be made from mixed feed Linear Alpha Olefins (LAOs) comprising at least two and up to 26 different linear alphaolefins selected from C_3 to C_{30} linear alphaolefins. In a preferred embodiment, the mixed feed LAO is obtained from an ethylene growth processing using an aluminum catalyst or a metallocene catalyst. The growth olefins comprise mostly C_6 to C_{18} LAO. LAOs from other processes can also be used.

[0078] The homo-polymer mPAO composition is made from single alphaolefin choosing from C_3 to C_{30} range, preferably C_3 to C_{16}, most preferably C_3 to C_{14} or C_3 to C_{12}. The homo-polymers can be isotactic, atactic, syndiotactic polymers or any other form of appropriate taciticity. Often the taciticity can be carefully tailored by the polymerization catalyst and polymerization reaction condition chosen or by the hydrogenation condition chosen.

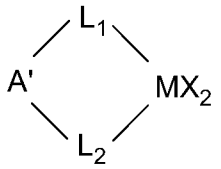
[0079] The alphaolefin(s) can be chosen from any component from a conventional LAO production facility or from a refinery. It can be used alone to make homo-polymer or together with another LAO available from a refinery or chemical plant, including propylene, 1-butene, 1-pentene, and the like, or with 1-hexene or 1-octene made from a dedicated production facility. In another embodiment, the alphaolefins can be chosen from the alphaolefins produced from Fischer-Tropsch synthesis (as reported in U.S. Patent 5,382,739). For example, C_3 to C_{16} alphaolefins, more preferably linear alphaolefins, are suitable

to make homo-polymers. Other combinations, such as C_4- and C_{14}-LAO, C_6- and C_{16}-LAO, C_8-, C_{10}-, C_{12}-LAO, or C_8- and C_{14}-LAO, C_6-, C_{10}-, C_{14}-LAO, C_4- and C_{12}-LAO, etc., are suitable to make copolymers.

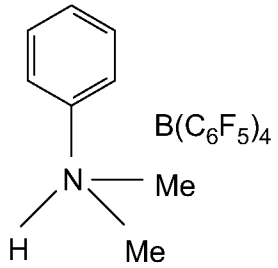
[0080] A feed comprising a mixture of LAOs selected from C_3 to C_{30} LAOs or a single LAO selected from C_3 to C_{16} LAO, is contacted with an activated metallocene catalyst under oligomerization conditions to provide a liquid product suitable for use in lubricant components or as functional fluids. This invention is also directed to a copolymer composition made from at least two alphaolefins of C_3 to C_{30} range and having monomers randomly distributed in the polymers. The phrase "at least two alphaolefins" will be understood to mean "at least two different alphaolefins" (and similarly "at least three alphaolefins" means "at least three different alphaolefins", and so forth).

[0081] The product obtained is an essentially random liquid copolymer comprising the at least two alphaolefins. By "essentially random" is meant that one of ordinary skill in the art would consider the products to be random copolymer. Likewise, the term "liquid" will be understood by one of ordinary skill in the art as meaning liquid under ordinary conditions of temperature and pressure, such as ambient temperature and pressure.

[0082] The process employs a catalyst system comprising a metallocene compound (Formula 1, below) together with an activator such as a non-coordinating anion (NCA) (Formula 2, below) or methylaluminoxane (MAO) 1111 (Formula 3, below):

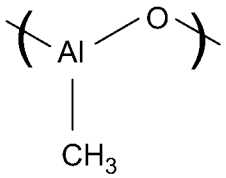


Formula 1



NCA

Formula 2



MAO

Formula 3

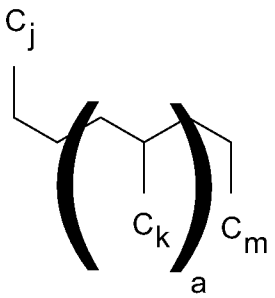
[0083] The term "catalyst system" is defined herein to mean a catalyst precursor/activator pair, such as a metallocene/activator pair. When "catalyst system" is used to describe such a pair before activation, it means the unactivated catalyst (precatalyst) together with an activator and, optionally, a co-activator (such as a trialkyl aluminum compound). When it is used to describe such a pair after activation, it means the activated catalyst and the activator or other charge-balancing moiety. Furthermore, this activated "catalyst system" may optionally comprise the co-activator and/or other charge-balancing moiety. Optionally and often, the co-activator, such as trialkyl aluminum compound, is also used as an impurity scavenger.

[0084] The metallocene is selected from one or more compounds according to Formula 1 above. In Formula 1, M is selected from Group 4 transition metals, preferably zirconium (Zr), hafnium (Hf) and titanium (Ti), L1 and L2 are

independently selected from cyclopentadienyl ("Cp"), indenyl, and fluorenyl, which may be substituted or unsubstituted, and which may be partially hydrogenated. A is an optional bridging group which, if present, in preferred embodiments is selected from dialkylsilyl, dialkylmethyl, diphenylsilyl or diphenylmethyl, ethylenyl (—CH_2-CH_2), alkylethylenyl (—CR_2-CR_2), where alkyl can be independently C_1 to C_{16} alkyl radical or phenyl, tolyl, xylyl radical and the like, and wherein each of the two X groups, Xa and Xb, are independently selected from halides OR (R is an alkyl group, preferably selected from C_1 to C_5 straight or branched chain alkyl groups), hydrogen, C_1 to C_{16} alkyl or aryl groups, haloalkyl, and the like. Usually relatively more highly substituted metallocenes give higher catalyst productivity and wider product viscosity ranges and are thus often more preferred.

[0085] Any of the polyalphaolefins preferably have a Bromine number of 1.8 or less as measured by ASTM D1159, preferably 1.7 or less, preferably 1.6 or less, preferably 1.5 or less, preferably 1.4 or less, preferably 1.3 or less, preferably 1.2 or less, preferably 1.1 or less, preferably 1.0 or less, preferably 0.5 or less, preferably 0.1 or less. If necessary, the polyalphaolefins can be hydrogenated to achieve a low bromine number.

[0086] Any of the mpolyalphaolefins (mPAO) described herein may have monomer units represented by Formula 4 in addition to the all regular 1,2-connection:



Formula 4

,

where j, k and m are each, independently, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21 or 22, n is an integer from 1 to 350 (preferably 1 to 300, preferably 5 to 50) as measured by proton NMR.

[0087] Any of the mpolyalphaolefins (mPAO) described herein preferably have an Mw (weight average molecular weight) of 100,000 or less, preferably between 100 and 80,000, preferably between 250 and 60,000, preferably between 280 and 50,000, preferably between 336 and 40,000 g/mol.

[0088] Any of the mpolyalphaolefins (mPAO) described herein preferably have a Mn (number average molecular weight) of 50,000 or less, preferably between 200 and 40,000, preferably between 250 and 30,000, preferably between 500 and 20,000 g/mol.

[0089] Any of the mpolyalphaolefins (mPAO) described herein preferably have a molecular weight distribution (MWD-Mw/Mn) of greater than 1 and less than 5, preferably less than 4, preferably less than 3, preferably less than 2.5. The MWD of mPAO is always a function of fluid viscosity. Alternately, any of the polyalphaolefins described herein preferably have an Mw/Mn of between 1 and 2.5, alternately between 1 and 3.5, depending on fluid viscosity.

[0090] Molecular weight distribution (MWD), defined as the ratio of weight-averaged MW to number-averaged MW (= Mw/Mn), can be determined by gel permeation chromatography (GPC) using polystyrene standards, as described in p. 115 to 144 , Chapter 6, The Molecular Weight of Polymers in "Principles of Polymer Systems" (by Ferdinand Rodrigues, McGraw-Hill Book, 1970). The GPC solvent was HPLC Grade tetrahydrofuran, uninhibited, with a column temperature of 30°C, a flow rate of 1 ml/min, and a sample concentration of 1 wt%, and the Column Set is a Phenogel 500 A, Linear, 10E6A.

