



(86) Date de dépôt PCT/PCT Filing Date: 2006/12/15
(87) Date publication PCT/PCT Publication Date: 2007/06/21
(85) Entrée phase nationale/National Entry: 2008/06/06
(86) N° demande PCT/PCT Application No.: US 2006/048056
(87) N° publication PCT/PCT Publication No.: 2007/070691
(30) Priorités/Priorities: 2005/12/15 (US60/750,562);
2006/12/12 (US11/637,342)

(51) Cl.Int./Int.Cl. *C10M 149/10* (2006.01)
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(54) Titre : FORMULES D'HUILE LUBRIFIANTE CONTENANT UNE OU DES BASES GTL ET/OU UNE OU DES HUILES
DE BASE ET DOTEES D'UNE MEILLEURE RESISTANCE A LA PERTE DE VISCOSITE ET DE POIDS, ET
PROCEDE D'AMELIORATION DE LA RESISTANCE A LA PERTE DE VISCOSITE ET DE POIDS DE FORMULES
D'HUILE LUBRIFIANTE CONTENANT UNE OU DES BAS
(54) Title: LUBRICANT OIL COMPOSITIONS CONTAINING GTL BASE STOCK(S)

(57) **Abrégé/Abstract:**

The present invention is directed to a method for improving the performance of lubricating oils of high viscosity comprising GTL base stock(s) and/or base oil(s) and lubricating oil comprising such base stock(s) and/or base oil(s) in combination with an effective amount of a polyolefin fluid having a kinematic viscosity at 100°C in the range between about 10 to about 200 mm²/s.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 June 2007 (21.06.2007)

PCT

(10) International Publication Number
WO 2007/070691 A3

(51) International Patent Classification:
C10M 149/10 (2006.01)

(21) International Application Number:
PCT/US2006/048056

(22) International Filing Date:
15 December 2006 (15.12.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/750,562 15 December 2005 (15.12.2005) US
11/637,342 12 December 2006 (12.12.2006) US

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(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

(88) Date of publication of the international search report:
27 December 2007

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: LUBRICANT OIL COMPOSITIONS CONTAINING GTL BASE STOCK(S)

(57) Abstract: The present invention is directed to a method for improving the performance of lubricating oils of high viscosity comprising GTL base stock(s) and/or base oil(s) and lubricating oil comprising such base stock(s) and/or base oil(s) in combination with an effective amount of a polyolefin fluid having a kinematic viscosity at 100°C in the range between about 10 to about 200 mm²/s.

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LUBRICANT OIL COMPOSITIONS CONTAINING GTL
BASE STOCK(S) AND/OR BASE OIL(S) AND HAVING
IMPROVED RESISTANCE TO THE LOSS OF VISCOSITY AND
WEIGHT AND A METHOD FOR IMPROVING THE RESISTANCE
TO LOSS OF VISCOSITY AND WEIGHT OF GTL BASE
STOCK(S) AND/OR BASE OIL(S) LUBRICANT OIL FORMULATIONS

Background of the Invention

Field of the Invention

[001] The present invention relates to high kinematic viscosity lubricating oils and lubricating oil formulations comprising wax hydroisomerate/hydrodewaxate base stock(s) and/or base oil(s) and the improvement of the oxidative stability/resistance to weight loss of such lubricating oils/lubricating oil formulations.

Description of the Related Art

[002] Base stocks/base oils that simultaneously have high quality and low cost are not readily available, thus limiting the quality and/or increasing the cost of high viscosity lubricants. Thermal stability, that is, the resistance to decomposition upon exposure to high temperatures but with minimal exposure to air, is an importance property of lubricating oils needed in industrial applications such as oils that circulate through industrial equipment, oils that lubricant gear boxes, oils that lubricant neutral gas engines, hydraulic oils, etc. Thermal decomposition of lubricants contribute to deposit formation. For example, in large marine engines, deposits formed in the hot regions of the engine can interfere with heat transfer in the piston cooling spaces. Additives are not readily available that improve thermal stability, but good oxidative stability and good low temperature properties and resistance to weight loss are still necessary/important properties of such lubricants.

[003] Heretofore only relatively low quality conventional Group I mineral oil base stocks and high quality/high cost poly-alpha-olefin (PAO) base stocks have been available at high viscosities (kinematic viscosities greater than about 120

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mm²/s at 40°C) in sufficient quantities to formulate such lubricants. Some hydroprocessed base stocks/base oils can be used to formulate high kinematic viscosity lubricants and lubricating oil formulations with better oxidative stability than most conventional mineral oil base stocks at cost somewhat below those of PAO base oils/base stocks, but are not available above about 120 mm²/s at 40°C (~600 SUS). Manufacturing base stocks/base oils with higher viscosities by hydroprocessing technology, however, is characterized by low yield and haze formation that interferes with lubricant filtration and contaminant detection.

[004] To produce high viscosity lubricants use has been made of thickener materials. Such thickener materials are characterized as relatively high molecular weight high viscosity polymeric materials such as polyisobutenes, styrene-isoprene copolymers, olefin copolymers, poly-alpha-olefins, polymethacrylates, polyacrylates, copolymers of vinyl acetate and ethylene, dialkylfumarate and vinyl acetate. The use of such thickener, however, while resulting in a formulation displaying high initial viscosity, produces formulation marked by significant loss in kinematic viscosity and in weight over time, i.e., during use.

[005] WO 03/076555 is directed to lubricant blend composition comprising two major components, a copolymer made from ethylene with one or more alpha olefins, the copolymer containing not more than 50 wt% ethylene and having a number average molecular weight from 400 to 10,000 and a polyalphaolefin fluid or a hydroprocessed oil having a VI greater than 80. The hydroprocessed oil is further described as being a Group II oil, a Group III oil, or a F-T wax isomerate. In the Examples the ethylene-alpha-olefin copolymers were combined only with Group III stocks having a KV @ 100°C of 3.98 or with Group II stocks.

[006] JP 2503536B2 is directed to base oils comprising 50-99.8 wt% of a base oil having kinematic viscosity @ 100°C in the range 1-20 mm²/s, said base oil being selected from synthetic hydrocarbons and esters, and an ethylene olefin

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copolymer having kinematic viscosity @ 100°C in the range 1,000 to 10,000 mm²/s. The object of adding the ethylene copolymer to the base oil is to achieve viscosity increase, superior shear stability, heat and oxidation resistance. The base oil, while identified as including synthetic hydrocarbons defines such synthetic hydrocarbons as being alpha olefin oligomers (i.e., PAO), alkyl-benzenes, alkyl naphthalene, "etc.", having a kinematic viscosity @ 100°C of 1 to 20 mm²/s. In the Examples, only PAO was used as base oil.

[007] USP 6,103,099 is directed to the production of synthetic lubricants and lubricant base stocks without dewaxing. The base stock is produced by hydroisomerizing a waxy hydrocarbon feed fraction having an initial boiling point in the 650-750°F range and an end point of at least 1050°F, synthesized by a slurry F-T hydrocarbon synthesis process, the hydroisomerization forming a hydroisomerate containing the desired base stock which is recovered without dewaxing the hydroisomerate. This base stock can be combined with conventional additives, including VI improvers or viscosity modifiers. VI improvers include acrylic polymers and copolymers, e.g., methacrylates and, polymethacrylates as well as olefin copolymers.

[008] USP 6,332,974 is directed to wide-cut lubricant base stocks made by hydroisomerizing and then catalytically dewaxing a waxy F-T synthesized hydrocarbon reaction feed. This base stock can be additized with VI improver and viscosity modifiers including acrylic polymers and copolymers such as polymethacrylates, and polyalkylmethacrylates as well as olefin copolymers. See also USP 6,090,989.

[009] WO 01/57166 is directed to formulated lubricant oils containing high performance base oils derived from highly paraffinic hydrocarbons comprising wax isomerate paraffinic hydrocarbon base stock components in combination with additives. Additives include viscosity modifier polymers having molecular weights typically in the range of about 10,000 to 1,000,000, and include hydro-

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generated styrene-isoprene block copolymers, rubbers based on ethylene and propylene (i.e., olefin copolymers), high molecular weight acrylate or methacrylates, polyisobutylenes, and other materials soluble in the base stock which, when added to the base stocks confer the required viscosity to achieve the desired high temperature viscosity grade.

[010] EP application 0 088 453 is directed to a lubricating composition containing PAO, ethylene-alphaolefin copolymer or hydrogenated polyisoprene having a kinematic viscosity @ 100°C of 40 to -1000 mm²/s, a low viscosity synthetic hydrocarbon and/or a low viscosity ester, and optionally an additive package. The low viscosity synthetic hydrocarbons are identified as having viscosities of from 1 to 10 mm²/s consisting primarily of oligomers of alpha-olefins and alkylated benzenes. In the example using ethylene-alpha olefin copolymers of different viscosities the base oil to which the copolymer is added is PAO. While the ethylene-alpha-olefin copolymer of EP 0 088 453 is shown to be more stable to viscosity and viscosity index losses from oxidation than was a commercial thickener, even the PAO-ethylene alpha olefin blends exhibited some significant deterioration in viscosity and VI after aging.

[011] USP 3,923,919 is directed to ethylene propylene copolymers as oils, the copolymers containing 29-71 mol percent ethylene. The copolymer of this patent is itself seen as being the oil having a viscosity at 210°F of 1-60 mm²/s maximum. When additized with an oxidation inhibitor (mixture of amines, catechol and a metallic dithiocarbamate) the ethylene-propylene copolymer of USP 3,923,919 exhibited oxidative stability superior to that exhibited by a Super Refined Mineral oil additized with the same antioxidant. Similarly an ethylene-propylene copolymer exhibited thermal and shear stability superior to that of Super Refined Mineral oil (no report of additives being present).

[012] USP 5,498,809 is directed to oil soluble copolymers, derived from ethylene and 1-butene, which have a number average molecular weight between

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1,500 and 7,500, at least about 30% of all polymer chains terminated with ethylvinylidene group, and ethylene-derived content of not greater than about 50 wt%. Lubricating oil additive can be prepared by functionalizing and dewaxing these copolymers.

Description of the Invention

[013] It has been discovered that lubricating oils of high viscosity in the range of about 2.0 to 1000 mm²/s, preferably 2 to 500 mm²/s, more preferably 2 to 350 mm²/s, still more preferably about 4 to 200 mm²/s @ 100°C prepared from GTL base stock(s) and/or base oil(s) having a viscosity in the range of 1.5 mm²/s to 50 mm²/s, preferably 2 to 35 mm²/s, more preferably 2 to 20 mm²/s @ 100°C additized with a polyolefin fluid having a viscosity at 100°C in the range of about 2 to 1,000 mm²/s exhibit improved oxidation stability, low temperature properties, viscosity retention and shear stability/weight retention superior to that exhibited by Gas-To-Liquids (GTL) base stock(s) and/or base oil(s) additized with conventional viscosity modifiers and superior to that exhibited by Group I and Group II oils additized with the same polyolefin fluid or with a known viscosity modifier.

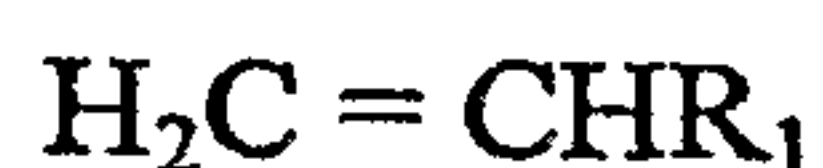
[014] The polyolefin fluid used as viscosity modifier in the present invention is characterized as having a kinematic viscosity in the range of about 2 to 1,000 mm²/s, preferably about 4 to 800 mm²/s, more preferably about 10 to 500 mm²/s, most preferably about 10 to 200 mm²/s at 100°C, and a molecular weight (number average) in the range of about 200 to 10,000, preferably about 400 to 4,000, more preferably about 600 to 3,000. The molecular weight distribution (MWD) of the polyolefin fluid ranges from 1.00 to 4, preferably 1.01 to 3, preferably 1.01 to 2.5. Usually narrower MWD is preferred. When the polyolefin fluid is a copolymer of ethylene with a second alpha olefin the polyolefin fluid is also characterized as containing not more than 50 wt% ethylene.

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[015] The polyolefin fluid can be derived from the copolymerization of a first alpha-olefin with one or more second alpha-olefins. The first alpha-olefin, typically ethylene, propylene, 1-butylene is polymerized with one or more second olefin(s) different from the first, said second olefin different from the first being selected from the group of C₂-C₃₀ straight or branched chain alpha olefins, and mixtures of such olefins, preferably C₂-C₁₄ straight or branched chain alpha-olefins and mixtures of said olefins. When the alpha olefin is branched, it is preferred that the branch be at least two carbons away from the double bond.

[016] The polyolefin fluid can also be a poly-alpha olefin wherein the polymer is a homopolymer made from one or more olefins selected from C₈-C₁₈ alpha olefin monomers or a copolymer of a mixture of such monomers. In the case of the homopolymers, they may be predominantly dimers, trimers and tetramers with minor amounts of higher oligomers.

