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

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
7 February 2008 (07.02.2008)

PCT

(10) **International Publication Number**
WO 2008/016484 A2

(51) **International Patent Classification:**
C10M 169/04 (2006.01) *C10N 30/02* (2006.01)

(21) **International Application Number:** PCT/US2007/016168

(22) **International Filing Date:** 17 July 2007 (17.07.2007)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
60/834,075 28 July 2006 (28.07.2006) 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, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, 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, LY, MA, MD, ME, 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, MT, 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:
— *without international search report and to be republished upon receipt of that report*

(54) Title: LUBRICANT COMPOSITIONS HAVING IMPROVED LOW TEMPERATURE PROPERTIES

(57) **Abstract:** The pour points of lubricating compositions are significantly improved when Group III and GTL base stocks are formulated with alkyl alkaline earth metal detergents. In a preferred embodiment, calcium alkyl salicylate detergents are used.

LUBRICANT COMPOSITIONS HAVING IMPROVED LOW TEMPERATURE PROPERTIES

FIELD OF THE INVENTION

[0001] The invention relates to lubricant compositions exhibiting good low temperature properties. More particularly, the invention relates to lubricant compositions having good pour points.

BACKGROUND OF THE INVENTION

[0002] Finished high performance and industrial lubricants consist of two main components. The first major component is the lubricating base oil. The second is the performance enhancing additives. The additive component is required to assure that the finished composition meets specifications set by government agencies, equipment manufacturers and other organizations. For example, many commercial lubricating compositions have specifications for pour point which is a measure of the temperature at which a sample of the lubricating composition will begin to flow under carefully controlled test conditions such as specified by the American Society for Testing Materials (ASTM).

[0003] Pour point depressants are additives known in the art and typically include polymethacrylates, polyacrylates, polyacrylamides, alkylated fumarate vinyl acetate copolymers, vinylcarboxylate polymers, terpolymers of dialkylfumarates, vinyl esters of fatty acids and ethylene-vinyl acetate copolymers to mention a few. Because of their polymeric nature, these pour point depressants are subject to shearing during their use, thereby impacting the useful life of the lubricating compositions containing them.

[0004] Experience has taught that the overall effect of additives may depend not only on the nature and concentration of the additives, but also on the nature of the oil as well. The invention disclosed herein lends support to the observation that the base oil of a lubricant formulation may have an influence on additive performance, especially on pour point depressant performance.

[0005] U.S. Patent Publication No. U.S. 2006/0116302 describes a detergent additive for lubricating oil compositions that comprises at least two of low, high and medium TBN (total base number) detergents, preferably calcium salicylate detergents. No reference is made to the pour points of lubricants formulated with the mixed detergents. Indeed, the claimed benefits of the mixed detergents related to piston cleanliness, film forming tendency and frictional properties.

[0006] Detergents are generally considered to be chemical compounds that chemically neutralize deposit precursors that form under high temperature conditions or as a result of burning fuels with high sulfur content or other materials that form acidic combustion by-products. Detergents have some ability to disperse and suspend contaminants. Detergents used in lubricant oil compositions are organic soaps and salts of alkaline earth metals such as barium, calcium and magnesium. Alkylated calcium and magnesium sulfonates, phenates and salicylates are widely used. The sulfonates, phenates and salicylates maybe neutral or over based which means that they may contain more of the alkaline metal than is required to neutralize the acidic components formed from the combustion of high sulfur fuels.

[0007] The use of pour point depressants (PPDs) to lower the pour point of engine oils is well known in the literature and the types of pour point depressants are varied. PPDs are lubricant additives designed to keep base oil flowing in cold weather. Typically, pour point depressants are viscous or solid high molecular weight polymers that are delivered in oils or solvents. PPDs are very effective in modifying the pour point of base oils with treat rates generally less than 0.5 wt%. The amount of pour point depressant used varies according to the type of base oil and the concentration of the polymer in the oil. Because of their polymeric nature, PPDs can shear during lubricant life. Commercially available pour point depressants include poly(methacrylates) known as Viscoplex® series 1,9,10, Viscoplex® 1-31, Viscoplex® 1-330 and Viscoplex® 5-557, Lubrizol® Lz 7749B, Lz® 7742, Lz® 7748, Texaco TC 5301 and TC 10314, C8-C18 dialkyl fumarate or maleate vinyl acetate copolymers such as Infineum® V385, Infineum® V387, Infineum® V390, styrene maleate copolymers such as Lz® 6662 and the like.