[0091] Any of the m-polyalphaolefins (mPAO) described herein may have a substantially minor portion of a high end tail of the molecular weight distribution. Preferably, the mPAO has not more than 5.0 wt% of polymer having a molecular weight of greater than 45,000 Daltons. Additionally or alternatively, the amount of the mPAO that has a molecular weight greater than 45,000 Daltons is not more than 1.5 wt%, or not more than 0.10 wt%. Additionally or alternatively, the amount of the mPAO that has a molecular weight greater than 60,000 Daltons is not more than 0.5 wt%, or not more than 0.20 wt%, or not more than 0.1 wt%. The mass fractions at molecular weights of 45,000 and 60,000 can be determined by GPC, as described above.

[0092] In a preferred embodiment of this invention, any PAO described herein may have a pour point of less than 0°C (as measured by ASTM D97), preferably less than -10°C, preferably less than 20°C, preferably less than -25°C, preferably less than -30°C, preferably less than -35°C, preferably less than -50°C, preferably between -10°C and -80°C, preferably between -15°C and -70°C.

[0093] Polyalphaolefins made using metallocene catalysis may have a kinematic viscosity at 100°C from about 1.5 to about 5,000 cSt, preferably from about 2 to about 3,000 cSt, preferably from about 3 cSt to about 1,000 cSt, more preferably from about 4 cSt to about 1,000 cSt, and yet more preferably from about 8 cSt to about 500 cSt as measured by ASTM D445.

[0094] PAOs useful in the present invention include those made by the process disclosed in U.S. Patent 4,827,064 and U.S. Patent 4,827,073. Those PAO materials, which are produced by the use of a reduced valence state chromium catalyst, are olefin oligomers of polymers which are characterized by very high viscosity indices which give them very desirable properties to be useful as lubricant base stocks and, with higher viscosity grades, as VI improvers. They are referred to as High Viscosity Index PAOs or HVI-PAOs.

The relatively low molecular weight high viscosity PAO materials were found to be useful as lubricant base stocks whereas the higher viscosity PAOs, typically with viscosities of 100 cSt or more, e.g. in the range of 100 to 1,000 cSt, were found to be very effective as viscosity index improvers for conventional PAOs and other synthetic and mineral oil derived base stocks.

[0095] Various modifications and variations of these high viscosity PAO materials are also described in the following U.S. Patents to which reference is made: 4,990,709; 5,254,274; 5,132,478; 4,912,272; 5,264,642; 5,243,114; 5,208,403; 5,057,235; 5,104,579; 4,943,383; 4,906,799. These oligomers can be briefly summarized as being produced by the oligomerization of 1-olefins in the presence of a metal oligomerization catalyst which is a supported metal in a reduced valence state. The preferred catalyst comprises a reduced valence state chromium on a silica support, prepared by the reduction of chromium using carbon monoxide as the reducing agent. The oligomerization is carried out at a temperature selected according to the viscosity desired for the resulting oligomer, as described in U.S. Patent Nos. 4,827,064 and 4,827,073. Higher viscosity materials may be produced as described in U.S. Patent No. 5,012,020 and U.S. Patent No. 5,146,021 where oligomerization temperatures below about 90°C are used to produce the higher molecular weight oligomers. In all cases, the oligomers, after hydrogenation when necessary to reduce residual unsaturation, have a branching index (as defined in U.S. Patent Nos. 4,827,064 and 4,827,073) of less than 0.19. Overall, the HVI-PAO normally have a viscosity in the range of about 12 to 5,000 cSt.

[0096] Furthermore, the HVI-PAOs generally can be characterized by one or more of the following: C_{30} to C_{1300} hydrocarbons having a branch ratio of less than 0.19, a weight average molecular weight of between 300 and 45,000, a number average molecular weight of between 300 and 18,000, a molecular weight distribution of between 1 and 5. Particularly preferred HVI-PAOs are

fluids with 100°C viscosity ranging from 5 to 5000 mm^2/s. In another embodiment, viscosities of the HVI-PAO oligomers measured at 100°C range from 3 mm^2/s to 15,000 mm^2/s. Furthermore, the fluids with viscosity at 100°C of 3 mm^2/s to 5000 mm^2/s have VI calculated by ASTM method D2270 greater than 130. Usually they range from 130 to 350. The fluids all have low pour points, below -15°C.

[0097] The HVI-PAOs can further be characterized as hydrocarbon compositions comprising the polymers or oligomers made from 1-alkenes, either by itself or in a mixture form, taken from the group consisting of C_6 to C_{20} 1-alkenes. Examples of the feeds can be 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, etc. or mixture of C_6 to C_{14} 1-alkenes or mixture of C_6 to C_{20} 1-alkenes, C_6 and C_{12} 1-alkenes, C_6 and C_{14} 1-alkenes, C_6 and C_{16} 1-alkenes, C_6 and C_{18} 1-alkenes, C_8 and C_{10} 1-alkenes, C_8 and C_{12} 1-alkenes, C_8, C_{10} and C_{12} 1-alkenes, and other appropriate combinations.

[0098] The lube products usually are distilled to remove any low molecular weight compositions such as those boiling below 600°F, or with carbon numbers less than C_{20}, if they are produced from the polymerization reaction or are carried over from the starting material.

[0099] The lube fluids made directly from the polymerization or oligomerization process usually have unsaturated double bonds or have olefinic molecular structure. The amount of double bonds or unsaturation or olefinic components can be measured by several methods, such as bromine number (ASTM D1159), bromine index (ASTM D2710) or other suitable analytical methods, such as NMR, IR, etc. The amount of the double bond or the amount of olefinic compositions depends on several factors – the degree of polymerization, the amount of hydrogen present during the polymerization process and the amount of other promoters which anticipate in the termination

steps of the polymerization process, or other agents present in the process. Usually the amount of double bonds or the amount of olefinic components is decreased by the higher degree of polymerization, the higher amount of hydrogen gas present in the polymerization process or the higher amount of promoters participating in the termination steps.

[00100] As with the other PAOs, the oxidative stability and light or UV stability of HVI-PAO fluids improves when the amount of unsaturation double bonds or olefinic contents is reduced. Therefore, it is necessary to further hydrotreat the polymer if they have high degree of unsaturation. Usually the fluids with bromine number of less than 5, as measured by ASTM D1159, is suitable for high quality base stock application. Of course, the lower the bromine number, the better the lube quality. Fluids with bromine numbers of less than 3 or 2 are common. The most preferred range is less than 1 or less than 0.1. The method to hydrotreat to reduce the degree of unsaturation is well known in literature (U.S. Patent No. 4,827,073, example 16). In some HVI-PAO products, the fluids made directly from the polymerization already have very low degree of unsaturation, such as those with viscosities greater than 150 cSt at 100°C. They have bromine numbers less than 5 or even below 2. In these cases, it can be used as is without hydrotreating, or it can be hydrotreated to further improve the base stock properties.

[00101] Regardless of the process or technique used for their production, if a PAO fluid is used as the sole or as one of a mixture of fluids constituting the first base stock of the bimodal mixture useful in the present invention, that PAO fluid is a low kinematic viscosity fluid, a PAO with a KV at 100°C in the range of 2 to 16 mm^2/s, preferably 2 to 12 mm^2/s.

[00102] The low viscosity fluid can be made up of a single base stock oil meeting the recited kinematic viscosity levels or be made up of two or more base

stocks/oils, each meeting the recited kinematic viscosity limits. Further, the low viscosity fluid can be made up of mixtures of one, two or more low viscosity stocks/oils, e.g. stocks/oils with kinematic viscosities in the range of 2 to 16 mm^2/s at 100°C, combined with one, two or more high viscosity stocks/oils, e.g. stocks/oils with kinematic viscosities greater than 16 mm^2/s at 100°C, such as stocks/oils with kinematic viscosities of 100 mm^2/s or greater, provided that the resulting mixture blend exhibits the target low kinematic viscosity of 2 to 16 mm^2/s recited as the viscosity range of the first low viscosity stock.

[00103] The second oil used in the bimodal blend is a high kinematic viscosity Group IV fluid, i.e. a PAO with a kinematic viscosity at 100°C in the range of at least 38 mm^2/s, preferably 38 to 1200 mm^2/s, more preferably 38 to 600 mm^2/s, still more preferably 38 to 300 mm^2/s, most preferably 38 to 150 mm^2/s.