[017] Preferably the polyolefin fluid is a copolymer of ethylene and an alpha olefin, the alpha olefin being represented by the formula



wherein R₁ is a straight or branched chain alkyl radical selected from the group of alkyl radicals having 1 to 22 carbons, or mixtures thereof, preferably 1 to 12 carbons or mixtures thereof, more preferably propylene or butylene, most preferably propylene or butylenes or the mixture of the two.

[018] The most suitable source of ethylene can be pure ethylene stream specially made for polymerization purpose (polymer grade ethylene). It can also be a dilute ethylene stream, from various source, such as refinery dilute ethylene stream, stream craker, or other source of ethylene. The alpha-olefins, such as propylene, 1-butene, can be available from petrochemical plant, light gas from catalytic fluid cracking process in refinery, from steam cracking of propane, butane, light naphtha, naphtha, etc. Most desirable source are those dilute

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propylene or butene stream, such PP stream containing propane/propylene or stream containing 1,2,i-butenes in butanes (BB stream) (C₄ stream, Raffinate 1 or Raffinate 2 stream from refinery). Other Linear Alpha Olefin (LAO) source from ethylene growth process, which produces 1-butene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, etc. are also most suitable. Other C₂ to C₁₈ LAO sources, such as from steam thermal cracking of wax, either petroleum derived wax or wax produced in a Fischer-Tropsch Hydrocarbon Synthesis process, are also suitable. The LAOs derived from steam thermal cracking of FT wax is most suitable because they are usually low in undesirable S, N, cyclic or aromatic components which is usually a deactivator for the polymerization reaction. LAO produced from metathesis of internal olefins with ethylene or LAO in the presence of other olefins or saturated hydrocarbons are also suitable for the reaction.

[019] The polyolefin fluid can be made by reacting the olefin monomers in the presence of a conventional Ziegler, Ziegler-Natta catalyst, e.g., TiCl₄, TiCl₃, VCl₄ or VOCl₃ with promoter, such as magnesium chloride, zinc chloride, etc and with activator(s), including trialkylaluminum, trialkylboron, and/or a halide such as organo-aluminum halides and/or hydrogen halides. There are many variations of Ziegler or Ziegler-Natta catalysts, as described in the book Ziegler-Natta Catalysts and Polymerizations by John Boor, Jr., Academic Press, NY, 1979.

[020] While the olefin copolymers (OCP) made using Ziegler-Natta catalysts tend to have number average molecular weight of about 10,000 or more, and many of the conventional VI Improver OCP are made by such method, as reviewed in Chapter 10 of Lubricant Additives, Chemistry and Applications. Ed. By L. R. Rudnick, Marcel Dekker, Inc., New York 2003, the process using Ziegler or Ziegler-Natta catalysts can be used to prepare the polyolefin fluid suitable for use in the present invention provided case is taken to produce a

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polyolefin fluid meeting the viscosity, molecular weight, MWD limits previously recited, and where appropriate the ethylene content limit.

[021] Preferably the polyolefin fluids used in the present invention are produced using a catalyst system comprising a metallocene and an aluminoxane. See, for example, USP 4,668,834; USP 4,704,491; WO 90/1503; USP 5,043,515; USP 5,859,159; USP 5,498,809. The polyolefin fluids which are preferred in the present invention are those synthesized using metallocene catalysts and are characterized as having a molecular weight distribution (MWD) defined as the ratio of the weight average molecular weight to the number average molecular weight of about 4 or less, preferably about 3 or less, more preferably about 2.5 or less. The polyolefin fluids have a MWD of from about 1 to 3.5, preferably from about 1 to 3. Both number average and weight average molecular weight can be determined by the technique of gel permeating chromatograph (GPC) with a suitable calibration curve, as is known to those skilled in the art.

[022] The polymerization reaction for the production of polyolefin fluids from a first alpha olefin such as ethylene, propylene, 1-butylene reacted with a second, different alpha olefin which is a straight or branched chain alpha olefin selected from C₂-C₃₀ alpha olefin and mixtures thereof, preferably C₁-C₁₄ straight or branched chain alpha olefin and mixtures thereof is conducted in the presence of a catalyst system comprising at least one metallocene (e.g., a cyclopentadienyl-transition metal compound) and preferably an activator, e.g., an alumoxane compound. The term metallocene refers to compounds containing a coordination bond between a transition metal and at least one cyclopentadiene ring structure. The term cyclopentadiene ring structure includes saturated or unsaturated polycyclic structures such as indenyl and fluorenyl which incorporate a five-membered ring. The co-monomer content can be controlled through the selection of the metallocene catalyst component and by controlling the relative proportions of the feed olefins, usually ethylene and an alpha-olefin,

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e.g., ethylene and 1-butene or ethylene and propylene, or ethylene and 1-pentene, or ethylene and propylene and 1-butene.

[023] The catalysts employed in the production of these polyolefin fluids, are organometallic coordination compounds which are cyclopentadienyl derivatives of a Group 4b metal of the Periodic Table of the Elements (56th Edition of Handbook of Chemistry and Physics, CRC Press, 1975) and include mono-, di- and tricyclopentadienyls and their derivatives of the transition metals.

Particularly desirable are the metallocenes of a Group 4b metal such as titanium, zirconium, and hafnium. These metallocenes are further activated with an alumoxane. The alumoxanes employed in forming the reaction product with the metallocenes are themselves the reaction products of an aluminum trialkyl with water or precursors which act as water source, such as copper sulfate hydrates.

[024] In general, at least one metallocene compound is employed in the formation of the catalyst. Metallocene is a metal derivative of a cyclopentadiene. The metallocenes usefully employed in accordance with this invention contain at least one cyclopentadiene ring. The metal is selected from the Group 4b preferably titanium, zirconium, and hafnium, and most preferably hafnium and zirconium. The cyclopentadienyl ring can be unsubstituted or contain one or more substituents (e.g., from 1 to 5 substituents) such as, for example, a hydrocarbyl substituent (e.g., up to 5 C₁ to C₅ hydrocarbyl substituents) or other substituents, e.g., such as, for example, a trialkyl silyl substituent. The metallocene can contain one, two, or three cyclopentadienyl rings; however, two rings are preferred.

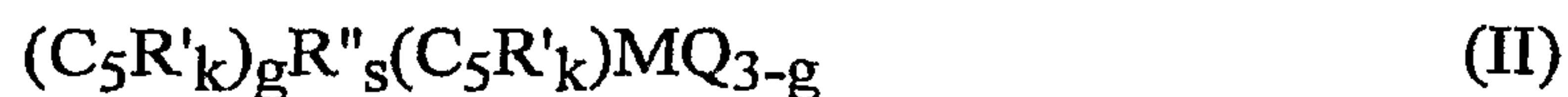
[025] Useful metallocenes can be represented by the general formulas:



wherein C_p is a cyclopentadienyl ring, M is a Group 4b transition metal, R is a hydrocarbyl group or hydrocarboxy group having from 1 to 20 carbon atoms, X

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is a halogen, and m is a whole number from 1 to 3, n is a whole number from 0 to 3, and q is a whole number from 0 to 3.



and



wherein $(C_5R'_k)$ is a cyclopentadienyl or substituted cyclopentadienyl, each R' is the same or different and is hydrogen or a hydrocarbyl radical such as alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radical containing from 1 to 20 carbon atoms, a silicon containing hydrocarbyl radical, or hydrocarbyl radicals wherein two carbon atoms are joined together to form a C_4 - C_6 ring, R'' is a C_1 - C_4 alkylene radical, a dialkyl germanium or silicon, or an alkyl phosphine or amine radical bridging two $(C_5R'_k)$ rings, Q is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl, or aryl alkyl radical having from 1-20 carbon atoms, hydrocarboxy radical having from 1-20 carbon atoms or halogen and can be the same or different from each other, Q' is an alkylidene radical having from 1 to about 20 carbon atoms, s is 0 or 1, g is 0, 1 or 2, s is 0 when g is 0, k is 4 when s is 1, and k is 5 when s is 0, and M is as defined above. Exemplary hydrocarbyl radicals are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl, phenyl and the like. Exemplary silicon containing hydrocarbyl radicals are trimethylsilyl, triethylsilyl and triphenylsilyl. Exemplary halogen atoms include chlorine, bromine, fluorine and iodine and of these halogen atoms, chlorine is preferred. Exemplary hydrocarboxy radicals are methoxy ethoxy, butoxy, amyloxy and the like. Exemplary of the alkylidene radicals is methylenidene, ethylenidene and propylenidene.

[026] The alumoxane compounds useful in the polymerization process may be cyclic or linear or the combination of the two. Cyclic alumoxanes may be represented by the general formula $(R-Al-O)_n$ while linear alumoxanes may be represented by the general formula $R(R-Al-O)_nAlR_2$. In the general formula R is a C_1 - C_5 alkyl group such as, for example, methyl, ethyl, propyl, butyl and

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pentyl, n is an integer of from 3 to 20, and n' is an integer from 1 to about 20. Preferably, R is methyl and n and n' are 4-18. Generally, in the preparation of alumoxanes from, for example, aluminum trimethyl and water, a mixture of the linear and cyclic compounds is obtained.

[027] The alumoxane can be prepared in various ways. Preferably, they are prepared by contacting water with a solution of aluminum trialkyl, such as, for example, aluminum trimethyl, in a suitable organic solvent such as toluene or an aliphatic hydrocarbon. For example, the aluminum alkyl is treated with water in the form of a moist solvent. In an alternative method, the aluminum alkyl such as aluminum trimethyl can be desirably contacted with a hydrated salt such as hydrated copper sulfate or ferrous sulfate. Preferably, the alumoxane is prepared in the presence of a hydrated ferrous sulfate. The method comprises treating a dilute solution of aluminum trimethyl in, for example, toluene, with ferrous sulfate represented by the general formula $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. The ratio of ferrous sulfate to aluminum trimethyl is desirably about 1 mole of ferrous sulfate for 6 to 7 moles of aluminum trimethyl. The reaction is evidenced by the evolution of methane. General method to produce methylaluminoxane (MAO) or other alumoxane can be found in many patents, US 5,663,394, US 5,693,838, US 6,194,340, US 6,518,445, etc.

[028] The mole ratio of aluminum in the alumoxane to total metal in the metallocenes which can be usefully employed can be in the range of about 0.5:1 to 5000:1, and desirably about 1:1 to 1000:1. Preferably, the mole ratio will be in the range of about 500:1 to 5:1 and most preferably about 250:1 to 5:1.

[029] The solvents used in the preparation of the catalyst system are inert hydrocarbons, in particular a hydrocarbon that is inert with respect to the catalyst system. Such solvents are well known and include, for example, isobutane, butane, pentane, hexane, heptane, octane, cyclohexane, methylcyclohexane, toluene, xylene and the like.

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[030] Polymerization is generally conducted at temperatures ranging between about 20°C and 300°C, preferably between about 30°C and 200°C. The polymerization feeds, including the olefins, the solvents and any other feed gases, preferably are purified by passing through molecular sieves and/or oxygenate removal catalyst beds, as typically practiced in polyolefins synthesis. The purpose of the purification is to remove water, oxygenates or any other trace polar components that can deactivate the polymerization catalysts. Usually highly purified feed streams result in high catalyst productivities and high lube selectivity, simplified work up or product isolation step, narrower molecular weight distribution. All these are beneficial for an economical process and more desirable product. Reaction time is not critical and may vary from several hours or more to several minutes or less, depending upon factors such as reaction temperature and the like. One of ordinary skill in the art may readily obtain the optimum reaction time for a given set of reaction parameters by routine experimentation.

[031] The catalyst systems described herein are suitable for the polymerization of ethylene and alpha-olefins in solution over a wide range of pressures. The polymerization can be completed at a pressure of from about 10 to 3,000 bar. The polymerization reaction can be conducted in batch mode, semi-batch or semi-continuous mode, or in continuous stir tank reactor (CSTR) mode.

[032] After polymerization and, optionally, deactivation of the catalyst (e.g., by conventional techniques such as contacting the polymerization reaction medium with water or an alcohol, such as methanol, propanol, isopropanol, etc., or cooling or flashing the medium to terminate the polymerization reaction), the product polymer can be recovered by distillation under vacuum to remove light fraction, which has a boiling point below 650°F at atmospheric pressure. The residual oil fraction can be used as is for this invention. Or more preferably, the residual oil fraction is further hydrogenated using standard hydrofinishing conditions, such as under 500-2000 psi H₂ pressure, 100-250°C and 2 wt% Nickel on

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Kieselguhr catalyst for proper amount of time to reduce the degree of unsaturation down to low bromine number, usually below 2. Usually, the lower the bromine number the better the product, especially the better oxidative stability.

[033] The polymerization may be conducted employing the liquid alpha-olefin reactant as solvent. For example, 1-butene or propylene or other appropriate alpha-olefin liquid, can be used as the reaction medium. Alternatively, polymerization may be accomplished in the presence of a hydrocarbon inert to the polymerization such as butane, isobutane, pentane, isopentane, hexane, isooctane, decane, toluene, xylene, and the like.