[0008] Accordingly, there is a need for a lubricant to provide good low temperature properties including pour point. This invention satisfies that need.

SUMMARY OF THE INVENTION

[0009] In one embodiment, a method for improving the pour point of a lubricating composition is disclosed. The lubricant comprising a major amount of a lubricating base oil and one or more detergents, the method comprising using a alkylated alkaline earth metal detergents as a pour point depressant.

[0010] In a second embodiment, a lubricating composition comprising a major amount of an oil of lubricating viscosity chosen from the group consisting of Group III, GTL and any combination thereof, an alkylated alkaline earth metal as a pour point depressant wherein the alkylated alkaline earth metal is greater than 0.4 and less than 10 weight percent, and a minor amount of at least one lubricant additives, the composition having a saturates content greater than

98%, a viscosity index (VI) greater than 120 and a sulfur content less than 0.03 wt%.

[0011] The foregoing summary and the following detailed description are exemplary of the various aspects and embodiments of the claimed invention.

DETAILED DESCRIPTION OF THE INVENTION

[0012] It has now been discovered that the pour point of lubricating oil compositions can be enhanced by formulating the composition with one or more alkylated alkaline earth metal detergents. More specifically, alkylated alkaline earth metal salicylates including calcium salicylate detergents were found to be effective in reducing then pout points of base oils.

[0013] The alkylated alkaline earth metal detergents are particularly effective in base oils or lubricant compositions having a saturates content greater than 98%, a viscosity index (VI) greater than 120 and a sulfur content less than 0.03 wt%. The alkylated alkaline earth metal detergents were found very effective in hydroisomerized or isodewaxed Fischer-Tropsch wax derived base oils (GTL). Therefore, the lubricating oil compositions of the invention comprise a major amount of a lubricating base oil which consists essentially of a Group III base stock and/or a GTL base stock.

[0014] This invention is suitable for lubricating oil compositions used for internal combustion engines, natural gas engines, turbine engines, automatic and manual transmissions, marine diesel engines, greases, gear boxes, hydraulic systems that require low temperature properties such as MRV, kinematic and Brookfield viscosities when formulated with highly saturated, Group III, base oils preferably hydroisomerized or isodewaxed Fischer-Tropsch wax derived base oils (GTL).

[0015] Groups I, II, III, IV and V are broad categories of base oil stocks defined by the American Petroleum Institute (API Publication 1509; www.API.org) to create guidelines for lubricant base oils. Table A summarizes properties of each of these five groups.

Table A: Base Stock Properties

	Saturates	Sulfur	Viscosity Index
Group I	< 90 wt% and/or	> 0.03 wt% and	≥ 80 and < 120
Group II	≥ 90 wt% and	≤ 0.03 wt% and	≥ 80 and < 120
Group III	≥ 90 wt% and	≤ 0.03 wt% and	≥ 120
Group IV	Polyalphaolefins (PAO)		
Group V	All other base oil stocks not included in Groups I, II, III, or IV		

[0016] One embodiment of the present invention, the base oil preferably is 100 wt% of a Group III base stock, or a base stock obtained by hydroisomerization or isodewaxing of a highly paraffinic wax such as a Fischer-Tropsch wax or a slack wax. Indeed, Group III base stocks derived from gases, i.e., Gas-to-Liquid (GTL) base stocks are most preferred.

[0017] 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) "hydrodewaxing" (or catalytic dewaxing): a catalytic process in which normal paraffins (wax) and/or waxy hydrocarbons are converted by cracking/fragmentation into lower molecular weight species, and by rearrangement/isomerization into more branched iso-paraffins;

(f) "hydroisomerization" (or isomerization or isodewaxing): a catalytic process in which normal paraffins (wax) and/or slightly branched iso-paraffins are converted by rearrangement/isomerization into more branched iso-paraffins;

(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.

[0018] The term “hydroisomerization/hydrodewaxing” is used to refer to one or more catalytic processes which have the combined effect of converting normal paraffins and/or waxy hydrocarbons by cracking/fragmentation into lower molecular weight species and, by rearrangement/isomerization, into more branched iso-paraffins. Such combined processes are sometimes described as “catalytic dewaxing” or “selective hydrocracking”.