[00104] When discussing PAO, the designation of a PAO as, e.g. PAO 150, means a PAO with a kinematic viscosity at 100°C of nominally 150 mm^2/s.

[00105] In regard to the second, high kinematic viscosity oil, it can be made up of a single PAO base stock/oil meeting the recited kinematic viscosity limit or it may be made up of two or more PAO base stocks/oils, each of which meet the recited kinematic viscosity limit. Conversely, this second, high kinematic viscosity base stock/oil can be a mixture of one, two or more lower kinematic viscosity PAO base stocks/oils, e.g., stocks/oils with kinematic viscosities of less than 38 mm^2/s at 100°C, mixed with one, two or more high kinematic viscosity PAO base stocks/oils, provided that the resulting mixture blend meets the target high kinematic viscosity of at least 38 mm^2/s at 100°C.

[00106] Such higher kinematic viscosity PAO fluids can be made using the same techniques previously recited for the production of the low kinematic viscosity PAO fluids (the first oil of the bimodal mixture).

[00107] Preferably the high kinematic viscosity PAO fluid which is the second fluid of the bimodal mixture is made employing metallocene catalysis or the process described in U.S. Patent 4,827,064 or U.S. Patent 4,827,073.

[00108] Regardless of the technique or process employed to make PAO, the PAO fluid used as the second base stock of the bimodal blend is a high kinematic viscosity PAO having a KV at 100°C of at least 38 mm^2/s.

[00109] The present invention achieves its reduction in traction coefficient by use of a lubricant comprising a bimodal blend of two different base oils, the first being one or more Group II, Group III or Group IV base oils, preferably Group III or Group IV base oils, having a KV at 100°C of from 2 to 16 mm^2/s, preferably 2 to 12 mm^2/s, and the second being one or more Group IV base oils having a KV at 100°C of at least 38 mm^2/s, provided there is a difference in KV between the first and second base stocks of the bimodal blend of at least 30 mm^2/s.

[00110] The reduction of traction coefficient employing the bimodal base stock blends recited above depends on the necessary presence of one or more alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, phenate, sulfonate, salicylate or carboxylate detergent as hereinbefore provided. The detergent need not be the salt of a single metal but can be a mixture of metal salts, e.g. a mixture of sodium salt and/or lithium salt and/or calcium salt and/or magnesium salt, only by way of example and not limitation.

[00111] In the present invention it has been discovered that traction coefficient at different surface speeds is improved by using various combinations of the first and second base stocks and of the detergents.

[00112] For surface speeds of at least 3 mm/s, preferably at least 10 mm/s, the base stock of the lubricating oil is a bimodal blend of a first base stock being one

or more oils selected from the group consisting of Group II base oils, Group III base oils and Group IV base oils, preferably Group III and Group IV base oils, more preferably Group III base oils having a kinematic viscosity at 100°C of from 2 to 16 mm^2/s, preferably 2 to 12 mm^2/s, and a second base oil selected from one or more oils selected from the group consisting of Group IV base oils having a kinematic viscosity at 100°C of at least 38 mm^2/s, preferably 38 to 1200 mm^2/s, more preferably 38 to 600 mm^2/s, still more preferably 38 to less than 300 mm^2/s, most preferably 38 to 150 mm^2/s, and a detergent selected from alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium salicylate, phenate, carboxylate, sulfonate, mixtures of alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium salicylates and phenates or mixtures of alkali and/or alkaline earth metal , preferably alkaline earth metal, more preferably calcium phenate and carboxylate, preferably the phenates, salicylates and carboxylates and mixtures of phenates and carboxylates or of phenates and salicylates in an amount of greater than 6 to 40 wt%, preferably 8 to 40 wt% based on active ingredient, more preferably 10 to 30 wt%, and wherein for the detergent mixtures the weight ratio of phenate to carboxylate or phenate to salicylate is 6:1 to 1:6, preferably 3:1 to 1:3, more preferably 2:1 to 1:2, most preferably 1:1. based on the total weight of the lubricating oil, the lubricating oil having a TBN of at least 5 mg KOH/g, preferably 40 to 70 mg KOH/g, more preferably 40 to 70 mg KOH/g, and a kinematic viscosity at 100°C of 13 to 30 mm^2/s, preferably 16 to 30 mm^2/s, more preferably 18 to 25 mm^2/s, most preferably 20 to 25 mm^2/s.

[00113] In another embodiment, for surface speeds of at least 3 mm/s, preferably at least 10 mm/s, the base stock is a bimodal blend of a first base stock being one or more oils selected from the group consisting of Group II base oils, Group III base oils and Group IV base oils, preferably Group III base oils, having a kinematic viscosity at 100°C of 2 to 16 mm^2/s, preferably 2 to 12 mm^2/s, and a

second base oil selected from one or more oils selected from Group IV base oils having a kinematic viscosity at 100°C of 38 to <300 mm^2/s, preferably 38 to 250 mm^2/s, more preferably 38 to 150 mm^2/s, and greater than 6 to 40 wt%, preferably 8 to 40 wt%, more preferably 10 to 30 wt%, still more preferably 12 to 25 wt%, based on the total weight of the lubricant of a detergent selected from a mixture of alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, sulfonate or a mixture of alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, phenates and sulfonates wherein the weight ratio of phenate to sulfonate is in the range of 5:1 to 1:3, preferably 4:1 to 1:2, most preferably 4:1 to 1:1, the lubricating oil having a TBN of at least 5 mg KOH/g, preferably 40 to 100 mg KOH/g, more preferably 40 to 70 mg KOH/g, and a kinematic viscosity at 100°C of 13 to30 mm^2/s, 16 to 30 mm^2/s, more preferably 18 to 25 mm^2/s.

[00114] In another embodiment, for surface speeds of at least 30 mm/s, preferably at least 60 mm/s, more preferably at least 75 mm/s, still more preferably at least 100 mm/s, the base stock of the lubricating oil is a bimodal blend of a first base stock being one or more oils selected from the group consisting of Group II base oils, Group III base oils and Group IV base oils, preferably Group III base oils, having a kinematic viscosity at 100°C of 2 to 16 mm^2/s, preferably 2 to 12 mm^2/s, and a second base oil selected from one or more oils selected from Group IV base oils having a kinematic viscosity at 100°C of at least 38 mm^2/s, preferably 38 to 1200 mm^2/s, more preferably 38 to 600 mm^2/s, still more preferably 38 to 300 mm^2/s, most preferably 38 to 100 mm^2/s, and greater than 6 to 40 wt%, preferably 8 to 40 wt%, more preferably 10 to 30 wt%, most preferably 12 to 25 wt% (active ingredient) based on the weight of the lubricating oil of a detergent selected from alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, salicylate, phenate, sulfonate, carboxylate and mixtures thereof, the lubricating oil having a TBN of

at least 5 mg KOH/g, preferably 40 to 100 mg KOH/g, more preferably 40 to 70 mg KOH/g, and a kinematic viscosity at 100°C of 6 to 30 mm^2/s, preferably 8 to 25 mm^2/s, more preferably 12 to 20 mm^2/s.

[00115] The method can use engine lubricating oils containing additional performance additives provided the base stock comprises the essential bimodal blend base stock and the aforesaid detergents. As indicated, the detergents employed are alkali and/or alkaline earth metal, preferably alkaline earth metal, more preferably calcium, salicylates, phenates, sulfonates, carboxylates used either singly or in various combinations. These detergents can be low, medium or high TBN detergents, i.e. detergents with base numbers ranging from about 5 to as high as 500 mg KOH/g, preferably about 5 to about 400 mg KOH/g.

[00116] The formulated lubricating oil useful in the present invention may additionally contain one or more of the other commonly used lubricating oil performance additives including but not limited to dispersants, additional other detergents, corrosion inhibitors, rust inhibitors, metal deactivators, other anti-wear and/or extreme pressure additives, anti-seizure agents, wax modifiers, viscosity index improvers, viscosity modifiers, fluid-loss additives, seal compatibility agents, other friction modifiers, lubricity agents, anti-staining agents, chromophoric agents, defoamants, demulsifiers, emulsifiers, densifiers, wetting agents, gelling agents, tackiness agents, colorants, and others. For a review of many commonly used additives, see Klamann in Lubricants and Related Products, Verlag Chemie, Deerfield Beach, FL; ISBN 0-89573-177-0. Reference is also made to "Lubricant Additives" by M. W. Ranney, published by Noyes Data Corporation of Parkridge, NJ (1973).