[034] Another method to produce these polyolefin fluids is by using Friedel-Crafts polymerization catalysts. For example, the high viscosity polyolefin fluids can be made from ethylene and alpha-olefins in range from 0% ethylene to 50 wt% ethylene as feed. The other alpha-olefins can be propylene, 1-butene, mixed butenes or mixed butanes in BB stream, linear alpha-olefins, including 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, or the mixture of them. The amount of these alpha-olefins in the feed ranges from 50 wt% to 100 wt%.

[035] The PAO's, which are known materials and fall within the present definition of polyolefin fluids as used herein are generally available on a major commercial scale from suppliers such as ExxonMobil Chemical Company, Chevron, BP, and others, typically vary in number average molecular weight from about 250 to about 3000, or higher, and PAO's may be made in kinematic viscosities up to about 100 mm²/s (100°C), or higher, but those having a number average molecular weight in the range 200 to 10,000, preferably 400 to 4,000, more preferably 600 to 3,000 and kinematic viscosity in the range 2 to 1,000, preferably 4 to 800 mm²/s, more preferably 4 to 500 mm²/s, most preferably 4 to 20 mm²/s at 100°C are the ones suitable for use herein. The PAO's are typically comprised of hydrogenated polymers or oligomers of alphaolefins with the

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individual alpha olefin monomers of about C₈ to about C₁₈ alphaolefins, such as 1-octene, 1-decene, 1-dodecene and the like, being preferred. The preferred polyalphaolefins are poly-1-octene, poly-1-decene and poly-1-dodecene and mixtures thereof and mixed olefin-derived polyolefins. However, the dimers of higher olefins in the range of about C₁₄ to C₁₈ may be used. Depending on the viscosity grade and the starting oligomer, the PAO's may be predominantly trimers and tetramers of the starting olefins, with minor amounts of the higher oligomers also being present.

[036] PAO fluids may be conveniently made by the polymerization of an alphaolefin in the presence of a polymerization catalyst such as the Friedel-Crafts catalysts including, for example, aluminum trichloride, boron trifluoride or complexes of boron trifluoride with water, alcohols such as ethanol, propanol or butanol, carboxylic acids or esters such as ethyl acetate or ethyl propionate. For example the methods disclosed by USP 4,149,178 or USP 3,382,291 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; 4,827,064; 4,827,073; 4,910,355; 4,956,122; and 5,068,487. The dimers of the C₁₄ to C₁₈ olefins are described in USP 4,218,330.

[037] Methods to produce these PAOs can be found in U.S. Patents 3,742,082, 5,068,487, etc. Some of these PAOs are available commercially. For example SpectraSynTM 40 and SpectraSynTM 100 are available from ExxonMobil Chemical Co. They are suitable as part of the components for this invention.

[038] The polyolefin fluid is combined with GTL base stock(s) and/or base oil(s) in an amount of from about 0.1 to 90 wt%, preferably about 20 to 80 wt%, more preferably about 40 to 60 wt% based on the total weight of the combination. The amount of polyolefin fluid used in the blends depends on the viscosities of the polyolefin fluid and the desirable finished lubricant viscosities.

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[039] Gas-To-Liquids (GTL) base stock and/or base oil include base stocks and/or base oils derived from one or more GTL materials.

[040] 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, gaseous hydrogen-containing compounds, and/or elements as feedstocks such as hydrogen, carbon dioxide, carbon monoxide, water, methane, ethane, ethylene, acetylene, propane, propylene, propane 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 feedstocks. GTL base stocks and/or base oils include oils boiling in the lube oil boiling range separated from GTL materials such as for example, by distillation, or thermal diffusion, etc., and subsequently subjected to well known solvent or catalytic dewaxing processes to produce lube oils of low pour point; synthesized wax isomerates, comprising, for example, hydrodewaxed or hydroisomerized/catalytic (or solvent) dewaxed synthesized waxy hydrocarbons; hydrodewaxed or hydroisomerized/catalytic (or solvent) dewaxed Fischer-Tropsch (F-T) material (i.e., hydrocarbons, waxy hydrocarbons, waxes and possible analogous oxygenates); preferably hydrodewaxed or hydroisomerized/catalytic (or solvent) dewaxed F-T waxy hydrocarbons, or hydrodewaxed or hydroisomerized/catalytic (or solvent) F-T waxes, hydrodewaxed or hydroisomerized/catalytic (or solvent) dewaxed synthesized waxes, or mixtures thereof. The GTL base stocks and/or base oil may be used as such or in combination with other hydrodewaxed or hydroisomerized/catalytic (or solvent) dewaxed waxy materials comprising, for example, hydrodewaxed or hydroisomerized/catalytic (or solvent) dewaxed mineral/petroleum-derived waxy hydrocarbons, hydrodewaxed or hydroisomerized/catalytic (or solvent) dewaxed

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waxy hydrocarbons, or mixtures thereof, derived from different feed materials including, feedstocks of mineral oil, non-mineral oil, non-petroleum, or natural source origin, e.g., feedstocks 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 hydrodewaxate or hydroisomerate base stocks and base oils.

[041] Slack wax is the wax recovered from petroleum oils by solvent or autorefrigerative 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 autorefrigerative dewaxing employs pressurized, liquefied low boiling hydrocarbons such as propane or butane.

[042] Slack waxes, being 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 hydrodewaxing or hydroisomerization catalyst.

[043] GTL base stock(s) and/or base oil(s) derived from GTL materials, especially, hydrodewaxed, or hydroisomerized/cat (or solvent) dewaxed F-T material derived base stock(s) and/or base oil(s), and other hydrodewaxed, or hydroisomerized/cat (or solvent) dewaxed wax derived base stock(s) and/or base oil(s) are characterized typically as having kinematic viscosities at 100°C of from about 2 mm²/s to about 50 mm²/s, preferably from about 3 mm²/s to about 50 mm²/s, more preferably from about 3.5 mm²/s to about 30 mm²/s, as exemplified by a GTL base stock derived by the isodewaxing of F-T wax, which

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has a kinematic viscosity of about 4 mm²/s at 100°C and a viscosity index of about 130 or greater. Preferably the wax treatment process is hydrodewaxing carried out in a process using a single hydrodewaxing catalyst. Reference herein to Kinematic viscosity refers to a measurement made by ASTM method D445.

[044] GTL base stock(s) and/or base oil(s) derived from GTL materials, especially hydrodewaxed, or hydroisomerized/cat (or solvent) dewaxed F-T material derived base stock(s) and/or base oil(s), and other hydrodewaxed, or hydroisomerized/cat (or solvent) dewaxed wax-derived base stock(s) and/or base oil(s), which can be used as base oil components of this invention are further characterized typically as having pour points of about -5°C or lower, preferably about -10°C or lower, more preferably about -15°C or lower, still more preferably about -20°C or lower, and under some conditions may have advantageous pour points of about -25°C or lower, with useful pour points of about -30°C to about -40°C or lower. If necessary, a separate dewaxing step may be practiced to achieve the desired pour point. In the present invention, however, the GTL or other hydrodewaxed, or hydroisomerized/cat (or solvent) dewaxed wax-derived base stock(s) and/or base oils used are those having pour points of about -30°C or higher, preferably about -25°C or higher, more preferably about -20°C or higher. References herein to pour point refer to measurement made by ASTM D97 and similar automated versions.

[045] The GTL base stock(s) and/or base oil(s) derived from GTL materials, especially hydrodewaxed or hydroisomerized/cat (or solvent) dewaxed F-T material derived base stock(s) and/or base oils, and other such wax-derived base stock(s) and/or base oils which are base oil components which can be used in this invention are also characterized typically as having viscosity indices of 80 or greater, preferably 100 or greater, and more preferably 120 or greater. Additionally, in certain particular instances, the viscosity index of this/these base stock(s) and/or base oils may be preferably 130 or greater, more preferably 135 or greater, and even more preferably 140 or greater. For example, GTL base

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stock(s) that derive from GTL materials preferably F-T materials especially F-T wax generally have a viscosity index of 130 or greater. References herein to viscosity index refer to ASTM method D2270.

[046] In addition, the GTL base stock(s) and/or base oils 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 stocks and/or base oils 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 and/or base oil obtained by the hydroisomerization/isodewaxing of F-T material, especially F-T wax is essentially nil.

[047] In a preferred embodiment, the GTL base stock(s) and/or base oils comprises paraffinic materials that consist predominantly of non-cyclic isoparaffins and only minor amounts of cycloparaffins. These GTL base stock(s) and/or base oils typically comprise paraffinic materials that consist of greater than 60 wt% non-cyclic isoparaffins, preferably greater than 80 wt% non-cyclic isoparaffins, more preferably greater than 85 wt% non-cyclic isoparaffins, and most preferably greater than 90 wt% non-cyclic isoparaffins.

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

[049] Wax hydrodewaxate or hydroisomerate base stocks and/or base oils derived from waxy feeds which are also suitable for use in this invention in

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combination with the aforesaid GTL base stocks and/or base oils, are paraffinic fluids of lubricating viscosity derived from hydrodewaxed or hydroisomerized/catalytic (or solvent) dewaxed waxy feedstocks of mineral or natural source origin, e.g., feedstocks such as one or more of gas oils, slack wax, waxy fuels hydrocracker bottoms, hydrocarbon raffinates, natural waxes, hydrocrackates, thermal crackates or other suitable mineral or non-mineral oil 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 stocks and base oils.

[050] As used herein, the following terms have the indicated meanings:

- a) “wax” - hydrocarbonaceous material having a high pour point, typically existing as a solid at room temperature, i.e., at a temperature in the range from about 15°C to 25°C, and consisting predominantly of paraffinic materials;
- b) “paraffinic” material: any saturated hydrocarbons, such as alkanes. Paraffinic materials may include linear alkanes, branched alkanes (iso-paraffins), cycloalkanes (cycloparaffins; mono-ring and/or multi-ring), and branched cycloalkanes;
- c) “hydroprocessing”: a refining process in which a feedstock is heated with hydrogen at high temperature and under pressure, commonly in the presence of a catalyst, to remove and/or convert less desirable components and to produce an improved product;
- d) “hydrotreating”: a catalytic hydrogenation process that converts sulfur- and/or nitrogen-containing hydrocarbons into hydrocarbon products with reduced sulfur and/or nitrogen content, and which generates hydrogen sulfide and/or ammonia (respectively) as byproducts; similarly, oxygen containing hydrocarbons can also be reduced to hydrocarbons and water;
- e) “catalytic dewaxing”: a conventional catalytic process in which normal paraffins (wax) and/or waxy hydrocarbons, e.g., slightly branched iso-

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paraffins, are converted by cracking/fragmentation into lower molecular weight species to insure that the final oil product (base stock or base oil) has the desired product pour point;

- f) “hydroisomerization” (or isomerization): a catalytic process in which normal paraffins (wax) and/or slightly branched iso-paraffins are converted by rearrangement/isomerization into branched or more branched iso-paraffins (the isomerate from such a process possibly requiring a subsequent additional wax removal step to ensure that the final oil product (base stock or base oil) has the desired product pour point);
- g) “hydrocracking”: a catalytic process in which hydrogenation accompanies the cracking/fragmentation of hydrocarbons, e.g., converting heavier hydrocarbons into lighter hydrocarbons, or converting aromatics and/or cycloparaffins (naphthenes) into non-cyclic branched paraffins.
- h) “hydrodewaxing”: (e.g., ISODEWAXING® of Chevron or MSDW™ of Exxon Mobil corporation) a very selective catalytic process which in a single step or by use of a single catalyst or catalyst mixture effects conversion of wax by isomerization/rearrangement of the n-paraffins and slightly branched isoparaffins into more heavily branched isoparaffins, the resulting product not requiring a separate conventional catalytic or solvent dewaxing step to meet the desired product pour point;
- i) the terms “hydroisomerate”, “isomerate”, “catalytic dewaxate”, and “hydrodewaxate” refer to the products produced by the respective processes, unless otherwise specifically indicated.

[051] Thus the term “hydroisomerization/cat dewaxing” is used to refer to catalytic processes which have the combined effect of converting normal paraffins and/or waxy hydrocarbons by rearrangement/isomerization, into more branched iso-paraffins, followed by (1) catalytic dewaxing to reduce the amount of any residual n-paraffins or slightly branched iso-paraffins present in the isomerate by cracking/fragmentation or by (2) hydrodewaxing to effect further

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isomerization and very selective catalytic dewaxing of the isomerate, to reduce the product pour point. When the term (or solvent), is included in the recitation, the process described involves hydroisomerization followed by solvent dewaxing which effects the physical separation of wax from the hydroisomerate so as to reduce the product pour point.