[0019] GTL materials are materials that are derived via one or more synthesis, combination, transformation, rearrangement, and/or degradation/deconstructive processes from gaseous carbon-containing compounds, hydrogen-containing compounds, and/or elements as feedstocks such as hydrogen, carbon dioxide, carbon monoxide, water, methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane, butylenes, and butynes. GTL base stocks and 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 stock(s) include oils boiling in the lube oil boiling range separated/fractionated from GTL materials such as by, for example, distillation or thermal diffusion, and subsequently subjected to well-known catalytic or solvent dewaxing processes to produce lube oils of reduced/low pour point; wax isomerates, comprising, for example, hydroisomerized or isodewaxed synthesized hydrocarbons; hydroisomerized or isodewaxed Fischer-Tropsch (F-T) material (i.e., hydrocarbons, waxy hydrocarbons, waxes and possible analogous oxygenates); preferably hydroisomerized or isodewaxed F-T hydrocarbons or hydroisomerized or isodewaxed F-T waxes, hydroisomerized or isodewaxed synthesized waxes, or mixtures thereof.

[0020] GTL base stock(s) derived from GTL materials, especially, hydroisomerized/isodewaxed F-T material derived base stock(s), and other hydroisomerized/isodewaxed wax derived base stock(s) are characterized typically as having kinematic viscosities at 100°C of from about 2 mm^2/s to about 50 mm^2/s, preferably from about 3 mm^2/s to about 50 mm^2/s, more preferably from about 3.5 mm^2/s to about 30 mm^2/s, as exemplified by a GTL base stock derived by the isodewaxing of F-T wax, which has a kinematic viscosity of about 4 mm^2/s at 100°C and a viscosity index of about 130 or greater. Reference herein to Kinematic viscosity refers to a measurement made by ASTM method D445.

[0021] GTL base stocks and base oils derived from GTL materials, especially hydroisomerized/isodewaxed F-T material derived base stock(s), and other hydroisomerized/isodewaxed wax-derived base stock(s), such as wax hydroisomerates/isodewaxates, which can be used as base stock 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. References herein to pour point refer to measurement made by ASTM D97 and similar automated versions.

[0022] The GTL base stock(s) derived from GTL materials, especially hydroisomerized/isodewaxed F-T material derived base stock(s), and other hydroisomerized/isodewaxed wax-derived base stock(s) which are base stock components which can be used in this invention are also characterized typically as having viscosity indices of 120 or greater in certain particular instances, viscosity index of these base stocks may be preferably 130 or greater, more preferably 135 or greater, and even more preferably 140 or greater. For example, GTL base 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.

[0023] In addition, the GTL base stock(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stocks and 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 base oil obtained by the hydroisomerization/isodewaxing of F-T material, especially F-T wax is essentially nil.

[0024] In a preferred embodiment, the GTL base stock(s) comprises paraffinic materials that consist predominantly of non-cyclic isoparaffins and only minor amounts of cycloparaffins. These GTL base stock(s) 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.

[0025] Useful compositions of GTL base stock(s), hydroisomerized or isodewaxed F-T material derived base stock(s), and wax-derived hydroisomerized/ isodewaxed base stock(s), such as wax isomerates/isodewaxates, are recited in U.S. Pat. Nos. 6,080,301; 6,090,989, and 6,165,949 for example.

[0026] Isomerate/isodewaxate base stock(s), derived from waxy feeds, which are also suitable for use in this invention, are paraffinic fluids of lubricating viscosity derived from hydroisomerized or isodewaxed waxy 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, hyrocrackates, thermal crackates, foots oil, wax from coal liquefaction or from shale oil, or other suitable mineral oil, non-mineral oil, non-petroleum, or natural source derived waxy materials, linear or branched hydrocarbyl compounds with carbon number of about 20 or greater, preferably about 30 or greater, and mixtures of such isomerate/isodewaxate base stocks and base oils.

[0027] Slack wax is the wax recovered from petroleum oils by solvent or auto-refrigerative dewaxing. Solvent dewaxing employs chilled solvent such as methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), mixtures of MEK/MIBK, mixtures of MEK and toluene, while autorefrigerative dewaxing employs pressurized, liquefied low boiling hydrocarbons such as propane or butane.

[0028] Slack wax(es), 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 hydroisomerization catalyst.

[0029] The term GTL base oil/base stock and/or wax isomerate base oil/base stock as used herein and in the claims is to be understood as embracing individual fractions of GTL base stock/base oil or wax isomerate base stock/base oil as recovered in the production process, mixtures of two or more GTL base stocks/base oil fractions and/or wax isomerate base stocks/base oil fractions, as well as mixtures of one or two or more low viscosity GTL base stock(s)/base oil fraction(s) and/or wax isomerate base stock(s)/base oil fraction(s) with one, two or more high viscosity GTL base stock(s)/base oil fraction(s) and/or wax isomerate base stock(s)/base oil fraction(s) to produce a dumbbell blend wherein the blend exhibits a viscosity within the aforesaid recited range.