[00117] The types and quantities of performance additives used in combination with the present invention in lubricant compositions are not limited by the examples shown herein as illustrations.

Viscosity Improvers

[00118] Viscosity improvers (also known as Viscosity Index modifiers, and VI improvers) provide lubricants with high and low temperature operability. These additives increase the viscosity of the oil composition at elevated temperatures which increases film thickness, while having limited effect on viscosity at low temperatures.

[00119] Suitable viscosity improvers include high molecular weight hydrocarbons, polyesters and viscosity index improver dispersants that function as both a viscosity index improver and a dispersant. Typical molecular weights of these polymers are between about 1,000 to 1,000,000, more typically about 2,000 to 500,000, and even more typically between about 2,500 and 200,000.

[00120] Examples of suitable viscosity improvers are polymers and copolymers of methacrylate, butadiene, olefins, or alkylated styrenes. Polyisobutylene is a commonly used viscosity improver. Another suitable viscosity index improver is polymethacrylate (copolymers of various chain length alkyl methacrylates, for example), some formulations of which also serve as pour point depressants. Other suitable viscosity index improvers include copolymers of ethylene and propylene, hydrogenated block copolymers of styrene and isoprene, and polyacrylates (copolymers of various chain length acrylates, for example). Specific examples include styrene-isoprene or styrene-butadiene based polymers of 50,000 to 200,000 molecular weight.

[00121] The amount of viscosity modifier may range from zero to 10 wt%, preferably zero to 6 wt%, more preferably zero to 4 wt% based on active ingredient and depending on the specific viscosity modifier used.

Anti-oxidants

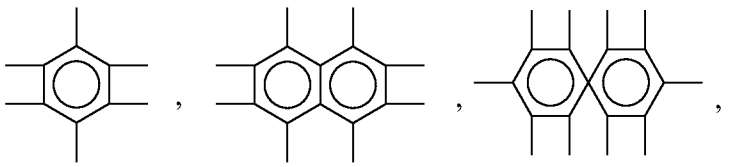
[00122] Typical anti-oxidant include phenolic anti-oxidants, aminic anti-oxidants and oil-soluble copper complexes.

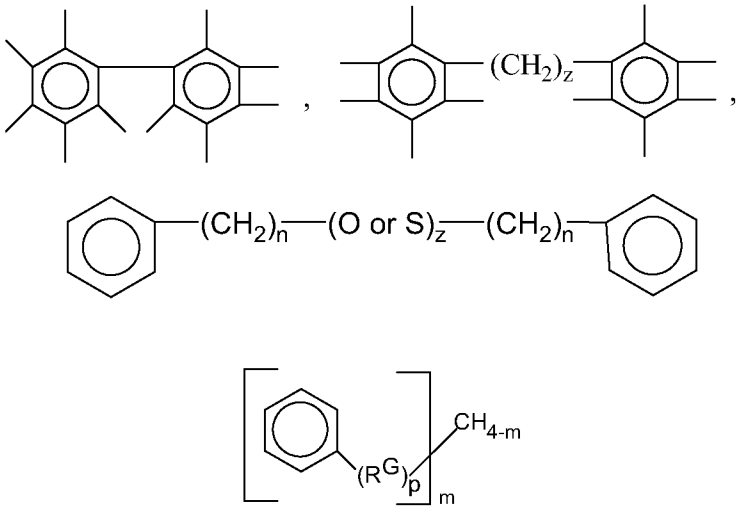
[00123] The phenolic anti-oxidants include sulfurized and non-sulfurized phenolic anti-oxidants. The terms "phenolic type" or "phenolic anti-oxidant" used herein includes compounds having one or more than one hydroxyl group bound to an aromatic ring which may itself be mononuclear, e.g., benzyl, or poly-nuclear, e.g., naphthyl and spiro aromatic compounds. Thus "phenol type" includes phenol per se, catechol, resorcinol, hydroquinone, naphthol, etc., as well as alkyl or alkenyl and sulfurized alkyl or alkenyl derivatives thereof, and bisphenol type compounds including such bi-phenol compounds linked by alkylene bridges sulfuric bridges or oxygen bridges. Alkyl phenols include mono- and poly-alkyl or alkenyl phenols, the alkyl or alkenyl group containing from about 3-100 carbons, preferably 4 to 50 carbons and sulfurized derivatives thereof, the number of alkyl or alkenyl groups present in the aromatic ring ranging from 1 to up to the available unsatisfied valences of the aromatic ring remaining after counting the number of hydroxyl groups bound to the aromatic ring.

[00124] Generally, therefore, the phenolic anti-oxidant may be represented by the general formula:

$$(R)_x—Ar—(OH)_y$$

where Ar is selected from the group consisting of:





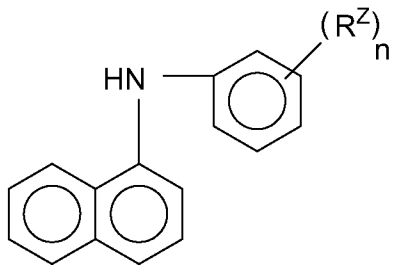
wherein R is a C_3-C_{100} alkyl or alkenyl group, a sulfur substituted alkyl or alkenyl group, preferably a C_4-C_{50} alkyl or alkenyl group or sulfur substituted alkyl or alkenyl group, more preferably C_3-C_{100} alkyl or sulfur substituted alkyl group, most preferably a C_4-C_{50} alkyl group, R^g is a C_1-C_{100} alkylene or sulfur substituted alkylene group, preferably a C_2-C_{50} alkylene or sulfur substituted alkylene group, more preferably a C_2-C_2 alkylene or sulfur substituted alkylene group, y is at least 1 to up to the available valences of Ar, x ranges from 0 to up to the available valances of Ar-y, z ranges from 1 to 10, n ranges from 0 to 20, and m is 0 to 4 and p is 0 or 1, preferably y ranges from 1 to 3, x ranges from 0 to 3, z ranges from 1 to 4 and n ranges from 0 to 5, and p is 0.

[00125] Preferred phenolic anti-oxidant compounds are the hindered phenolics 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 anti-oxidants include the hindered phenols substituted with C_1+ 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; 2-methyl-6-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4 methyl phenol; 2,6-di-t-butyl-4-ethyl phenol; and 2,6-di-t-butyl 4 alkoxy phenol.

[00126] Phenolic type anti-oxidants are well known in the lubricating industry and commercial examples such as Ethanox® 4710, Irganox® 1076, Irganox® L1035, Irganox® 1010, Irganox® L109, Irganox® L118, Irganox® L135 and the like are familiar to those skilled in the art. The above is presented only by way of exemplification, not limitation on the type of phenolic anti-oxidants which can be used.

[00127] Aromatic amine anti-oxidants include phenyl-α-naphthyl amine which is described by the following molecular structure:



wherein R^Z is hydrogen or a C_1 to C_{14} linear or C_3 to C_{14} branched alkyl group, preferably C_1 to C_{10} linear or C_3 to C_{10} branched alkyl group, more preferably linear or branched C_6 to C_8 and n is an integer ranging from 1 to 5 preferably 1. A particular example is Irganox L06.

[00128] Other aromatic amine anti-oxidants include other alkylated and non-alkylated aromatic amines such as aromatic monoamines of the formula $R^8R^9R^{10}N$ where R^8 is an aliphatic, aromatic or substituted aromatic group, R^9 is an aromatic or a substituted aromatic group, and R^{10} is H, alkyl, aryl or

$R^{11}S(O)_XR^{12}$ where R^{11} is an alkylene, alkenylene, or aralkylene group, R^{12} is a higher alkyl group, or an alkenyl, aryl, or alkaryl group, and x is 0, 1 or 2. The aliphatic group R^8 may contain from 1 to about 20 carbon atoms, and preferably contains from about 6 to 12 carbon atoms. The aliphatic group is a saturated aliphatic group. Preferably, both R^8 and R^9 are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring aromatic group such as naphthyl. Aromatic groups R^8 and R^9 may be joined together with other groups such as S.