[052] The term GTL base stock and/or base oil and/or wax hydrodewaxate or hydroisomerate base stock and/or base oil as used herein and in the claims is to be understood as embracing individual fractions of GTL base stock and/or base oil and/or of wax-derived hydrodewaxed or hydroisomerized/cat (or solvent) dewaxed base stock and/or base oil as recovered in the production process, mixtures of two or more GTL base stocks and/or base oil(s) fractions and/or wax-derived hydrodewaxed, or hydroisomerized/cat (or solvent) dewaxed base stock(s) and/or base oil(s) fractions, as well as mixtures of one or two or more low viscosity GTL base stock(s) and/or base oil(s) fraction(s) and/or wax-derived hydrodewaxed, or hydroisomerized/cat (or solvent) dewaxed base stock(s) and/or base oil(s) fraction(s) with one, two or more higher viscosity GTL base stock(s) and/or base oil(s) fraction(s) and/or wax-derived hydrodewaxed, or hydroisomerized/cat (or solvent) dewaxed base stock(s) and/or base oil(s) fraction(s) to produce a dumbbell blend wherein the blend exhibits a kinematic viscosity within the aforesaid recited range.

[053] 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.

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[054] In an F-T synthesis process, a synthesis gas comprising a mixture of H_2 and CO is catalytically converted into hydrocarbons and preferably liquid hydrocarbons. The mole ratio of the hydrogen to the carbon monoxide may broadly range from about 0.5 to 4, but is more typically within the range of from about 0.7 to 2.75 and preferably from about 0.7 to 2.5. As is well known, F-T synthesis processes include processes in which the catalyst is in the form of a fixed bed, a fluidized bed or as a slurry of catalyst particles in a hydrocarbon slurry liquid. The stoichiometric mole ratio for a F-T synthesis reaction is 2.0, but there are many reasons for using other than a stoichiometric ratio as those skilled in the art know. In cobalt slurry hydrocarbon synthesis process the feed mole ratio of the H_2 to CO is typically about 2.1/1. The synthesis gas comprising a mixture of H_2 and CO is bubbled up into the bottom of the slurry and reacts in the presence of the particulate F-T synthesis catalyst in the slurry liquid at conditions effective to form hydrocarbons, a portion of which are liquid at the reaction conditions and which comprise the hydrocarbon slurry liquid. The synthesized hydrocarbon liquid is separated from the catalyst particles as filtrate by means such as filtration, although other separation means such as centrifugation can be used. Some of the synthesized hydrocarbons pass out the top of the hydrocarbon synthesis reactor as vapor, along with unreacted synthesis gas and other gaseous reaction products. Some of these overhead hydrocarbon vapors are typically condensed to liquid and combined with the hydrocarbon liquid filtrate. Thus, the initial boiling point of the filtrate may vary depending on whether or not some of the condensed hydrocarbon vapors have been combined with it. Slurry hydrocarbon synthesis process conditions vary somewhat depending on the catalyst and desired products. Typical conditions effective to form hydrocarbons comprising mostly C_{5+} paraffins, (e.g., C_{5+} - C_{200}) and preferably C_{10+} paraffins, in a slurry hydrocarbon synthesis process employing a catalyst comprising a supported cobalt component include, for example, temperatures, pressures and hourly gas space velocities in the range of from

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about 320-850°F, 80-600 psi and 100-40,000 V/hr/V, expressed as standard volumes of the gaseous CO and H₂ mixture (0°C, 1 atm) per hour per volume of catalyst, respectively. The term "C₅₊" is used herein to refer to hydrocarbons with a carbon number of greater than 4, but does not imply that material with carbon number 5 has to be present. Similarly other ranges quoted for carbon number do not imply that hydrocarbons having the limit values of the carbon number range have to be present, or that every carbon number in the quoted range is present. It is preferred that the hydrocarbon synthesis reaction be conducted under conditions in which limited or no water gas shift reaction occurs and more preferably with no water gas shift reaction occurring during the hydrocarbon synthesis. It is also preferred to conduct the reaction under conditions to achieve an alpha of at least 0.85, preferably at least 0.9 and more preferably at least 0.92, so as to synthesize more of the more desirable higher molecular weight hydrocarbons. This has been achieved in a slurry process using a catalyst containing a catalytic cobalt component. Those skilled in the art know that by alpha is meant the Schultz-Flory kinetic alpha. While suitable F-T reaction types of catalyst comprise, for example, one or more Group VIII catalytic metals such as Fe, Ni, Co, Ru and Re, it is preferred that the catalyst comprise a cobalt catalytic component. In one embodiment the catalyst comprises catalytically effective amounts of Co and one or more of Re, Ru, Fe, Ni, Th, Zr, Hf, U, Mg and La on a suitable inorganic support material, preferably one which comprises one or more refractory metal oxides. Preferred supports for Co containing catalysts comprise Titania, particularly. Useful catalysts and their preparation are known and illustrative, but nonlimiting examples may be found, for example, in U.S. Pat. Nos. 4,568,663; 4,663,305; 4,542,122; 4,621,072 and 5,545,674.

[055] As set forth above, the waxy feed from which the base stock(s) and/or base oil(s) is/are derived is a wax or waxy feed from mineral oil, non-mineral oil, non-petroleum, or other natural source, especially slack wax, or GTL

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material, preferably F-T material, referred to as F-T wax. F-T wax preferably has an initial boiling point in the range of from 650-750°F and preferably continuously boils up to an end point of at least 1050°F. A narrower cut waxy feed may also be used during the hydroisomerization. A portion of the n-paraffin waxy feed is converted to lower boiling isoparaffinic material. Hence, there must be sufficient heavy n-paraffin material to yield an isoparaffin containing isomerate boiling in the lube oil range. If catalytic dewaxing is also practiced after isomerization/isodewaxing, some of the isomerate/isodewaxate will also be hydrocracked to lower boiling material during the conventional catalytic dewaxing. Hence, it is preferred that the end boiling point of the waxy feed be above 1050°F (1050°F+).

[056] When a boiling range is quoted herein it defines the lower and/or upper distillation temperature used to separate the fraction. Unless specifically stated (for example, by specifying that the fraction boils continuously or constitutes the entire range) the specification of a boiling range does not require any material at the specified limit has to be present, rather it excludes material boiling outside that range.

[057] The waxy feed preferably comprises the entire 650-750°F+ fraction formed by the hydrocarbon synthesis process, having an initial cut point between 650°F and 750°F determined by the practitioner and an end point, preferably above 1050°F, determined by the catalyst and process variables employed by the practitioner for the synthesis. Such fractions are referred to herein as “650-750°F+ fractions”. By contrast, “650-750°F” fractions” refers to a fraction with an unspecified initial cut point and an end point somewhere between 650°F and 750°F. Waxy feeds may be processed as the entire fraction or as subsets of the entire fraction prepared by distillation or other separation techniques. The waxy feed also typically comprises more than 90%, generally more than 95% and preferably more than 98 wt% paraffinic hydrocarbons, most of which are normal paraffins. It has negligible amounts of sulfur and nitrogen compounds (e.g., less

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than 1 wppm of each), with less than 2,000 wppm, preferably less than 1,000 wppm and more preferably less than 500 wppm of oxygen, in the form of oxygenates. Waxy feeds having these properties and useful in the process of the invention have been made using a slurry F-T process with a catalyst having a catalytic cobalt component, as previously indicated.

[058] The process of making the lubricant oil base stocks from waxy stocks, e.g., slack wax or F-T wax, 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, as indicated above, 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. Conversion temperatures range from about 150°C to about 500°C at pressures ranging from about 500 to 20,000 kPa. This process may be operated in the presence of hydrogen, and hydrogen partial pressures range from about 600 to 6000 kPa. The ratio of hydrogen to the hydrocarbon feedstock (hydrogen circulation rate) typically range from about 10 to 3500 n.l.l.⁻¹ (56 to 19,660 SCF/bbl) and the space velocity of the feedstock typically ranges from about 0.1 to 20 LHSV, preferably 0.1 to 10 LHSV.

[059] Following any needed hydrodenitrogenation or hydrodesulfurization, the hydroprocessing used for the production of base stocks from such waxy feeds may use an amorphous hydrocracking/hydroisomerization catalyst, such as a

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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.

[060] Other isomerization catalysts and processes for hydrocracking, hydro-dewaxing, or hydroisomerizing GTL materials and/or waxy materials to base stock or base oil are described, for example, in U.S. Pat. Nos. 2,817,693; 4,900,407; 4,937,399; 4,975,177; 4,921,594; 5,200,382; 5,516,740; 5,182,248; 5,290,426; 5,580,442; 5,976,351; 5,935,417; 5,885,438; 5,965,475; 6,190,532; 6,375,830; 6,332,974; 6,103,099; 6,025,305; 6,080,301; 6,096,940; 6,620,312; 6,676,827; 6,383,366; 6,475,960; 5,059,299; 5,977,425; 5,935,416; 4,923,588; 5,158,671; and 4,897,178; EP 0324528 (B1), EP 0532116 (B1), EP 0532118 (B1), EP 0537815 (B1), EP 0583836 (B2), EP 0666894 (B2), EP 0668342 (B1), EP 0776959 (A3), WO 97/031693 (A1), WO 02/064710 (A2), WO 02/064711 (A1), WO 02/070627 (A2), WO 02/070629 (A1), WO 03/033320 (A1) as well as in British Patents 1,429,494; 1,350,257; 1,440,230; 1,390,359; WO 99/45085 and WO 99/20720. Particularly favorable processes are described in European Patent Applications 464546 and 464547. Processes using F-T wax feeds are described in U.S. Pat. Nos. 4,594,172; 4,943,672; 6,046,940; 6,475,960; 6,103,099; 6,332,974; and 6,375,830.

[061] 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 USP 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.

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[062] In one embodiment, conversion of the waxy feedstock may be conducted over a combination of Pt/zeolite beta and Pt/ZSM-23 catalysts 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 the hydrodewaxing 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 stock and/or base oil products may be obtained. Catalyst ZSM-48 is described in USP 5,075,269. The use of the Group VIII metal loaded ZSM-48 family of catalysts, preferably platinum on ZSM-48, in the hydroisomerization of the waxy feedstock eliminates the need for any subsequent, separate dewaxing step, and is preferred.

[063] A dewaxing step, when needed, may be accomplished using one or more of solvent dewaxing, catalytic dewaxing or hydrodewaxing processes and either the entire hydroisomerate or the 650-750°F+ fraction may be dewaxed, depending on the intended use of the 650-750°F- material present, if it has not been separated from the higher boiling material prior to the dewaxing. In solvent dewaxing, the hydroisomerate may be contacted with chilled solvents such as acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), mixtures of MEK/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. Autorefrigerative dewaxing using low molecular weight hydrocarbons, such as propane, can also be used in which the hydroisomerate is mixed with, e.g., liquid propane, a 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

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then stripped out of the raffinate, which is then fractionated to produce the preferred base stocks useful in the present invention. Also well known is catalytic dewaxing, in which 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, in the boiling range, for example, 650-750°F-, which are separated from the heavier 650-750°F+ base stock fraction and the base stock fraction fractionated into two or more base stocks. Separation of the lower boiling material may be accomplished either prior to or during fractionation of the 650-750°F+ material into the desired base stocks.

[064] 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 TON, and the silicoaluminophosphates known as SAPO's. 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 400-600°F, a pressure of 500-900 psig, H₂ treat rate of 1500-3500 SCF/B for flow-through reactors and LHSV of 0.1-10, preferably 0.2-2.0. 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 650-750°F to material boiling below its initial boiling point.

[065] GTL base stock(s) and/or base oil(s), hydrodewaxed, or hydroisomerized/cat (or solvent) dewaxed wax-derived base stock(s) and/or base

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oil(s), have a beneficial kinematic viscosity advantage over conventional API Group II and Group III base stocks, and so may be very advantageously used with the instant invention. Such GTL base stock(s) and/or base oil(s) can have significantly higher kinematic viscosities, up to about 20-50 mm²/s at 100°C, whereas by comparison commercial Group II base oils can have kinematic viscosities, up to about 15 mm²/s at 100°C, and commercial Group III base oils can have kinematic viscosities, up to about 10 mm²/s at 100°C. The higher kinematic viscosity range of GTL base stock(s) and/or base oil(s), compared to the more limited kinematic viscosity range of Group II and Group III base stocks and base oils, in combination with the instant invention can provide additional beneficial advantages in formulating lubricant compositions.

[066] In the present invention the GTL base stock(s) and/or base oil(s) can constitute all or part of the base stock oil to which the PAO is added.

[067] The GTL base stock(s) and/or base oil(s) can constitute from 5 to 100%, preferably 40 to 100%, more preferably 70 to 100%, still more preferably 90 to 100% by weight of the total of the base oil, the amount employed being left to the practitioner in response to the requirements of the finished lubricant, the balance being mineral oil stocks, e.g., Group I, Group II, Group III stocks as defined by API base stock classification, and/or wax hydrodewaxate or hydroisomerate derived from waxes or waxy feeds derived from mineral oil, non-mineral oil or natural sources, e.g., slack wax, foot oil, waxy raffinate, wax from coal liquefaction or shale oil processing, etc.

[068] These GTL, and optionally other base oils including hydrodewaxate or hydroisomerate derived from the waxes or waxy feeds, and polyolefin fluid blends can be also mixed with other desirable components to further improve the properties. These other components include many of the Group V base stocks as defined by API base stock classification. Typical group V base stocks include esters fluids, alkylaromatic fluids, polyalkylene glycol fluids, etc.