[0030] In a preferred embodiment, the GTL material, from which the GTL base stock(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 alpha for producing the more desirable higher molecular weight paraffins. This process is also well known to those skilled in the art.

[0031] 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 which 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 an 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 about 320-850°F, 80-600 psi and 100-40,000 V/hr/V, expressed as standard volumes of the gaseous CO and H_2 mixture (0°C, 1 atm) per hour per volume of catalyst, respectively. The term "C_{5+}" 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.

[0032] As set forth above, the waxy feed from which the base stock(s) is/are derived is wax or waxy feed from mineral oil, non-mineral oil, non-petroleum, or other natural source, especially slack wax, or GTL 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+).

[0033] 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 sepcified limit has to be present, rather it excludes material boiling outside that range.

[0034] 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 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.

[0035] The process of making the lubricant oil base stocks from waxy stocks, e.g., slack wax or F-T wax, may be characterized as a hydrodewaxing 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/ 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 removal of oxygenates while others may benefit from oxygenates treatment. The 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.

[0036] 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 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.

[0037] Other isomerization catalysts and processes for hydrocracking/ hydroisomerized/isodewaxing 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.

[0038] 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.

[0039] 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 Group VIII metal loaded ZSM-48, preferably Group VIII noble metal loaded ZSM-48, more preferably Pt/ZSM-48 in either one stage or two stages. In any case, useful hydrocarbon base oil products may be obtained. Catalyst ZSM-48 is described in 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.

[0040] A dewaxing step, when needed, may be accomplished using either well known solvent or catalytic dewaxing 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. Low molecular weight hydrocarbons, such as propane, are also used for dewaxing, in which the hydroisomerate is mixed with 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 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.

[0041] 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, H_2 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.

[0042] GTL base stock(s), isomerized or isodewaxed wax-derived base stock(s), have a beneficial kinematic viscosity advantage over conventional Group II and Group III base stocks and base oils, and so may be very advantageously used with the instant invention. Such GTL base stocks and base oils can have significantly higher kinematic viscosities, up to about 20-50 mm^2/s at 100°C, whereas by comparison commercial Group II base oils can have kinematic viscosities, up to about 15 mm^2/s at 100°C, and commercial Group III base oils can have kinematic viscosities, up to about 10 mm^2/s at 100°C. The higher kinematic viscosity range of GTL base stocks and base oils, 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.

[0043] In the present invention the one or more isomerate/isodewaxate base stock(s), the GTL base stock(s), or mixtures thereof, preferably GTL base stock(s) can constitute all or part of the base oil.

[0044] One or more of the wax isomerate/isodewaxate base stocks and base oils can be used as such or in combination with the GTL base stocks and base oils.

[0045] One or more of these waxy feed derived base stocks and base oils, derived from GTL materials and/or other waxy feed materials can similarly be used as such or further in combination with other base stocks and base oils of mineral oil origin, natural oils and/or with synthetic base oils.

[0046] The preferred base stocks or base oils derived from GTL materials and/or from waxy feeds are characterized as having predominantly paraffinic compositions and are further characterized as having high saturates levels, low-to-nil sulfur, low-to-nil nitrogen, low-to-nil aromatics, and are essentially water-white in color.

[0047] The GTL base stock/base oil and/or wax hydroisomerate/isodewaxate, preferably GTL base oils/base stocks obtained from F-T wax, more preferably GTL base oils/base stocks obtained by the hydroisomerization/isodewaxing of F-T wax, can constitute from 5 to 100 wt%, preferably 40 to 100 wt%, more preferably 70 to 100 wt% 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.

[0048] 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 ($CH_2 \geq 4$), are such that: (a) $BI-0.5(CH_2 \geq 4) > 15$; and (b) $BI+0.85(CH_2 \geq 4) < 45$ as measured over said liquid hydrocarbon composition as a whole.

[0049] The preferred GTL 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 $\mathrm{BI} \geqq 25.4$ and $(\mathrm{CH}_2 \geq 4) \leq 22.5$. They have a nominal boiling point of $370°\mathrm{C}^+$, 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: DV (at -40°C) < 2900 (KV @ 100°C) - 7000.

[0050] The preferred GTL 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.