[00129] Typical aromatic amines anti-oxidants 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 such other additional amine anti-oxidants which may be present include diphenylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more of such other additional aromatic amines may also be present. Polymeric amine anti-oxidants can also be used.

[00130] Another class of anti-oxidant used in lubricating oil compositions and which may be present in addition to the necessary phenyl-α-naphthylamine is oil-soluble copper compounds. Any oil-soluble suitable copper compound may be blended into the lubricating oil. Examples of suitable copper anti-oxidants include copper dihydrocarbyl thio- or dithio-phosphates and copper salts of carboxylic acid (naturally occurring or synthetic). Other suitable copper salts include copper dithiacarbamates, sulphonates, phenates, and acetylacetonates. Basic, neutral, or acidic copper Cu(I) and or Cu(II) salts derived from alkenyl succinic acids or anhydrides are know to be particularly useful.

[00131] Such anti-oxidants may be used in an amount of about 0.10 to 5 wt%, preferably about 0.30 to 3 wt% (on an as-received basis).

Dispersant

[00132] 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.

[00133] 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.

[00134] 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.

[00135] 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.

[00136] 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.

[00137] 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.

[00138] 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.

[00139] The molecular weight of the alkenyl succinic anhydrides 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.

[00140] Mannich base dispersants are made from the reaction of alkylphenols, formaldehyde, and amines. 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.

[00141] Typical high molecular weight aliphatic acid modified Mannich condensation products can be prepared from high molecular weight alkyl-substituted hydroxyaromatics or $HN(R)_2$ group-containing reactants.

[00142] 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 polypropylene, polybutylene, and other polyalkylene compounds to give alkyl substituents on the benzene ring of phenol having an average 600-100,000 molecular weight.

[00143] Examples of $HN(R)_2$ group-containing reactants are alkylene polyamines, principally polyethylene polyamines. 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., 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.

[00144] Examples of alkylene polyamine 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 $H_2N\text{-}(Z\text{-}NH\text{-})_nH$, 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 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.

[00145] 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.

[00146] 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%, more preferably about 1 to 6 wt% (on an as-received basis) based on the weight of the total lubricant.

Pour Point Depressants

[00147] Conventional pour point depressants (also known as lube oil flow improvers) may also be present. Pour point depressant may be added to lower the minimum temperature at which the fluid will flow or can be poured. Examples of suitable pour point depressants include alkylated naphthalenes 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.

[00148] Such additives may be used in amount of about 0.0 to 0.5 wt%, preferably about 0 to 0.3 wt%, more preferably about 0.001 to 0.1 wt% on an as-received basis.

Corrosion Inhibitors/Metal Deactivators

[00149] Corrosion inhibitors are used to reduce the degradation of metallic parts that are in contact with the lubricating oil composition. Suitable corrosion inhibitors include aryl thiazines, alkyl substituted dimercapto thiodiazoles thiadiazoles and mixtures thereof.

[00150] Such additives may be used in an amount of about 0.01 to 5 wt%, preferably about 0.01 to 1.5 wt%, more preferably about 0.01 to 0.2 wt%, still more preferably about 0.01 to 0.1 wt% (on an as-received basis) based on the total weight of the lubricating oil composition.

Seal Compatibility Additives

[00151] Seal compatibility agents help to swell elastomeric seals by causing a chemical reaction in the fluid or physical change in the elastomer. Suitable seal compatibility agents for lubricating oils include organic phosphates, aromatic esters, aromatic hydrocarbons, esters (butylbenzyl phthalate, for example), and polybutenyl succinic anhydride. Such additives may be used in an amount of about 0.01 to 3 wt%, preferably about 0.01 to 2 wt% on an as-received basis.

Anti-Foam Agents

[00152] 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, preferably 0.001 to about 0.5 wt%, more preferably about 0.001 to about 0.2 wt%, still more preferably about 0.0001 to 0.15 wt% (on an as-received basis) based on the total weight of the lubricating oil composition.

Inhibitors and Anti-Rust Additives

[00153] Anti-rust additives (or corrosion inhibitors) are additives that protect lubricated metal surfaces against chemical attack by water or other contaminants. One type of anti-rust additive is a polar compound that wets the metal surface preferentially, protecting it with a film of oil. Another type of anti-rust additive absorbs water by incorporating it in a water-in-oil emulsion so that only the oil touches the surface. Yet another type of anti-rust additive chemically adheres to the metal to produce a non-reactive surface. Examples of suitable additives include zinc dithiophosphates, metal phenolates, basic metal sulfonates, fatty acids and amines. Such additives may be used in an amount of about 0.01 to 5 wt%, preferably about 0.01 to 1.5 wt% on an as-received basis.

[00154] Anti-wear additives can also advantageously be present. Anti-wear additives are exemplified by metal dithiophosphate, metal dithiocarbamate, metal dialkyl dithiophosphate, metal xanthage where the metal can be zinc or molybdenum. Tricresylphosphates are another type of anti-wear additive. Such anti-wear additives can be present in an amount of about 0.05 to 1.5 wt%, preferably about 0.1 to 1.0 wt%, more preferably about 0.2 to 0.5 wt% (as received).

Comparative Examples and Examples

[00155] A series of engine oils was evaluated in regard to the effect base stock composition and detergent type has on traction coefficient. The engine oils were either a commercially available oil (Reference Oil A (Ref. A)) or base stock blends using combinations of a first base stock or base stocks of different kinematic viscosities and a second base stock or base stocks of different kinematic viscosities only (Reference Oil B (Ref. B)) or in combination with different detergents or mixtures of detergents at different loading/treat levels producing lubricating oils of different kinematic viscosities, all formulations containing detergent having a Base Number (BN) of 40 or 70 mg KOH/g. The traction coefficient was measured employing the MTM Traction Rig which is a fully automated Mini Traction Machine traction measurement instrument. The rig is manufactured by PCS Instruments and identified as Model MTM. The test specimens and apparatus configuration are such that realistic pressures, temperatures and speeds can be attained without requiring very large loads, motors or structures. A small sample of fluid (50 ml) is placed in the test cell and the machine automatically runs through a range of speeds, slide-to-roll ratios, temperatures and loads to produce a comprehensive traction map for the test fluid without operational intervention. The standard test specimens are a polished 19.05 mm 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 ball is loaded against the face of the disc and the ball and disc are driven independently 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 disk test specimen is fixed. However, the shaft and drive system which supports the ball 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. The ball and disk are driven in the same 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. The traction coefficient is the ratio of the traction force to the applied load. As shown in Figures 1-9, the traction coefficient was measured over a range of speeds. In Figures 1-9, the speed on the x-axis is the entrainment speed, which is half the sum of the ball and disk speeds. These entrainment speeds simulate the range of surface speeds, or at least a portion of the range of surface speeds, reached when the engine is operating.

[00156] The test results presented herein were generated under the following test conditions:

Temperature	100°C
Load	1.0 GPa
Slide-to-roll ratio (SRR)	50%
Speed gradient	0-3000 mm/sec in 480 seconds

Two different machines of the same model, Model MTM, were used in these evaluations and the identity of the machine used (machine 1 or machine 2) is indicated on the figures.

[00157] The lubricating oils are described in Table 1.