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[069] A preferred GTL liquid hydrocarbon composition is one comprising paraffinic hydrocarbon components in which the extent of branching, as measured by the percentage of methyl hydrogens (BI), and the proximity of branching, as measured by the percentage of recurring methylene carbons which are four or more carbons removed from an end group or branch ($\text{CH}_2 \geq 4$), are such that: (a) $\text{BI} - 0.5(\text{CH}_2 \geq 4) > 15$; and (b) $\text{BI} + 0.85(\text{CH}_2 \geq 4) < 45$ as measured over said liquid hydrocarbon composition as a whole.

[070] The preferred GTL base stock and/or base oil can be further characterized, if necessary, as having less than 0.1 wt% aromatic hydrocarbons, less than 20 wppm nitrogen containing compounds, less than 20 wppm sulfur containing compounds, a pour point of less than -18°C , preferably less than -30°C , a preferred $\text{BI} \geq 25.4$ and $(\text{CH}_2 \geq 4) \leq 22.5$. They have a nominal boiling point of 370°C^+ , on average they average fewer than 10 hexyl or longer branches per 100 carbon atoms and on average have more than 16 methyl branches per 100 carbon atoms. They also can be characterized by a combination of dynamic viscosity, as measured by CCS at -40°C , and kinematic viscosity, as measured at 100°C represented by the formula: $\text{DV (at } -40^\circ\text{C}) < 2900 (\text{KV at } 100^\circ\text{C}) - 7000$.

[071] The preferred GTL base stock and/or base oil is also characterized as comprising a mixture of branched paraffins characterized in that the lubricant base oil contains at least 90% of a mixture of branched paraffins, wherein said branched paraffins are paraffins having a carbon chain length of about C_{20} to about C_{40} , a molecular weight of about 280 to about 562, a boiling range of about 650°F to about 1050°F , and wherein said branched paraffins contain up to four alkyl branches and wherein the free carbon index of said branched paraffins is at least about 3.

[072] In the above the Branching Index (BI), Branching Proximity ($\text{CH}_2 \geq 4$), and Free Carbon Index (FCI) are determined as follows:

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Branching Index

[073] A 359.88 MHz ^1H solution NMR spectrum is obtained on a Bruker 360 MHz AMX spectrometer using 10% solutions in CDCl_3 . TMS is the internal chemical shift reference. CDCl_3 solvent gives a peak located at 7.28. All spectra are obtained under quantitative conditions using 90 degree pulse (10.9 μs), a pulse delay time of 30 s, which is at least five times the longest hydrogen spin-lattice relaxation time (T_1), and 120 scans to ensure good signal-to-noise ratios.

[074] H atom types are defined according to the following regions:

- 9.2-6.2 ppm hydrogens on aromatic rings;
- 6.2-4.0 ppm hydrogens on olefinic carbon atoms;
- 4.0-2.1 ppm benzylic hydrogens at the α -position to aromatic rings;
- 2.1-1.4 ppm paraffinic CH methine hydrogens;
- 1.4-1.05 ppm paraffinic CH_2 methylene hydrogens;
- 1.05-0.5 ppm paraffinic CH_3 methyl hydrogens.

[075] The branching index (BI) is calculated as the ratio in percent of non-benzylic methyl hydrogens in the range of 0.5 to 1.05 ppm, to the total non-benzylic aliphatic hydrogens in the range of 0.5 to 2.1 ppm.

Branching Proximity ($\text{CH}_2 \geq 4$)

[076] A 90.5 MHz ^{13}C CMR single pulse and 135 Distortionless Enhancement by Polarization Transfer (DEPT) NMR spectra are obtained on a Bruker 360 MHz AMX spectrometer using 10% solutions in CDCl_3 . TMS is the internal chemical shift reference. CDCl_3 solvent gives a triplet located at 77.23 ppm in the ^{13}C spectrum. All single pulse spectra are obtained under quantitative conditions using 45 degree pulses (6.3 μs), a pulse delay time of 60 s, which is at least five times the longest carbon spin-lattice relaxation time (T_1), to ensure complete relaxation of the sample, 200 scans to ensure good signal-to-noise ratios, and WALTZ-16 proton decoupling.

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[077] The C atom types CH₃, CH₂, and CH are identified from the 135 DEPT ¹³C NMR experiment. A major CH₂ resonance in all ¹³C NMR spectra at ≈29.8 ppm is due to equivalent recurring methylene carbons which are four or more removed from an end group or branch (CH₂ > 4). The types of branches are determined based primarily on the ¹³C chemical shifts for the methyl carbon at the end of the branch or the methylene carbon one removed from the methyl on the branch.

[078] Free Carbon Index (FCI). The FCI is expressed in units of carbons, and is a measure of the number of carbons in an isoparaffin that are located at least 5 carbons from a terminal carbon and 4 carbons way from a side chain. Counting the terminal methyl or branch carbon as "one" the carbons in the FCI are the fifth or greater carbons from either a straight chain terminal methyl or from a branch methane carbon. These carbons appear between 29.9 ppm and 29.6 ppm in the carbon-13 spectrum. They are measured as follows:

- a) calculate the average carbon number of the molecules in the sample which is accomplished with sufficient accuracy for lubricating oil materials by simply dividing the molecular weight of the sample oil by 14 (the formula weight of CH₂);
- b) divide the total carbon-13 integral area (chart divisions or area counts) by the average carbon number from step a. to obtain the integral area per carbon in the sample;
- c) measure the area between 29.9 ppm and 29.6 ppm in the sample; and
- d) divide by the integral area per carbon from step b. to obtain FCI.

[079] Branching measurements can be performed using any Fourier Transform NMR spectrometer. Preferably, the measurements are performed using a spectrometer having a magnet of 7.0T or greater. In all cases, after verification by Mass Spectrometry, UV or an NMR survey that aromatic carbons were absent, the spectral width was limited to the saturated carbon region, about 0-80 ppm vs. TMS (tetramethylsilane). Solutions of 15-25 percent by weight in

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chloroform-d1 were excited by 45 degrees pulses followed by a 0.8 sec acquisition time. In order to minimize non-uniform intensity data, the proton decoupler was gated off during a 10 sec delay prior to the excitation pulse and on during acquisition. Total experiment times ranged from 11-80 minutes. The DEPT and APT sequences were carried out according to literature descriptions with minor deviations described in the Varian or Bruker operating manuals.

[080] DEPT is Distortionless Enhancement by Polarization Transfer. DEPT does not show quaternaries. The DEPT 45 sequence gives a signal for all carbons bonded to protons. DEPT 90 shows CH carbons only. DEPT 135 shows CH and CH₃ up and CH₂ 180 degrees out of phase (down). APT is Attached Proton Test. It allows all carbons to be seen, but if CH and CH₃ are up, then quaternaries and CH₂ are down. The sequences are useful in that every branch methyl should have a corresponding CH and the methyls are clearly identified by chemical shift and phase. The branching properties of each sample are determined by C-13 NMR using the assumption in the calculations that the entire sample is isoparaffinic. Corrections are not made for n-paraffins or cycloparaffins, which may be present in the oil samples in varying amounts. The cycloparaffins content is measured using Field Ionization Mass Spectroscopy (FIMS).

[081] GTL base stock(s) and/or base oil(s), and hydrodewaxed, or hydroisomerized/cat (or solvent) dewaxed wax base stock(s) and/or base oil(s), for example, hydroisomerized or hydrodewaxed waxy synthesized hydrocarbon, e.g., Fischer-Tropsch waxy hydrocarbon base stock(s) and/or base oil(s) are of low or zero sulfur and phosphorus content. There is a movement among original equipment manufacturers and oil formulators to produce formulated oils of ever increasingly reduced sulfated ash, phosphorus and sulfur content to meet ever increasingly restrictive environmental regulations. Such oils, known as low SAPS oils, would rely on the use of base oils which themselves, inherently, are of low or zero initial sulfur and phosphorus content. Such oils when used as

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base oils can be formulated with additives. Even if the additive or additives included in the formulation contain sulfur and/or phosphorus the resulting formulated lubricating oils will be lower or low SAPS oils as compared to lubricating oils formulated using conventional mineral oil base stocks.

[082] Low SAPS formulated oils for vehicle engines (both spark ignited and compression ignited) will have a sulfur content of 0.7 wt% or less, preferably 0.6 wt% or less, more preferably 0.5 wt% or less, most preferably 0.4 wt% or less, an ash content of 1.2 wt% or less, preferably 0.8 wt% or less, more preferably 0.4 wt% or less, and a phosphorus content of 0.18% or less, preferably 0.1 wt% or less, more preferably 0.09 wt% or less, most preferably 0.08 wt% or less, and in certain instances, even preferably 0.05 wt% or less.

[083] These mostly paraffinic GTL base stock(s) and/or base oil(s), when blended with the polyolefin fluids yield unique blend compositions. These blend compositions have unexpected high thermal, oxidative stability and excellent viscometrics (wide viscosity range, high VI and low pour point). This blend composition is characterized by wide range of kinematic viscosity (from 2 mm²/s to 1000 mm²/s at 100°C or 3 mm²/s to 50,000 mm²/s at 40°C, high VI and low pour points) and low amount of any other undesirable components - low S, N, low aromatics, low cyclic hydrocarbons or naphthenic components. Such compositions are not previously known.

[084] These mixtures of GTL base stock(s) and/or base oil(s) with polyolefin fluids may be blended with effective amounts of one or more suitable additives to form lubricant compositions.

[085] Examples of typical additives include, but are not limited to, oxidation inhibitors, antioxidants, dispersants, detergents, corrosion inhibitors, rust inhibitors, metal deactivators, anti-wear agents, extreme pressure additives, anti-seizure agents, pour point depressants, wax modifiers, other viscosity index improvers, other viscosity modifiers, fluid-loss additives, seal compatibility

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agents, friction modifiers, lubricity agents, anti-staining agents, chromophoric agents, defoamants, demulsifiers, emulsifiers, densifiers, wetting agents, gelling agents, tackiness agents, colorants, and others. For a review of many commonly used additives, see Klamann in *Lubricants and Related Products*, Verlag Chemie, Deerfield Beach, FL; ISBN 0-89573-177-0. Reference is also made to "Lubricant Additives" by M. W. Ranney, published by Noyes Data Corporation of Parkridge, NJ (1973).

[086] Finished lubricants comprise the lubricant base stock or base oil, plus at least one performance additive.

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

Antiwear and EP Additives

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

[089] While there are many different types of antiwear additives, for several decades the principal antiwear additive for internal combustion engine crankcase oils is a metal alkylthiophosphate and more particularly a metal dialkyldithiophosphate in which the primary metal constituent is zinc, or zinc dialkyldithiophosphate (ZDDP). ZDDP compounds generally are of the formula $\text{Zn}[\text{SP}(\text{S})(\text{OR}^1)(\text{OR}^2)]_2$ where R^1 and R^2 are C_1 - C_{18} alkyl groups, preferably C_2 - C_{12} alkyl groups. These alkyl groups may be straight chain or branched. The ZDDP is typically used in amounts of from about 0.4 to 1.4 wt% of the total lube oil composition, although more or less can often be used advantageously.

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[090] However, it is found that the phosphorus from these additives has a deleterious effect on the catalyst in catalytic converters and also on oxygen sensors in automobiles. One way to minimize this effect is to replace some or all of the ZDDP with phosphorus-free antiwear additives.

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



[092] where each of R^3 - R^6 are independently hydrogen or a hydrocarbon radical. Preferred hydrocarbon radicals are alkyl or alkenyl radicals. Any two of R^3 - R^6 may be connected so as to form a cyclic ring. Additional information concerning sulfurized olefins and their preparation can be found in USP 4,941,984, incorporated by reference herein in its entirety.

[093] The use of polysulfides of thiophosphorus acids and thiophosphorus acid esters as lubricant additives is disclosed in U.S. Patents 2,443,264; 2,471,115; 2,526,497; and 2,591,577. Addition of phosphorothionyl disulfides as an antiwear, antioxidant, and EP additive is disclosed in USP 3,770,854. Use of alkylthiocarbamoyl compounds (bis(dibutyl)thiocarbamoyl, for example) in combination with a molybdenum compound (oxymolybdenum diisopropylphosphorodithioate sulfide, for example) and a phosphorous ester (dibutyl hydrogen phosphite, for example) as antiwear additives in lubricants is disclosed in USP 4,501,678. USP 4,758,362 discloses use of a carbamate additive to provide improved antiwear and extreme pressure properties. The use of thiocarbamate as an antiwear additive is disclosed in USP 5,693,598. Thiocarbamate/molybdenum complexes such as moly-sulfur alkyl dithio-

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carbamate trimer complex ($R=C_8-C_{18}$ alkyl) are also useful antiwear agents. The use or addition of such materials should be kept to a minimum if the object is to produce low SAP formulations.

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

[095] ZDDP is combined with other compositions that provide antiwear properties. USP 5,034,141 discloses that a combination of a thiodixanthogen compound (octylthiodixanthogen, for example) and a metal thiophosphate (ZDDP, for example) can improve antiwear properties. USP 5,034,142 discloses that use of a metal alkyoxyalkylxanthate (nickel ethoxyethylxanthate, for example) and a dixanthogen (diethoxyethyl dixanthogen, for example) in combination with ZDDP improves antiwear properties.