[0051] In the above the Branching Index (BI), Branching Proximity $(\mathrm{CH}_2 \geq 4)$, and Free Carbon Index (FCI) are determined as follows:

Branching Index

[0052] A 359.88 MHz 1 H 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.

[0053] 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.

[0054] 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 ($CH_2 \geq 4$)

[0055] A 90.5 MHz^{3}CMR single pulse and 135 Distortionless Enhancement by Polarization Transfer (DEPT) NMR spectra are obtained on a Brucker 360 MHzAMX 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.

[0056] The C atom types CH_3, CH_2, and CH are identified from the 135 DEPT ^{13}C NMR experiment. A major CH_2 resonance in all ^{13}C 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 ^{13}C chemical shifts for the methyl carbon at the end of the branch or the methylene carbon one removed from the methyl on the branch.

[0057] 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 CH_2);

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.

[0058] 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 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.

[0059] 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 CH_3 up and CH_2 180 degrees out of phase (down). APT is Attached Proton Test. It allows all carbons to be seen, but if CH and CH_3 are up, then quaternaries and CH_2 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).

[0060] GTL base oils and base oils derived from synthesized hydrocarbons, for example, hydroisomerized or isodewaxed waxy synthesized hydrocarbon, e.g., Fischer-Tropsch waxy hydrocarbon base oils 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 sulfur, sulfated ash and phosphorus content to meet ever increasingly restrictive environmental regulations. Such oils, known as low SAP 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 base oils can be formulated with the catalytic antioxidant additive disclosed herein replacing or used part of the heretofore additive such as ZDDP previously employed in stoichimetric or super stoichiometric amounts. Even if the remaining additive or additives included in the formulation contain sulfur and/or phosphorus the resulting formulated oils will be lower or low SAP.

[0061] As indicated, the base oil of the compositions of the invention may also contain a Group IV base stock, i.e., a polyalphaolefin or PAO. The preferred PAOs are those prepared from C_8 to C_{12} mono olefins.

[0062] The process of over basing a metal detergent means that a stoechiometric excess of the metal is present over what is required to neutralize the anion of the salt. It is the excess metal from over basing that has the effect of neutralizing acids which may build up. The alkylated alkaline earth metal detergents useful in this invention may also be borated. Such process for borating alkylated alkaline earth metal detergents has been described in U.S. Patent 4,965,004. The amount of alkylated alkaline earth metal detergent in the lubricating oil composition will be from about 0.4 wt% to about 10 wt%, preferably from about 0.5 wt% to about 5 wt% of the total weight of the lubricating oil composition. Preferably, the alkylated alkaline earth metal salicylate is the sole metal lubricating detergent present in the lubricating oil composition but other metal detergents such as metal sulfonates or phenates may also be present.

[0063] The compositions of the invention may include one or more lubricant additives, such as, dispersants, detergents, antioxidants, antiwear agents, viscosity index improvers, friction modifiers and defoamants.

[0064] Dispersants useful in this invention are borated and non-borated nitrogen-containing compounds that are oil soluble salts, amides, imides and esters made from high molecular weight mono and di-carboxylic acids and various amines. Preferred dispersants are the reaction product of acid anhydrides of polyolefins having an average molecular weight in the range from about 800 to about 3000, such as isobutenyl succinic anhydride with an alkoxyl or alkylene polyamine, such as tetraethylenepentamine. The borated dispersants contain boron in an amount from about 0.5 to 5.0 wt% based on dispersants. Dispersants, borated and/or non-borated or mixture thereof, are used generally in amounts from about 0.5 to about 10 wt% based on the total weight of the lubricating oil composition.

[0065] Examples of suitable antioxidants are hindered phenols, such as 2,6-di-tert-butylphenol, 4,4'- methylene bis (2,6-di-tert-butylphenol) 2,6-di-tert-butyl-p-cresol and the like, amine antioxidants such as alkylated naphthylamines, alkylated diphenylamines and the like and mixtures thereof. Antioxidants are used generally in amounts from about 0.01 to about 5 wt% based on the total weight of the lubricating oil composition.

[0066] Anti-wear agents generally are oil-soluble zinc dihydrocarbyl-dithiophosphates having at least a total of 5 carbon atoms, the alkyl group being preferably C_2 - C_8 that is primary, secondary, branched or linear. There are typically present in amounts of from about 0.01 to 5 wt%, preferably 0.4 to 1.5 wt% based on total weight of the lubricating oil composition.