Table 1

Oil Designation	Detergent System (wt% Active) (TBN of Full Blend)	Base Stock	Lubricating Oil KV @ 100°C
Ref. A	Overbased Calcium Phenate (11.5%), Overbased Ca Sulfonate (3.1%) (70)	Group I (12 mm^2/s)/ PIB (2200 MW)	20 mm^2/s
Oil I-A	Overbased Calcium Phenate (11.5%), Overbased Ca Sulfonate (3.1%) (70)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil I-B	Re-blend of Oil I-A	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil II	Overbased Calcium Phenate (11.5%), Overbased Ca Sulfonate (3.1%) (70)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	16.5 mm^2/s
Oil III	Overbased Calcium Phenate (11.5%), Overbased Ca Sulfonate (3.1%) (70)	Group III (6.5 mm^2/s)/ Group IV (300 mm^2/s)	20 mm^2/s
Oil IV	Overbased Ca Salicylate (12.5%) (70)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil V	Overbased Ca Sulfonate (8.2%) (70)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil VI	Overbased Ca Carboxylate (13.6%) (70)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil VII	Overbased Ca Phenate (18.4%) (70)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil VIII-A	Overbased Ca Phenate (11.5%)/ Overbased Ca Salicylate (4.7%) (70 BN)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil VIII-B	Re-blend of Oil IX-A	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil IX-A	Overbased Ca Phenate (11.5%)/ Overbased Ca Salicylate (4.7%) (70 BN)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	13 mm^2/s
Oil IX-B	Overbased Ca Phenate (11.5%)/ Overbased Ca Salicylate (4.7%) (70 BN)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	16.5 mm^2/s
Oil X	Overbased Ca Phenate (11.5%)/ Overbased Ca Salicylate (4.7%) (70 BN)	Group III (6.5 mm^2/s)/ Group IV (300 mm^2/s)	20 mm^2/s
Oil XI	Overbased Ca Phenate (11.5%)/ Overbased Ca Salicylate (4.7%) (70 BN)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	25 mm^2/s
Oil XII	Overbased Ca Phenate (11.5%)/ Overbased Ca Salicylate (4.7%) (70 BN)	Group III (6.5 mm^2/s)/ Group IV (40 mm^2/s)	20 mm^2/s
Ref. B	Base Oil Only	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	16 mm^2/s
Oil XIII	Overbased Ca Phenate (11.5%)/ Overbased Ca Salicylate (4.7%) (70 BN)	Group I (8 mm^2/s)/ Group I (32 mm^2/s)	22 mm^2/s

Table 1 (Continued)

Oil Designation	Detergent System (wt% Active) (TBN of Full Blend)	Base Stock	Lubricating Oil KV @ 100°C
Oil XIV	Overbased Ca Phenate (11.5%)/ Overbased Ca Salicylate (4.7%) (70 BN)	Group IV (8 mm^2/s)/ Group IV (40 mm^2/s)	21 mm^2/s
Oil XV	Overbased Ca Phenate (11.5%)/ Overbased Ca Salicylate (4.7%) (70 BN)	Group IV (8 mm^2/s)/ Group IV (40 mm^2/s)	13 mm^2/s
Oil XVI	Overbased Ca Phenate (11.5%)/ Overbased Ca Salicylate (4.7%) (70 BN)	Group I (12 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil XVII	Overbased Ca Phenate (11.5%)/ Overbased Ca Salicylate (4.7%) (70 BN)	Group II (12 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil XVIII	Overbased Ca Phenate (11.5%)/ Overbased Ca Salicylate (4.7%) (70 BN)	Group II (3 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil XIX	Overbased Ca Phenate (11.5%)/ Overbased Ca Salicylate (4.7%) (70 BN)	Group II (3 mm^2/s)/ Group IV (40 mm^2/s)	20 mm^2/s
Oil XX	Overbased Ca Phenate (11.5%)/ Overbased Ca Carboxylate (3.7%) (70 BN)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil XXI	Overbased Ca Phenate (11.5%)/ Overbased Ca Salicylate (3%)/ Overbased Ca Sulfonate (1.1%)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil XXII	Overbased Ca Phenate (11.5%)/ Overbased Ca Salicylate (1.5%)/ Overbased Ca Sulfonate (2.1%)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil XXIII	Overbased Ca Phenate (11.5%)/ Overbased Ca Salicylate (0.5%) Overbased Ca Sulfonate (2.7%)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil XXIV	Overbased Ca Phenate (14./7%)/ Overbased Ca Salicylate (2.5%)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil XXV	Overbased Ca Phenate (7.4%)/ Overbased Ca Salicylate (7.5%)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil XXVI	Overbased Ca Phenate (3.7%)/ Overbased Ca Salicylate (10%)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil XXVII	Overbased Ca Phenate (15%)/ Overbased Ca Sulfonate (1.5%)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil XXVIII	Overbased Ca Phenate (8.3%)/ Overbased Ca Sulfonate (4.5%)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil XXIX	Overbased Ca Phenate (5%)/ Overbased Ca Sulfonate (6%)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s
Oil XXX (40 BN)	Overbased Ca Phenate (6.6%)/ Overbased Ca Salicylate (2.7%)	Group III (6.5 mm^2/s)/ Group IV (150 mm^2/s)	20 mm^2/s

[00158] The formulations in addition to the different base oils, mixtures of base oils and detergents also all contained the same amounts in all formulations of other additives such as dispersants, anti-oxidants and extreme pressure/anti-wear additives, etc., except for Ref. B which contained no additive.

[00159] The effect of formulation variables on lubricant performance in terms of traction coefficient at different speeds is seen by reference to the Figures. In the following, for those Oils identified as containing a Group III oil, the Group III oil used was a slack wax isomerate made by subjecting slack wax to hydrotreating to remove any sulfur and nitrogen compounds, which desulfurized and denitrogenated slack wax was then hydroisomerized followed by hydrofinishing.

[00160] The Group IV base oil was PAO. The kinematic viscosity is identified by the designation, e.g. PAO 150, identifying the PAO as having a KV at 100°C of nominally 150 mm^2/s.

[00161] In Figure 1, Oils I-A, I-B, II and III are compared against Reference Oil A. All four formulations and the Reference Oil have the same detergents and other additives except that Reference Oil A is a blend of a Group I base oil and PIB while Oils I-A to III are formulations containing blends of Group III base oil with Group IV base oil (PAO).

[00162] From Figure 1 it is seen that all of the oils, I-A to III, blended with the bimodal blend of Group III (6.5 mm^2/s)/Group IV (150 mm^2/s), produced a large improvement in traction coefficient relative to Ref. Oil A at speeds of 80 mm/s and higher. The effect on traction coefficient at different speeds versus

Reference Oil A is also dependent on the final kinematic viscosity of the blended oil, and the kinematic viscosity of the second, high viscosity oil of the blend.

[00163] For formulation Oils I-A and I-B employing blends of kinematic viscosity of 20 mm^2/s and a mixture of phenate and sulfonate detergents, the traction coefficients were lower than that of the reference oil at all speeds when the second high viscosity component of the blend had a kinematic viscosity at 100°C of 150 mm^2/s.

[00164] For formulation Oil II employing a blend of kinematic viscosity at 100°C of 16 mm^2/s and a mixture of phenate and sulfonate the traction coefficient was consistently lower than that of Reference Oil A only at higher speeds of about 60 mm/s and higher.

[00165] Finally, for formulation Oil III employing a blend of kinematic viscosity at 100°C of 20 mm^2/s and wherein the second high viscosity oil component of the blend had a kinematic viscosity at 100°C of 300 mm^2/s and containing a mixture of phenate and sulfonate detergent, the traction coefficient was consistently lower than that of the Reference Oil A only at higher speeds of about 70 mm/s and higher.

[00166] In Figure 2, formulation Oils IV to VII are compared against each other and against Reference Oil A and Reference Oil B.

[00167] Figure 2 shows the effect of single detergent type on formulated oil traction coefficient at different speeds.

[00168] It is seen that for formulation Oils IV to VII all based on blends having a kinematic viscosity at 100°C of 20 mm^2/s and all made using the same combination of Group III (6.5 mm^2/s) base stock and Group IV base stock (PAO 150) and all containing only single detergent additives plus the same

amounts of other additives, the traction coefficient of the formulated Oils IV, VI and VII were lower than that of Reference Oil A over the entire engine speed range regardless of whether the single detergent was a salicylate, a carboxylate or a phenate. While formulation Oils IV, VI and VII were all superior to Reference Oil A over the entire speed range, the formulation oils which performed best contained salicylate (Oil IV) and carboxylate (Oil VI) detergents.