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

Viscosity Index Improvers

[097] Viscosity index improvers (also known as VI improvers, viscosity modifiers, and viscosity improvers) provide lubricants with high and low

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temperature operability. These additives impart shear stability at elevated temperatures and acceptable viscosity at low temperatures.

[098] Suitable viscosity index improvers include high molecular weight hydrocarbons, polyesters and viscosity index improver dispersants that function as both a viscosity index improver and a dispersant. Typical molecular weights of these polymers are between about 10,000 to 1,000,000, more typically about 20,000 to 500,000, and even more typically between about 50,000 and 200,000.

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

[0100] Viscosity index improvers may be used in an amount of about 0.01 to 8 wt%, preferably about 0.01 to 4 wt%.

Antioxidants

[0101] Antioxidants retard the oxidative degradation of base oils during service. Such degradation may result in deposits on metal surfaces, the presence of sludge, or a viscosity increase in the lubricant. One skilled in the art knows a wide variety of oxidation inhibitors that are useful in lubricating oil compositions. See, Klamann in *Lubricants and Related Products*, op cite, and U.S. Patents 4,798,684 and 5,084,197, for example.

[0102] Useful antioxidants include hindered phenols. These phenolic antioxidants may be ashless (metal-free) phenolic compounds or neutral or basic

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metal salts of certain phenolic compounds. Typical phenolic antioxidant compounds are the hindered phenolics which are the ones which contain a sterically hindered hydroxyl group, and these include those derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or p-position to each other. Typical phenolic antioxidants include the hindered phenols substituted with C₆+ alkyl groups and the alkylene coupled derivatives of these hindered phenols. Examples of phenolic materials of this type 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-t-butyl-4-heptyl phenol; and 2-methyl-6-t-butyl-4-dodecyl phenol. Other useful hindered mono-phenolic antioxidants may include for example hindered 2,6-di-alkyl-phenolic propionic ester derivatives. Bis-phenolic antioxidants may also be advantageously used in combination with the instant invention. Examples of ortho-coupled phenols include: 2,2'-bis(4-heptyl-6-t-butyl-phenol); 2,2'-bis(4-octyl-6-t-butyl-phenol); and 2,2'-bis(4-dodecyl-6-t-butyl-phenol). Para-coupled bisphenols include for example 4,4'-bis(2,6-di-t-butyl phenol) and 4,4'-methylene-bis(2,6-di-t-butyl phenol).

[0103] Non-phenolic oxidation inhibitors which may be used include aromatic amine antioxidants and these may be used either as such or in combination with phenolics. Typical examples of non-phenolic antioxidants include: alkylated and non-alkylated aromatic amines such as aromatic monoamines of the formula $R^8R^9R^{10}N$ where R^8 is an aliphatic, aromatic or substituted aromatic group, R^9 is an aromatic or a substituted aromatic group, and R^{10} is H, alkyl, aryl or $R^{11}S(O)_xR^{12}$ where R^{11} is an alkylene, alkenylene, or aralkylene group, R^{12} is a higher alkyl group, or an alkenyl, aryl, or alkaryl group, and x is 0, 1 or 2. The aliphatic group R^8 may contain from 1 to about 20 carbon atoms, and preferably contains from about 6 to 12 carbon atoms. The aliphatic group is a saturated aliphatic group. Preferably, both R^8 and R^9 are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring aromatic group such as

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naphthyl. Aromatic groups R^8 and R^9 may be joined together with other groups such as S.

[0104] Typical aromatic amines antioxidants have alkyl substituent groups of at least about 6 carbon atoms. Examples of aliphatic groups include hexyl, heptyl, octyl, nonyl, and decyl. Generally, the aliphatic groups will not contain more than about 14 carbon atoms. The general types of amine antioxidants useful in the present compositions include diphenylamines, phenyl naphthylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more aromatic amines are also useful. Polymeric amine antioxidants can also be used. Particular examples of aromatic amine antioxidants useful in the present invention include: p,p'-dioctyldiphenylamine; t-octylphenyl-alpha-naphthylamine; phenyl-alphanaphthylamine; and p-octylphenyl-alpha-naphthylamine.

[0105] Sulfurized alkyl phenols and alkali or alkaline earth metal salts thereof also are useful antioxidants.

[0106] Another class of antioxidant used in lubricating oil compositions is oil-soluble copper compounds. Any oil-soluble suitable copper compound may be blended into the lubricating oil. Examples of suitable copper antioxidants include copper dihydrocarbyl thio- or dithio-phosphates and copper salts of carboxylic acid (naturally occurring or synthetic). Other suitable copper salts include copper 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 known to be particularly useful.

[0107] Preferred antioxidants include hindered phenols, arylamines. These antioxidants may be used individually by type or in combination with one another. Such additives may be used in an amount of about 0.01 to 5 wt%, preferably about 0.01 to 1.5 wt%, more preferably zero to less than 1.5 wt%, most preferably zero.

Detergents

[0108] Detergents are commonly used in lubricating compositions. A typical detergent is an anionic material that contains a long chain hydrophobic portion of the molecule and a smaller anionic or oleophobic hydrophilic portion of the molecule. The anionic portion of the detergent is typically derived from an organic acid such as a sulfur acid, carboxylic acid, phosphorous acid, phenol, or mixtures thereof. The counterion is typically an alkaline earth or alkali metal.

[0109] Salts that contain a substantially stoichiometric amount of the metal are described as neutral salts and have a total base number (TBN, as measured by ASTM D2896) of from 0 to 80. Many compositions are overbased, containing large amounts of a metal base that is achieved by reacting an excess of a metal compound (a metal hydroxide or oxide, for example) with an acidic gas (such as carbon dioxide). Useful detergents can be neutral, mildly overbased, or highly overbased.

[0110] It is desirable for at least some detergent to be overbased. Overbased detergents help neutralize acidic impurities produced by the combustion process and become entrapped in the oil. Typically, the overbased material has a ratio of metallic ion to anionic portion of the detergent of about 1.05:1 to 50:1 on an equivalent basis. More preferably, the ratio is from about 4:1 to about 25:1. The resulting detergent is an overbased detergent that will typically have a TBN of about 150 or higher, often about 250 to 450 or more. Preferably, the overbasing cation is sodium, calcium, or magnesium. A mixture of detergents of differing TBN can be used in the present invention.

[0111] Preferred detergents include the alkali or alkaline earth metal salts of sulfonates, phenates, carboxylates, phosphates, and salicylates.

[0112] Sulfonates may be prepared from sulfonic acids that are typically obtained by sulfonation of alkyl substituted aromatic hydrocarbons. Hydrocarbon examples include those obtained by alkylating benzene, toluene, xylene,

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naphthalene, biphenyl and their halogenated derivatives (chlorobenzene, chlorotoluene, and chloronaphthalene, for example). The alkylating agents typically have about 3 to 70 carbon atoms. The alkaryl sulfonates typically contain about 9 to about 80 carbon or more carbon atoms, more typically from about 16 to 60 carbon atoms.

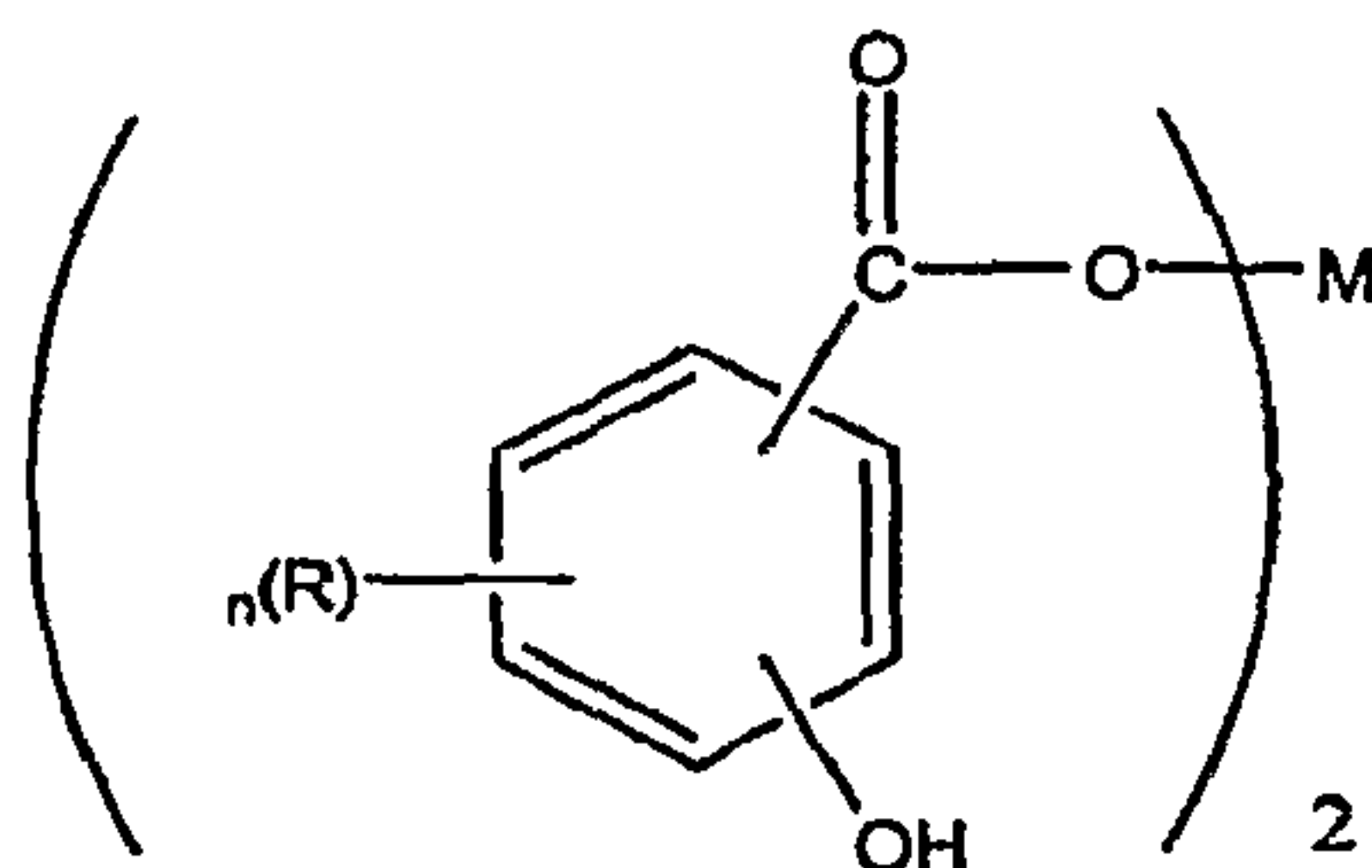
[0113] Klamann in *Lubricants and Related Products*, op cit discloses a number of overbased metal salts of various sulfonic acids which are useful as detergents and dispersants in lubricants. The book entitled "Lubricant Additives", C. V. Smallheer and R. K. Smith, published by the Lezius-Hiles Co. of Cleveland, Ohio (1967), similarly discloses a number of overbased sulfonates that are useful as dispersants/detergents.

[0114] Alkaline earth phenates are another useful class of detergent. These detergents can be made by reacting alkaline earth metal hydroxide or oxide (CaO, Ca(OH)₂, BaO, Ba(OH)₂, MgO, Mg(OH)₂, for example) with an alkyl phenol or sulfurized alkylphenol. Useful alkyl groups include straight chain or branched C₁-C₃₀ alkyl groups, preferably, C₄-C₂₀. Examples of suitable phenols include isobutylphenol, 2-ethylhexylphenol, nonylphenol, dodecyl phenol, and the like. It should be noted that starting alkylphenols may contain more than one alkyl substituent that are each independently straight chain or branched. When a non-sulfurized alkylphenol is used, the sulfurized product may be obtained by methods well known in the art. These methods include heating a mixture of alkylphenol and sulfurizing agent (including elemental sulfur, sulfur halides such as sulfur dichloride, and the like) and then reacting the sulfurized phenol with an alkaline earth metal base.

[0115] Metal salts of carboxylic acids are also useful as detergents. These carboxylic acid detergents may be prepared by reacting a basic metal compound with at least one carboxylic acid and removing free water from the reaction product. These compounds may be overbased to produce the desired TBN level.

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Detergents made from salicylic acid are one preferred class of detergents derived from carboxylic acids. Useful salicylates include long chain alkyl salicylates. One useful family of compositions is of the formula



where R is a hydrogen atom or an alkyl group having 1 to about 30 carbon atoms, n is an integer from 1 to 4, and M is an alkaline earth metal. Preferred R groups are alkyl chains of at least C₁₁, preferably C₁₃ or greater. R may be optionally substituted with substituents that do not interfere with the detergent's function. M is preferably, calcium, magnesium, or barium. More preferably, M is calcium.