[0067] Suitable conventional viscosity index (VI) improvers are the olefin polymers such as polybutene, ethylene-propylene copolymers,hydrogenated polymers and copolymers and terpolymers of styrene with isoprene and/or butadiene, A-B block copolymer such as those made by polymerization of dienes such as butadiene and/or isoprene with vinyl aromatics such as styrene known as Shell Vis (star polymers), polymers of alkyl acrylates or alkyl methacrylates, copolymers of alkylmethacrylates with N-vinyl pyrrolidone or dimethylamino-alkyl methacrylate, post grafted polymers of ethylene-propylene with an active monomer such as maleic anhydride which may be further reacted with an alcohol or an alkylene polyamine, styrene-maleic anhydride polymers post-reacted with alcohols and amines and the like. These additives are used in amounts from about 1.5 to about 15 wt% based on total weight of the lubricating oil composition. The amounts also depend on the desired viscosity specifications.

[0068] Friction modifiers useful in this invention include polyol esters such as glycerol esters more specifically fatty acid esters mono, di and tri-esters and a combination therof. Examples include but are not limited to glycerol monostearate, monooleate and the like. Other friction modifiers useful in this invention comprise molybdenum dithiocarbamates, molybdenum amine complexes and molybdenum dithiophosphates. Examples of molybdenum dithiocarbamates include C_6-C_{18} dialkyl or diaryldithiocarbamates, or alkylaryldithiocarbamates such as dibutyl, diamyl, diamyl-di-(2-ethylhexyl), dilauryl, dioleyl and dicyclohexyl dithiocarbamate. The amount of friction modifiers present in the oil, ranges from about 0.05 to about 1 wt% based on total weight of lubricating oil composition. The molybdenum content can range from about 20 to about 500 ppm, most preferably from about 50 to about 120 ppm.

[0069] Defoamants, typically silicone compounds such as polydimethyl-siloxane polymers and polyacrylate esters 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 wt% and often less than 0.2 wt% based on total weight of lubricating composition.

[0070] The compositions of the invention will also include a pour point depressant consisting of an alkylated alkaline earth metal detergent. The alkylated alkaline earth metal detergents, more preferably the alkylated calcium salicylates have been found to be particularly effective in the hydroisomerized or isodewaxed Fischer-Tropsch wax derived base oils having a kinematic viscosity in the range from about 2 mm^2/s to about 4.5 mm^2/s. The effectiveness of the alkylated alkaline earth metal detergent to reduce the pour point of the base oil appears to depend on the amount and the chain length of the wax molecules. For the hydroisomerized or isodewaxed Fischer-Tropsch wax derived base oil of kinematic viscosity 3-4 mm^2/s, the neutral and over based n-C_{14} alkyl calcium salicylates were the most effective. The over based alkylated calcium phenates and over based alkylated calcium sulfonates were not very effective in reducing the pour point of the 3-4 mm^2/s GTL base oil. Accordingly, the alkylated alkaline earth metal detergents useful in this invention are neutral and over based.

[0071] The alkylated alkaline earth metal detergents can also be sulfurized. The process for sulfurizing alkaline earth metal detergent especially metal phenate detergents is well known to those skilled in the art. The preparation of alkylated alkaline earth metal detergents is well known and has been documented e.g. in U.S. Patents 6,642,190, 6,599,867 and EP 1,233,053. The alkyl group on the aromatic ring is linear with a carbon number from C_8 to C_{30} but more preferably from C_{12} to C_{18} or a mixture thereof. Preferably the detergent will be a calcium and/or magnesium salicylate, neutral and over based, and will have a Total Base Number (TBN) from about 40 to about 700 but preferably from about 50 to about 350.

[0072] The alkylated alkaline earth metal detergents of this invention are particularly useful but not limited to finished lubricants such as piston engine oils, circulatory oils, automatic transmission fluids, gear oils, greases, hydraulic fluids, turbine oils, natural gas engine oils and metal working fluids that typically require pour point depressant to achieve low temperature properties.

The alkylated alkaline earth metal detergents particularly the alkylated alkaline earth metal salicylate detergents are more effective than the alkylated alkaline earth metal sulfonates and phenates in reducing the pour point of base oils. Moreover, the alkylated alkaline earth metal salicylate detergents were more effective in reducing the pour point of GTL and Group III base oils over the Group I and Group II base oils.