[00169] The formulation oil containing the sulfonate detergent (Oil V) performed better than the reference oil at low speed (about 3 to 60 mm/s) and at higher speed (about 100 mm/s or higher) showing a fluctuation in performance indicating this formulation is best suited for use only under continuous higher speed operating conditions (100 mm/s or more) or continuous low speed operating conditions (3 to 50-60 mm/s). The formulation oils containing salicylates (Oil IV), sulfonates (Oil V) or carboxylates (Oil VI) all performed better at low speeds (about 3 to 12 mm^2/s) than Reference Oil B (base stock only).

[00170] Figures 3A and 3B show the effect varying blend kinematic viscosity and second oil component kinematic viscosity of blends using the same combination of phenate and salicylate detergent, and other additives and the effect formulation BN has on traction coefficient at different speeds.

[00171] In Figure 3B it is seen that formulation Oils VIII-A, XI and XII (blend KV at 100°C of 20 to 25 mm^2/s, second high viscosity oil KV at 100°C of 40 or 150 mm^2/s) and formulation Oil XXX (blend KV at 100°C of 20 mm^2/s, second high viscosity oil KV at 100°C of 150 mm^2/s, formulation blend BN of 40 containing the same mixture of phenate and salicylate detergents and other additives consistently outperformed Reference Oil A at all speeds in terms of lowering the traction coefficient. Formulation Oils XI and XII also outperformed

Reference Oil B ((Ref. B) base stock only) under low speed (3 to 10 mm/s) conditions.

[00172] In Figure 3A it is seen that formulation Oils IX-A and IX-B (blend KV at 100°C of 13 and 16.5 mm^2/s, second high viscosity oil KV at 100°C of 150 mm^2/s) containing the same mixture of salicylate and phenate detergents and other additives consistently outperformed Reference Oil A only at higher speeds of about 50 mm/s and higher (Oil IX-B) or 100 mm/s and higher (Oil IX-A).

[00173] Formulation Oil X (blend KV at 100°C of 20 mm^2/s, second high viscosity at KV at 100°C of 300 mm^2/s) containing the same mixture of salicylate and phenate detergent and other additives similarly consistently outperformed Reference Oil A only at higher speeds of about 20 mm/s and higher.

[00174] Thus, while all the formulations in Figures 3A and 3B outperformed Reference Oil A at higher speeds, formulation Oils VIII-A, IX-B, XI, XII and XXX matched or outperformed Reference Oil A over the entire speed range on both figures, with all of these formulation oils containing the same mixture of salicylate and phenate detergents, and having kinematic viscosities at 100°C of 20 to 25 mm^2/s and employing the second Group IV base oil (PAO 40 or PAO 150) blending component.

[00175] In Figure 4 formulation Oils XIII to XV are compared against each other and Reference Oil A and Reference Oil B.

[00176] Figure 4 shows the effect using Group I/Group I and Group IV/Group IV combinations of base oils with the same phenate/salicylate detergent mixture and other additives at different blend kinematic viscosities, all formulations with BN of 70, has on traction coefficient at different speeds.

[00177] Only formulation Oil XIV employing the mixture of Group IV (PAO8) base oil and Group IV base oil (PAO 40) blended to 21 mm^2/s kinematic viscosity at 100°C outperformed Reference Oil A in terms of traction coefficient over the entire speed range while also outperforming Reference Oil B (base oils only) under low speed (3 to 12 mm^2/s) conditions.

[00178] Formulation Oil XIII, using the same phenate/salicylate detergent combination in a mixture of Group I (8 mm^2/s)/Group I (32 mm^2/s) base stocks, blended to 22 mm^2/s, outperformed Reference Oil A only under low to moderate speed (3 to 50 mm/s) conditions. Formulation Oil XV, which is the same as Oil XIV except that it was blended to a KV at 100°C of 13 mm^2/s (rather than 21 mm^2/s) outperformed Reference Oil A under moderate to high speed (80 mm/s and higher) conditions only.

[00179] In Figure 5, formulation Oils XVI, XVII, XVIII and XIX are compared against each other and against Reference Oils A and B.

[00180] Figure 5 shows the effect using Group I/Group IV and Group II/Group IV base oil combinations with the same phenate/salicylate detergent combinations and other additives, all with formulation Base Numbers of 70, and blended to a KV at 100°C of 20 mm^2/s.

[00181] Only formulation Oil XIX, a formulation employing the base oil combination of Group II (3 mm^2/s) base oil and Group IV base oil (PAO 40) outperformed Reference Oil A in terms of coefficient of friction over the entire speed range. It also outperformed Reference Oil B (Group III/Group IV base oil combinations only) in the low to moderate speed range (3 to 20 mm^2/s).

[00182] Formulation Oil XVIII, which is the same as Oil XIX except that the second base oil component is Group IV base oil (PAO 150) (instead of PAO 40), outperformed Reference Oil A only in the moderate to high speed region (about

20 mm/s and higher) and was superior to Oil XVI (Group I/Group IV formulation). Oil XVII, which is the same as Oil XVIII except that it used a higher kinematic viscosity Group II (12 mm^2/s) base stock instead of the 3 mm^2/s Group II base stock of formulation Oil XVIII as the first base oil component, exhibited only a slight traction coefficient benefit over Reference Oil A under low to moderate speed conditions (3 to 10 mm/s) and only a very slight benefit under high speed (100+ mm/s) conditions. Group II base oils with kinematic viscosities of less than 12 mm^2/s, therefore, are preferred to obtain a significant traction coefficient benefit at higher (100 mm/s and higher) speeds.

[00183] Figures 6A and 6B show a comparison of different phenate/co-detergent blends, all formulations of BN 70, in Group III (6.5 mm^2/s) base stock/Group IV base stock (PAO 150) mixtures blended to a blend KV at 100°C of 20 mm^2/s, the comparison being to each other and to Reference Oils A and B.

[00184] Figure 6A shows that both Oil I-A (phenate/sulfonate) and Oil VIII-A (phenate/salicylate) provide a large improvement in traction coefficient relative to Reference Oil A (phenate/sulfonate in Group I/PIB blend) over the entire speed range. Oil VIII-A outperforms Oil I-A at low to moderate speeds (about 3 to 80-90 mm^2/s).

[00185] Figure 6B shows that the phenate/carboxylate detergent combination in Group III (6.5 mm^2/s) base oil/Group IV base oil (PAO 150) blend also provides a large improvement in traction coefficient relative to Reference Oil A over the entire speed range. However, under very low speed conditions (about 3 to 7 mm/s), the phenate/carboxylate detergent combination while still effective does not provide as much of a benefit as the phenate/salicylate combination.

[00186] In Figure 7, formulation Oils IV, VIII-A, XXI, XXII, XXIII and VII are compared against each other and Reference Oils A and B.

[00187] Figure 7 shows the effect of varying the amount of salicylate and sulfonate detergents employed in blends containing a combination of phenate, salicylate and sulfonate detergents has on the traction coefficient. These formulations were all blended to the same kinematic viscosity at 100°C of 20 mm^2/s using the same low KV and higher KV first and second base stocks. As can be seen, formulation Oil IV, containing only the salicylate detergent, exhibited the greatest reduction in traction coefficient over the entire speed range, while those formulations containing a mixture of salicylate, phenate and sulfonate detergents (salicylate replacing a portion of the sulfonate detergent) exhibited performance which varied with the amount of salicylate present with at least 1.5 wt% salicylate needed to show an improvement over Reference Oil A under low to moderate speeds (3 to 50 mm/s).

[00188] Formulations containing only salicylate or mixtures of salicylate and phenate or mixtures of sulfonate and phenate are preferred over formulations containing mixtures of salicylate, phenate and sulfonate.

[00189] In Figure 8, formulation Oils VII, XXIV, VIII-A, XXV, XXVI and IV are compared against each other and Reference Oils A and B.

[00190] Figure 8 shows the effect varying the amount of salicylate detergent with respect to the phenate detergent has on traction coefficient on formulations otherwise the same in terms of blend KV and of the low KV and higher KV base oils used. As can be seen, the greater the salicylate/phenate ratio, the better the traction coefficient performance. However, maximizing the phenate concentration in the formation is important for other performance characteristics.