[0116] Hydrocarbyl-substituted salicylic acids may be prepared from phenols by the Kolbe reaction. See USP 3,595,791, which is incorporated herein by reference in its entirety, for additional information on synthesis of these compounds. The metal salts of the hydrocarbyl-substituted salicylic acids may be prepared by double decomposition of a metal salt in a polar solvent such as water or alcohol.

[0117] Alkaline earth metal phosphates are also used as detergents.

[0118] Detergents may be simple detergents or what is known as hybrid or complex detergents. The latter detergents can provide the properties of two detergents without the need to blend separate materials. See USP 6,034,039 for example.

[0119] Preferred detergents include calcium phenates, calcium sulfonates, calcium salicylates, magnesium phenates, magnesium sulfonates, magnesium salicylates and other related components (including borated detergents).

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

Dispersant

[0120] 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.

[0121] 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.

[0122] Chemically, many dispersants may be characterized as phenates, sulfonates, sulfurized phenates, salicylates, naphthenates, stearates, carbamates, thiocarbamates, phosphorus derivatives. A particularly useful class of dispersants are the alkenylsuccinic derivatives, typically produced by the reaction of a long chain substituted alkenyl succinic compound, usually a substituted succinic anhydride, with a polyhydroxy or polyamino compound. The long chain group constituting the oleophilic portion of the molecule which confers solubility in the oil, is normally a polyisobutylene group. Many examples of this type of dispersant are well known commercially and in the literature. Exemplary U.S. patents describing such dispersants are 3,172,892; 3,2145,707; 3,219,666; 3,316,177; 3,341,542; 3,444,170; 3,454,607; 3,541,012; 3,630,904; 3,632,511; 3,787,374 and 4,234,435. Other types of dispersant are described in U.S. Patents 3,036,003; 3,200,107; 3,254,025; 3,275,554;

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3,438,757; 3,454,555; 3,565,804; 3,413,347; 3,697,574; 3,725,277; 3,725,480; 3,726,882; 4,454,059; 3,329,658; 3,449,250; 3,519,565; 3,666,730; 3,687,849; 3,702,300; 4,100,082; 5,705,458. A further description of dispersants may be found, for example, in European Patent Application No. 471 071, to which reference is made for this purpose.

[0123] 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.

[0124] Succinimides are formed by the condensation reaction between alkenyl succinic anhydrides and amines. Molar ratios can vary depending on the polyamine. For example, the molar ratio of alkenyl succinic anhydride to TEPA can vary from about 1:1 to about 5:1. Representative examples are shown in U.S. Patents 3,087,936; 3,172,892; 3,219,666; 3,272,746; 3,322,670; and 3,652,616, 3,948,800; and Canada Pat. No. 1,094,044.

[0125] 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.

[0126] Succinate ester amides are formed by condensation reaction between alkenyl succinic anhydrides and alkanol amines. For example, suitable alkanol amines include ethoxylated polyalkylpolyamines, propoxylated polyalkylpolyamines and polyalkenylpolyamines such as polyethylene polyamines. One example is propoxylated hexamethylenediamine. Representative examples are shown in USP 4,426,305.

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[0127] The molecular weight of the alkenyl succinic anhydrides used in the preceding paragraphs will typically range between 800 and 2,500. The above products can be post-reacted with various reagents such as sulfur, oxygen, formaldehyde, carboxylic acids such as oleic acid, and boron compounds such as borate esters or highly borated dispersants. The dispersants can be borated with from about 0.1 to about 5 moles of boron per mole of dispersant reaction product.

[0128] Mannich base dispersants are made from the reaction of alkylphenols, formaldehyde, and amines. See USP 4,767,551, which is incorporated herein by reference. Process aids and catalysts, such as oleic acid and sulfonic acids, can also be part of the reaction mixture. Molecular weights of the alkylphenols range from 800 to 2,500. Representative examples are shown in U.S. Patents 3,697,574; 3,703,536; 3,704,308; 3,751,365; 3,756,953; 3,798,165; and 3,803,039.

[0129] Typical high molecular weight aliphatic acid modified Mannich condensation products useful in this invention can be prepared from high molecular weight alkyl-substituted hydroxyaromatics or HN(R)_2 group-containing reactants.

[0130] 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.

[0131] 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 prepara-

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tion 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.

[0132] Examples of alkylene polyamide reactants include ethylenediamine, diethylene triamine, triethylene tetraamine, tetraethylene pentaamine, pentaethylene hexamine, hexaethylene heptaamine, heptaethylene octaamine, octaethylene nonaamine, nonaethylene decamine, and decaethylene undecamine and mixture of such amines having nitrogen contents corresponding to the alkylene polyamines, in the formula $H_2N-(Z-NH-)_nH$, 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-, penta-propylene tri-, tetra-, penta- and hexamines 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.

[0133] 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.

[0134] Hydrocarbyl substituted amine ashless dispersant additives are well known to one skilled in the art; see, for example, U.S. Patents 3,275,554;

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3,438,757; 3,565,804; 3,755,433, 3,822,209, and 5,084,197, which are incorporated herein in their entirety by reference.

[0135] 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%.

Pour Point Depressants

[0136] Conventional pour point depressants (also known as lube oil flow improvers) may be added to the compositions of the present invention if desired. These pour point depressant may be added to lubricating compositions of the present invention to lower the minimum temperature at which the fluid will flow or can be poured. Examples of suitable pour point depressants include polymethacrylates, polyacrylates, polyarylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, and terpolymers of dialkylfumarates, vinyl esters of fatty acids and allyl vinyl ethers. USP Nos. 1,815,022; 2,015,748; 2,191,498; 2,387,501; 2,655, 479; 2,666,746; 2,721,877; 2,721,878; and 3,250,715 describe useful pour point depressants and/or the preparation thereof. Such additives may be used in an amount of about 0.01 to 5 wt%, preferably about 0.01 to 1.5 wt%.

Corrosion Inhibitors

[0137] Corrosion inhibitors are used to reduce the degradation of metallic parts that are in contact with the lubricating oil composition. Suitable corrosion inhibitors include thiadiazoles. See, for example, USP Nos. 2,719,125;

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2,719,126; and 3,087,932, which are incorporated herein by reference in their entirety. Such additives may be used in an amount of about 0.01 to 5 wt%, preferably about 0.01 to 1.5 wt%.

Seal Compatibility Additives

[0138] 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%.

Anti-Foam Agents

[0139] Anti-foam agents may advantageously be added to lubricant compositions. These agents retard the formation of stable foams. Silicones and organic polymers are typical anti-foam agents. For example, polysiloxanes, such as silicon oil or polydimethyl siloxane, provide antifoam properties. Anti-foam agents are commercially available and may be used in conventional minor amounts along with other additives such as demulsifiers; usually the amount of these additives combined is less than 1 percent and often less than 0.1 percent.

Inhibitors and Antirust Additives

[0140] Antirust additives (or corrosion inhibitors) are additives that protect lubricated metal surfaces against chemical attack by water or other contaminants. A wide variety of these are commercially available; they are referred to in Klamann in Lubricants and Related Products, op cit.

[0141] One type of antirust additive is a polar compound that wets the metal surface preferentially, protecting it with a film of oil. Another type of antirust additive absorbs water by incorporating it in a water-in-oil emulsion so that only the oil touches the metal surface. Yet another type of antirust additive chemically adheres to the metal to produce a non-reactive surface. Examples of

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suitable additives include zinc dithiophosphates, metal phenolates, basic metal sulfonates, fatty acids and amines. Such additives may be used in an amount of about 0.01 to 5 wt%, preferably about 0.01 to 1.5 wt%.

Friction Modifiers

[0142] A friction modifier is any material or materials that can alter the coefficient of friction of a surface lubricated by any lubricant or fluid containing such material(s). Friction modifiers, also known as friction reducers, or lubricity agents or oiliness agents, and other such agents that change the ability of base oils, formulated lubricant compositions, or functional fluids, to modify the coefficient of friction of a lubricated surface may be effectively used in combination with the base oils or lubricant compositions of the present invention if desired. Friction modifiers that lower the coefficient of friction are particularly advantageous in combination with the base oils and lube compositions of this invention. Friction modifiers may include metal-containing compounds or materials as well as ashless compounds or materials, or mixtures thereof. Metal-containing friction modifiers may include metal salts or metal-ligand complexes where the metals may include alkali, alkaline earth, or transition group metals. Such metal-containing friction modifiers may also have low-ash characteristics. Transition metals may include Mo, Sb, Sn, Fe, Cu, Zn, and others. Ligands may include hydrocarbyl derivative of alcohols, polyols, glycerols, partial ester glycerols, thiols, carboxylates, carbamates, thiocarbamates, dithiocarbamates, phosphates, thiophosphates, dithiophosphates, amides, imides, amines, thiazoles, thiadiazoles, dithiazoles, diazoles, triazoles, and other polar molecular functional groups containing effective amounts of O, N, S, or P, individually or in combination. In particular, Mo-containing compounds can be particularly effective such as for example Mo-dithiocarbamates, Mo(DTC), Mo-dithiophosphates, Mo(DTP), Mo-amines, Mo (Am), Mo-alcoholates, Mo-alcohol-amides, etc. See USP 5,824,627; USP 6,232,276; USP 6,153,564; USP 6,143,701; USP 6,110,878; USP 5,837,657; USP 6,010,987; USP

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5,906,968; USP 6,734,150; USP 6,730,638; USP 6,689,725; USP 6,569,820; WO 99/66013; WO 99/47629; WO 98/26030.

[0143] Ashless friction modifiers may have also include lubricant materials that contain effective amounts of polar groups, for example, hydroxyl-containing hydrocarbyl base oils, glycerides, partial glycerides, glyceride derivatives, and the like. Polar groups in friction modifiers may include hydrocarbyl groups containing effective amounts of O, N, S, or P, individually or in combination. Other friction modifiers that may be particularly effective include, for example, salts (both ash-containing and ashless derivatives) of fatty acids, fatty alcohols, fatty amides, fatty esters, hydroxyl-containing carboxylates, and comparable synthetic long-chain hydrocarbyl acids, alcohols, amides, esters, hydroxy carboxylates, and the like. In some instances fatty organic acids, fatty amines, and sulfurized fatty acids may be used as suitable friction modifiers.

[0144] Useful concentrations of friction modifiers may range from about 0.01 wt% to 10-15 wt% or more, often with a preferred range of about 0.1 wt% to 5 wt%. Concentrations of molybdenum-containing materials are often described in terms of Mo metal concentration. Advantageous concentrations of Mo may range from about 10 ppm to 3000 ppm or more, and often with a preferred range of about 20-2000 ppm, and in some instances a more preferred range of about 30-1000 ppm. Friction modifiers of all types may be used alone or in mixtures with the materials of this invention. Often mixtures of two or more friction modifiers, or mixtures of friction modifier(s) with alternate surface active material(s), are also desirable.

Typical Additive Amounts

[0145] When lubricating oil compositions contain one or more of the additives discussed above, the additive(s) are blended into the composition in an amount sufficient for it to perform its intended function. Typical amounts of such additives useful in the present invention are shown in Table 1 below.

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[0146] Note that many of the additives are shipped from the manufacturer and used with a certain amount of base oil solvent in the formulation. Accordingly, the weight amounts in the table below, as well as other amounts mentioned in this patent, are directed to the amount of active ingredient (that is the non-solvent portion of the ingredient). The wt% indicated below are based on the total weight of the lubricating oil composition.

TABLE 1
Typical Amounts of Various Lubricant Oil Components

<u>Compound</u>	<u>Approximate Wt% (Useful)</u>	<u>Approximate Wt% (Preferred)</u>
Detergent	0.01-6	0.01-4
Dispersant	0.1-20	0.1-8
Friction Reducer	0.01-5	0.01-1.5
Supplementary Viscosity Index Improver	0.0-40	0.01-30, more preferably 0.01-15
Antioxidant	0.0-5	0.0-1.5
Corrosion Inhibitor	0.01-5	0.01-1.5
Anti-wear Additive	0.01-6	0.01-4
Pour Point Depressant	0.0-5	0.01-1.5
Anti-foam Agent	0.001-3	0.001-0.15
Base Oil	Balance	Balance

EXAMPLES

[0147] GTL base stocks were produced by hydroisomerizing Fischer-Tropsch wax in a pilot plant to prepare, e.g., a base stock with kV @ 100°C of 6 mm²/s.

[0148] EBC base stocks produced in a pilot plant with 28 and 114 mm²/s at 100°C were used for the lubricant formulation. These samples were prepared in the following manner:

Example A - Preparation of 28 cSt EBC sample

[0149] 1-butene was charged at 100 ml/hour, ethylene was charged at 30 gram/hour and hydrogen gas was charged at 21.8 ml per minute into a 600 ml autoclave containing a catalyst solution of 20 mg zirconocene dichloride, 4.0 gram of 10 wt% methylaluminoxane in toluene and 50 gram toluene, and cooled

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in an ice water bath. The reaction mixture quickly warmed to 25°C. The reaction temperature was maintained at close to room temperature with water/ice cooling. The feeds were discontinued after four hours. After 12 hours of reaction at room temperature or below, the reaction was stopped by addition of air to the reactions system. The viscous liquid product was isolated in 73% yield by distillation at 140°C/0.1 millitorr for 2 hours to remove any light end. The isolated ethylene-butene copolymer product had the following properties: 100°C Kv = 28.0 cS, 40°C Kv = 234.2 cS, VI = 156. This polymer was used in the blend study. The polymer contained about 33 wt% ethylene.