[0073] Finished engine oil lubricants apply to both straight and multigrade and include those of SAE Viscosity Grade of 0W-10 0W-20, 0W-30, 0W-40, 0W-50, 0W-60, 5W, 5W-20, 5W-30, 5W-40, 5W-50, 5W-60, 10W, 10W-20, 10W-30, 10W-40, 10W-50, 15W, 15W-20, 15W-30 or 15W-40. The lubricating oil composition can contain from about 4 to about 10 wt% of a secondary API Group V base stock such as alkylated aromatic, trimethylol propane ester...etc. but base stock component is preferably a long chain alkylated aromatic, such as an alkylated naphthalenes. In one engine oil embodiment, the base oils contain other Group III base oils such as those from slack wax isomerization and hydrocracked processes and polyalphaolefins (PAOs). Polyalphaolefins are prepared by polymerization of 1-alkenes using typically Lewis acid or Ziegler catalysts. Their preparation and properties are described by J. Brennan in Ind. Eng. Chem. Prod. Res. Dev., 19080, 19, pp 2-6. The polyalphaolefins are prepared preferably from C_8 to C_{12} monoolefins. The preferred base oils will have a saturates content of 99% minimum, a VI greater than 120 and a sulfur content less than 0.03 wt%.

EXAMPLES

[0074] The invention is further illustrated by the following examples in which the low temperature properties of various lubrication compositions were determined and given in the tables herein. These examples are not intended to limit the scope of the invention.

Example 1

[0075] In this Example, engine oil additives were added to the GTL 3.6 mm^2/s base oil at the typical treat rate used in an engine oil formulation. The pour point of the base oil -additive mixture was determined by ASTM D 97. A pour point difference of 3°C was not considered a significant difference as it is within test repeatability. The results in Table 1 shows that only that out of all the additives tested, only alkylated calcium salicylate detergent was effective in reducing the pour point of the base oil.

Table 1

Component, wt%	**Oil 1**	**Oil 2**	**Oil 3**	**Oil 4**	**Oil 5**	**Oil 6**	**Oil 7**
GTL Base Oil	100	91.7	95.2	96.5	98.0	99.0	99.8
Viscosity Improver I		8.3					
Dispersant			4.8				
Ca Salicylate Detergent				3.5			
Viscosity Improver II					2.0		
Borated Dispersant						1.0	
Polyol Ester							0.2
Pour Point, °C	-27	-27	-30	-57	-30	-30	-30
Pour Point Delta, °C	0	0	-3	-30	-3	-3	-3

Example 2

[0076] This Example shows that at a given treat rate in the GTL 3.6 mm^2/s viscosity base oil, the alkylated calcium sulfonate ("D1") and the alkylated calcium phenate ("D2") detergents were not as effective as the alkylated calcium salicylate ("D3") in reducing the pour point of the base oil as shown in Table 2.

Table 2

Components, wt%	**Oil 1**	**Oil 4**	**Oil 5**	**Oil 6**
	wt%	**wt%**	**wt%**	**wt%**
GTL Base Oil	100.0	96.5	96.5	96.5
D3, alkylated calcium salicylate		3.5		
D1, alkylated calcium sulfonate			3.5	
D2, alkylated calcium phenate				3.5
Pour Point, °C	-27	-57	-42	-30
Pour Point Delta, C	0	-30	-15	-3

Example 3

[0077] This Example shows that the alkylated calcium salicylate is less effective for reducing the pour point in Group I and Group II base oils when compared to Group III as shown in Table 3.

Table 3

Component, wt%	**Oil 7**	**Oil 8**	**Oil 9**	**Oil 10**	**Oil 11**	**Oil 12**
Group I	100.0	96.5				
Group II			100.0	96.5		
Group III					100.0	96.5
D3, alkylated calcium salicylate		3.5		3.5		3.5
Pour Point, °C	-12	-15	-18	-24	-21	-33
Pour Point Delta, °C	0	-3	0	-6	0	-12

Example 4

[0078] This Example shows that the alkylate calcium salicylate significantly reduced the pour point of the GTL 3.6 base oil at even 0.5 wt% treat rate as shown in Table 4 below.

Table 4

Component	**Oil 1**	**Oil 13**	**Oil 14**	**Oil 15**	**Oil 4**
	wt%	**wt%**	**wt%**	**wt%**	**wt%**
GTL Base Oil	100.0	99.5	99.0	98.5	96.5
D3 calcium salicylate		0.5	1.0	1.5	3.5
Pour Point, °C	-27	-51	-51	-54	-57
Pour Point Delta, °C	0	-24	-24	-27	-30

Example 5

[0079] This Example shows that both neutral and overbased alkyl calcium salicylates in TBN ranges from 56 to 280 were all as effective in reducing the pour point of the GTL 3.6 base oil as shown in Table 5.