[00191] Formulation Oil XXV, which contained about 7.5 wt% salicylate and 7.4 wt% phenate detergents (weight ratio about 1:1), exhibited among the best overall traction coefficient improvements relative to Reference Oil A. Decreasing the salicylate/phenate ratio slightly in Oil VIII-A which contained

about 4.7 wt% salicylate and 11.5 wt% phenate (salicylate:phenate weight ratio about 1:2.5) degraded traction coefficient performance at low speeds (3 to 10 mm/s) relative to Oil XXV and Oil XXVI. It is desirable, therefore, to maximize the phenate content and the effect on traction coefficient by employing a salicylate/phenate detergent blend employing a weight ratio of salicylate/phenate between 1:1 and 1:2.5.

[00192] It must be noted that all the formulations exceeded Reference Oil A in terms of their effect on traction coefficient at all speeds, and Oils VII, XXV, XXVI and IV exceeds the traction coefficient performance of Reference Oil B, base stocks only) under low speed conditions (3 to 10 mm/s). It should be noted that the 100% phenate formulation (Oil VII) provided better traction coefficient performance than Oil XXIV (2.5 wt% salicylate/14.7 wt% phenate), Oil VIII-A (4.7 wt% salicylate and 11.5 wt% phenate), and Oil XXVI (10 wt% salicylate and 3.7 wt% phenate) under low to moderate speeds (about 8 to 70-100 mm/s).

[00193] In Figure 9 formulation Oils V, VII, XXVII, XXVIII and XXIX are compared against each other and Reference Oils A and B.

[00194] Figure 9 shows the effect varying the amount of sulfonate detergent with respect to phenate detergent has on traction coefficient in formulations otherwise the same in terms of blend KV and of the low KV and high KV base oils used. Of the formulations containing mixtures of sulfonate and phenate detergents, the higher the sulfonate/phenate ratios tested, the better the traction coefficient performance relative to Reference Oil A under all speeds However, sulfonate-only detergent is not desirable not only because no phenate is present but Figure 9 shows that while the all-sulfonate oil, Oil V, provides a large traction coefficient benefit over Reference Oil A at low speeds (3 to 12 mm/s) and high speeds (100+ mm/s), the benefit is much reduced relative to oils containing mixtures of phenate and sulfonate, or even nil relative to Reference

Oil A at moderate speeds (20 to 100 mm/s). The phenate-only detergent formulation (Oil VII) outperforms that of the sulfonate/phenate blends at low to moderate speeds (~3 to 10 mm/s). Only Oil XXIX (6 wt% sulfonate/5 wt% phenate) slightly outperforms Oil VII under high speeds (100+ mm/s).

CLAIMS:

1. A method for improving the fuel economy of large low, medium and high speed engines that reach surface speeds of at least about 3 mm/s and are lubricated by an engine oil by reducing the traction coefficient of the engine oil used to lubricate the engine by employing as the engine oil a lubricating oil having a kinematic viscosity at 100°C of 13 to 30 mm^2/s and a base number of at least 5 mg KOH/g comprised of a base oil comprising a bimodal blend of two different base oils, a first base oil being one or more oils selected from the group consisting of Group II base oils, Group III base oils and Group IV base oils having a kinematic viscosity at 100°C of from 2 to 16 mm^2/s and a second base oil selected from one or more oils selected from the group consisting of Group IV base oil having a kinematic viscosity at 100°C of at least 38 mm^2/s, wherein the difference in kinematic viscosity between the first and second base oils in the bimodal blend are at least 30 mm^2/s, and a detergent selected from alkali and/or alkaline earth metal salicylates, phenates, carboxylates, sulfonates, mixtures of phenates and salicylates or mixtures of phenates and carboxylates at a total treat level in an amount of greater than 6 to 40 wt% (active ingredient), based on the total weight of the lubricating oil wherein the improvement in fuel economy is evidenced by the traction coefficient of the engine oil employing the bimodal blend being lower than the traction coefficient of engine oils which are not bimodal blends or which are based on only Group I and/or Group II base oils or which contain no Group IV base oils having a KV at 100°C of at least 38 mm^2/s.

2. A method for improving the fuel economy of large engines that reach surface speeds of at least about 30 mm/s and are lubricated by an engine oil by reducing the traction coefficient of the engine oil used to lubricate the engine by employing as the engine oil a lubricating oil having a kinematic viscosity at 100°C of 6 to 30 mm^2/s and a base number of at least 5 mg KOH/g comprised of a base oil comprising a bimodal blend of two different base oils, a

first base oil being one or more oils selected from the group consisting of Group II base oils, Group III base oils and Group IV base oils having a kinematic viscosity at 100°C of from 2 to 16 mm^2/s and a second base oil selected from one or more oils selected from the group consisting of Group IV base oil having a kinematic viscosity at 100°C of at least 38 mm^2/s, wherein the difference in kinematic viscosity between the first and second base oils in the bimodal blend is at least 30 mm^2/s, and a detergent selected from the group consisting of alkali and/or alkaline earth metal salicylates, phenates, sulfonates, carboxylates and mixtures thereof, wherein the total amount of detergent employed is in the range of greater than 6 to 40 wt% (active ingredient), based on the total weight of the lubricating oil wherein the improvement in fuel economy is evidenced by the traction coefficient of the engine oil employing the bimodal blend being lower than the traction coefficient of engine oils which are not bimodal blends or which are based on only Group I and/or Group II base oils or which contain no Group IV base oils having a KV at 100°C of at least 38 mm^2/s.

3. A method for improving the fuel economy of large low, medium and high speed engines that reach surface speeds of at least about 3 mm/s and are lubricated by an engine oil by reducing the traction coefficient of the engine oil used to lubricate the engine by employing as the engine oil a lubricating oil having a kinematic viscosity at 100°C of 13 to 30 mm^2/s and a base number of at least 5 mg KOH/g comprised of a base oil comprised of a bimodal blend of two different base oils, a first base oil being one or more oils selected from the group consisting of Group II, Group III and Group IV base oils having a kinematic viscosity at 100°C of from 2 to 16 mm^2/s and a second base oil selected from one or more oils selected from the group consisting of Group IV base oil having a kinematic viscosity at 100°C of 38 to <300 mm^2/s wherein the difference in kinematic viscosity between the first and second base oils in the bimodal blend is at least 30 mm^2/s, and a detergent selected from the group consisting of alkali and/or alkaline earth metal sulfonates or mixtures phenates and sulfonates, the

total amount of detergent being in the range greater than 6 to 40 wt% (active ingredient), based on the total weight of the lubricating oil wherein the improvement in fuel economy is evidenced by the traction coefficient of the engine oil employing the bimodal blend being lower than the traction coefficient of engine oils which are not bimodal blends or which are based on only Group I and/or Group II base oils or which contain no Group IV base oils having a KV at 100°C of at least 38 mm^2/s.

4. The method of claim 1 wherein the first base oil is selected from Group III and Group IV base stock oils.

5. The method of claim 2 wherein the first base oil is selected from Group III and Group IV base stock oils.

6. The method of claim 3 wherein the first base oil is selected from Group III and Group IV base stock oils.

7. The method of claim 1, 2 or 3 wherein the detergent is present in an amount in the range 8 to 40 wt% (active ingredient).

8. The method of claim 1 wherein the lubricant kinematic viscosity at 100°C is in the range 16 to 30 mm^2/s.

9. The method of claim 1 wherein the lubricant kinematic viscosity at 100°C is in the range 18 to 25 mm^2/s.

10. The method of claim 2 wherein the lubricant kinematic viscosity at 100°C is in the range 8 to 25 mm^2/s.

11. The method of claim 3 wherein the lubricant kinematic viscosity at 100°C is in the range 16 to 30 mm^2/s.

12. The method of claim 3 wherein the lubricant kinematic viscosity at 100°C is in the range 18 to 25 mm^2/s.

13. The method of claim 1, 2 or 3 wherein the second base oil is a PAO base oil.

14. The method of claim 13 wherein the PAO base oil is made using metallocene catalysis.

15. The method of claim 13 wherein the PAO base oil is characterized by not more than 5.0 wt% of the polymer having a molecular weight of greater than 45,000 Daltons.