Example B

[0150] This polymer was prepared in a continuous mode of operation. In this reaction, polymer grade ethylene, polymer grade 1-butene and polymer grade iso-butane solvent were charged into a 200 gallon reactor after purification through molecular sieve and treatment by injecting 50 ppm tri-t-butylaluminum. The feed rates for ethylene, 1-butene and iso-butane were 12, 120 and 180 lb/hour, respectively. A catalyst solution, containing 5×10^{-6} g-mole/liter of dimethylsilylbis (4,5,6,7 tetrahydro-indenyl) zirconium dichloride and methylaluminoxane of 1/400 Zr/Al molar ratio in toluene, was charged into the reactor at 13.5 ml/minute. The reactor temperature was maintained 89.4°C and 95.6°C, pressure 237-261 psi and average residence time 2 hours. The crude reaction product was withdrawn from the reactor continuously and washed with 0.4 wt% sodium hydroxide solution followed with a water wash. A viscous liquid product was obtained by devolatilization to remove iso-butane solvent, light stripping at 66°C/5 psig followed by deep stripping at 140°C/1 millitorr. The residual viscous liquid was then hydro-finished at 200°C, 800-1200 psi H₂ pressure with 2 wt% Ni-on-Kieselguhr catalyst for eight hours. The hydro-generated product contains 34 wt% ethylene content and had the following

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properties: 100°C Kv = 114.0 mm²/s, 40°C Kv = 1946.5 mm²/s, VI = 145 and pour point = -24°C. This polymer has Mn of 2374 and MWD of 1.88.

[0151] The Group I mineral oil bright stock to which the inventive samples were compared has the following properties:

kinematic viscosity at 100°C = 3.13 mm²/s, kinematic viscosity at 40°C = 454.5 mm²/s, VI = 97, pour point = -9°C.

[0152] The Group II hydroprocessed base stock is a commercial base stock with kV @ 40°C of 11 mm²/s.

[0153] Identical additives were used within each series of examples 1 and 2, which, in combination with the listed base stocks produced a premium multi-purpose lubricant suitable for circulating, gear, hydraulic, and other applications.

[0154] The thermal stability test procedure used in Examples 1 and 2 is described below:

1. Record the weight of flask and stirrer and the weight of adapter and thermal well.
2. In a small flask with a small stirrer, weigh 10 grams of sample oil.
3. Assemble the flask with stirrer and oil, adapter and thermal well - record the total weight.
4. Attach the assembly to vacuum and nitrogen lines that can be isolated from the sample. Connect thermocouple for temperature measurement. Stir at low speed.
5. Evacuate, then refill the flask with nitrogen. Repeat the evacuation and filling with nitrogen 2 more times. Leave the flask open to nitrogen atmosphere and to a nitrogen bubbler.
6. Wrap the flask with thermal insulating cloth. Heat the flask to 300°C. Hold at those conditions for 24 hours after the temperature reached 300°C.

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7. Cool down under nitrogen until near room temperature. Weigh complete assembly.
8. Measure the oil viscosity at 100°C and 40°C.

Example 1

[0155] Lubricant formulations with $kV @ 40^{\circ}C$ of about $220 \text{ mm}^2/\text{s}$ were obtained by blending ethylene-butene copolymers (EBC) and a GTL base stock, or by blending a $100 \text{ mm}^2/\text{s}$ poly-alpha-olefin (PAO) and GTL base stock for comparison against lubricant formulations of a heavy Group I mineral oil base stock (bright stock), or with a blend of a Group I/GTL base stock with 20% PIB thickeners. The GTL/EBC and GTL/PAO blends both have superior oxidative stability as shown by the long RBOT time by ASTM D2272 method. This RBOT time is much longer than that of the fluid prepared from Group I bright stock [2126 minute and 2252 minutes versus 750-760 minutes]. By the addition of GTL to a blend of Group I bright stock and PIB, a conventionally used thickener, the oxidative stability by RBOT was improved slightly [991-963 minutes vs. 750-760 minutes]. However, compared to the GTL/EBC and GTL/PAO products, the Group I/GTL/PIB product [the PIB-thickened fluid] lost much more viscosity and weight during the thermal stability test than did the EBC or PAO thickened product. These results demonstrated that the EBC and PAO thickened GTL-based lubricants have unexpected improvement in properties in the retention of viscosity and weight (see Table A).

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TABLE A

Wt%	GTL/EBC	GTL/PAO	Group I	Gp I/GTL/PIB
EBC 114 mm ² /s	45.8			
EBC 28 mm ² /s	11.4			
GTL 6 mm ² /s	20	20		16.6
PAO-100 mm ² /s		57.2		
Bright stock			76.7	40.1
PIB				20.0
Additives	23.3	23.3	23.3	23.3
KV @ 40°C (mm ² /s)	243	249	211	230
D2272 (RBOT), min	2126, 2193	2229, 2252	750, 760	991, 963
Pour point, °C	-31	-34	-22	-26
Weight				
After thermal stability test, 1 day at 300°C				
% loss in Kv at 40°C	-4.7	-1.7	-4.2	15.0
% weight loss	1.6	1.4	0.0	5.0

Example 2

[0156] Lubricant formulations with kv @ 40°C of about 220 mm²/s were prepared by blending a combination of EBC and Group II base stock for comparison with a Group I bright stock per se and with a mixture of Group I/Group II oil thickened with 20% PIB. The oxidative stability of the EBC-Group II blend is superior to that of the conventional Group I bright stock mineral oil as shown by the RBOT data while both the oxidative and thermal stability of the EBC-Group II blend are superior to that of the PIB thickened Group I/Group II blend shown by both the RBOT data and its resistance to loss of both viscosity and weight. Use of Group II hydroprocessed base stock and PIB to displace some of the conventional mineral oil in the all conventional Group I bright stock mineral oil formulation improved the oxidative stability and pour point, but the thermal stability was not as good as that of the Group II-EBC combination nor as good as that of the Group I bright stock mineral oil formulations itself. The resistance to viscosity and weight loss was not as good as that secured with the GTL/EBC or GTL/PAO blend formulations of Example 1 (see Table B).

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TABLE B

Wt%	Group II/EBC	Group I	Group II/Group I/PIB
EBC 114 mm ² /s (Example B)	35.9		
EBC 28 mm ² /s (Example A)	9.0		
Hydroprocessed base stock (Group II)	31.8		33.1
Bright stock (Group I)		76.7	23.5
PIB			20.0
Additives	23.3	23.3	23.3
KV @ 40°C (mm ² /s)	241	211	246
D2272 (RBOT), min	1906, 2147	750, 760	1055, 1153
Pour point, °C	-28	-22	-24
After thermal stability test, 1 day at 300°C			
% loss in kinematic viscosity at 40°C	5.2	-4.2	26.0
% weight loss	0.0	0.0	1.6

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CLAIMS:

1. A method for reducing the loss of viscosity and weight and improving the oxidation stability and low temperature properties of lubricating oil formulation by employing a base stock comprising a GTL base stock and/or base oil in combination with a polyolefin fluid, said polyolefin fluid being characterized by a viscosity in the range of about 2 to 1000 mm²/s at 100°C, a number average molecular weight in the range of about 200 to 10,000.

2. The method of claim 1 wherein the lubricating oil formulation has a viscosity in the range of about 2 to 1000 mm²/s at 100°C.

3. The method of claim 1 wherein the polyolefin fluid is combined with the GTL in an amount in the range of about 0.1 to 90 wt% based on the weight of the combination.

4. The method of claim 1 wherein the polyolefin fluid is a copolymer of a first alpha olefin selected from ethylene, propylene, 1-butylene and a second alpha olefin different from the first selected from the group of C₂-C₃₀ straight or branched chain alphaolefins and mixtures thereof wherein when one of the alpha olefin used is ethylene the ethylene content of the poly olefin fluid is not more than 50 wt%.

5. The method of claim 1 wherein the polyolefin fluid is a poly alpha olefin homo or copolymer made from alpha olefins selected from the group of C₈ to C₁₈ alpha olefins and mixtures thereof.

6. The method of claim 1, 2, 3, 4 or 5 wherein the polyolefin fluid has a molecular weight distribution (MWD) of from 1.00 to 4.

7. The method of claim 1, 2, 3, 4 or 5 wherein the GTL base stock and/or base oil is a hydrodewaxed or hydroisomerized Fischer-Tropsch material.

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8. The method of claim 7 wherein the Fischer-Tropsch material is Fischer-Tropsch wax.

9. The method of claim 1, 2, 3, 4 or 5 wherein the lubricating oil formulation has a kinematic viscosity in the range of about 2 to 500 mm²/s at 100°C.

10. The method of claim 9 wherein the GTL base oil has a kinematic viscosity in the range of about 1.5 to 50 mm²/s at 100°C.

11. The method of claim 1, 2, 3, 4 or 5 wherein the polyolefin fluid has a kinematic viscosity in the range about 4 to 800 mm²/s at 100°C.

12. The method of claim 1, 2, 3, 4 or 5 wherein the polyolefin fluid has a kinematic viscosity in the range of about 10 to 500 mm²/s at 100°C.

13. The method of claim 1, 2, 3, 4 or 5 wherein the polyolefin fluid has a kinematic viscosity in the range of about 10 to 200 mm²/s at 100°C.

14. The method of claim 1 wherein the base stock further contains a hydrodewaxate or hydroisomerate of waxy feed derived from mineral oil.

15. The method of claim 1 or 14 wherein the base stock further contains a mineral oil base stock, a Group V synthetic base stock or mixture thereof.

16. The method of claim 15 wherein the GTL base stock and/or base oil constitutes 5 to 100 wt% of the total of the base oil.

17. The method of claim 16 wherein the GTL base stock and/or base oil constitutes 40 to 100 wt% of the total of the base oil.

18. The method of claim 16 wherein the GTL base stock and/or base oil constitute 70 to 100 wt% of the total of the base oil.

19. The method of claim 16 wherein the GTL base stock and/or base oil constitutes 90 to 100 wt% of the total of the base oil.

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20. A base stock exhibiting an enhanced resistance to reduction in the loss of weight and viscosity and improved oxidation stability and low temperature properties comprising a mixture of GTL base stock and/or base oil in combination with a polyolefin fluid, said polyolefin fluid being characterized by a viscosity in the range of about 2 to 1000 mm²/s at 100°C and a number average molecular weight in the range of about 200 to 10,000 and a molecular weight distribution of 1.00 to 4.

21. The base stock of claim 20 wherein the polyolefin fluid is present in an amount in the range of about 0.1 to 90 wt% based on the total weight of the base stock.

22. The base stock of claim 20 wherein the polyolefin fluid is a copolymer of a first alpha olefin selected from ethylene, propylene, 1-butylene and a second alpha olefin different from the first selected from the group of C₂-C₃₀ straight or branched chain alpha-olefin and mixtures thereof wherein when one of the alpha olefins used is ethylene, the ethylene content of the polyolefin fluid is not more than 50 wt%.

23. The base stock of claim 20 wherein the polyolefin fluid is a polyalpha olefin homo- or copolymer made from C₈ to C₁₈ alpha olefin.

24. The base stock of claim 20, 21, 22 or 23 wherein the GTL base stock and/or base oil is a hydrodewaxed or hydroisomerized Fischer-Tropsch liquid hydrocarbon composition comprising paraffinic hydrocarbon components in which the extent of branching, as measured by the percentage of methyl hydrogens (BI), and the proximity of branching, as measured by the percentage of recurring methylene carbons which are four or more carbons removed from an end group or branch ($\text{CH}_2 \geq 4$), are such that:

(a) $\text{BI} - 0.5 (\text{CH}_2 \geq 4) > 15$; and

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- (b) $BI + 0.85 (CH_2 \geq 4) < 45$ as measured over said liquid hydrocarbon composition as a whole and further characterized as a mixture of branched paraffinic characterized in that the GTL base oil contains at least 90% of a mixture of branched paraffins wherein said branched paraffins are paraffinic having a carbon chain length of about C_{20} to about C_{40} , a molecular weight of about 280 to about 562, a boiling range of about 650°F to about 1050°F, and wherein said branched paraffins contain up to four alkyl branches and wherein the free carbon index of said branched paraffins is at least about 3.

25. The base stock of claim 24 wherein the GTL base stock and/or base oil has a kinematic viscosity in the range of about 1.5 to 50 mm²/s @ 100°C.

26. The base stock of claim 25 wherein the polyolefin fluid has a kinematic viscosity in the range of about 4 to 800 mm²/s @ 100°C.

27. The base stock of claim 25 wherein the polyolefin fluid has a kinematic viscosity in the range of about 10 to 500 mm²/s @ 100°C.

28. The base stock of claim 25 wherein the polyolefin fluid has a kinematic viscosity in the range of about 10 to 200 mm²/s @ 100°C.