Table 5

Component	**Oil 1**	**Oil 4**	**Oil 16**	**Oil 17**	**Oil 18**
	wt%	**wt%**	**wt%**	**wt%**	**wt%**
GTL Base Oil	100.0	96.5	96.5	96.5	96.5
D3, TBN = 205		3.5			
D4, TBN = 280			3.5		
D5, TBN = 65 (neutral)				3.5	
D6, TBN = 68					3.5
Pour Point, °C	-27	-57	-57	-54	-54
Pour Point Delta, °C	0	-30	-30	-27	-27

Example 5

[0080] This Example shows that metal detergent retains the favorable pour point improvement in a fully formulated oil of viscosity grade 0W-30. The engine oil contains no pour point depressant other then the alkylated alkaline earth metal with a GTL base stock having a kinematic viscosity of 3.6 mm2/s at 100°c.

Table 6

Oil	Formulated Engine Oil
KV @ 40°C, mm^2/s	50.36
KV @ 100°C, mm^2/s	10.15
Pour Point, °C	-54

CLAIMS:

1. A method for improving the pour point of a lubricating composition comprising a major amount of a lubricating base oil and one or more detergents, the method comprising using a alkylated alkaline earth metal detergents as a pour point depressant.

2. The method of Claim 1 wherein at least one alkaline earth metal detergents has a TBN of at least 65 and less than 280

3. The method of Claim 2 wherein the alkyl salicylate detergent is a calcium salicylate.

4. The method of Claim 2 wherein the alkaline earth metal is a calcium sulfonate.

5 . The method of Claim 2 wherein the alkaline earth metal is a calcium phenate.

6. The method of Claim 1 wherein the base oil is chosen from the group consisting of Group III, GTL, and any combination thereof.

7. A lubricating composition comprising:

(a) a major amount of an oil of lubricating viscosity chosen from the group consisting of Group III, GTL and any combination thereof,

(b) an alkylated alkaline earth metal as a pour point depressant wherein the alkylated alkaline earth metal is greater than 0.4 and less than 10 weight percent, and

(c) a minor amount of at least one lubricant additives,

the composition having a saturates content greater than 98%, a viscosity index (VI) greater than 120 and a sulfur content less than 0.03 wt%.

8. The composition of Claim 7 wherein the alkylated alkaline earth metal is chosen from the group consisting of calcium salicylate, calcium sulfonate, calcium phenate, and any combination thereof.

9. The composition of Claim 8 wherein the alkylated earth metal is a calcium salicylate.

10. The composition of Claim 7 wherein the composition is substantially free of any detergents and pour point depressants except for the alkylated alkaline earth metal.

11. The composition of Claim 9 wherein the calcium salicylate detergent comprises a mixture of calcium salicylates, one having a TBN greater than 200, a second having a TBN of about 100 to 200 and a third having a TBN of less than 100.

12. The composition of Claim 7 further comprising a Group IV base stock wherein the Group IV base stock is at least 4 and less than 10 weight percent of the composition.

13. The composition of Claim 7 further comprising a PAO.

14. A lubricating composition comprising:

(a) greater than 50 weight percent of a base oil of lubricating viscosity selected from the group consisting of Group III, GTL, and any combination thereof; and

(b) an alkylated alkaline earth metal as a pour point depressant wherein the alkylated alkaline earth metal is greater than 0.4 and less than 10 weight percent;

(c) at least one lubricant performance enhancing additives, the composition having a saturates content greater than 98%, a viscosity index (VI) greater than 120 and a sulfur content less than 0.03 wt%.

15. In the lubrication of an engine with a crankcase lubricant wherein the lubricant additionally is used to perform a hydraulic function, the improvement comprising using as the crankcase lubricant the composition of any one of Claims 7 to 14.

16. The composition of Claim 14 wherein the alkylated alkaline earth metal is chosen from the group consisting of calcium salicylate, calcium sulfonate, calcium phenate, and any combination thereof.

17. The composition of Claim 14 wherein the alkylated earth metal is a calcium salicylate.

18. The composition of Claim 14 wherein the composition is substantially free of any detergents and pour point depressants except for the alkylated alkaline earth metal.

19. The composition of Claim 14 wherein the calcium salicylate detergent comprises a mixture of calcium salicylates, one having a TBN greater than 200, a second having a TBN of about 100 to 200 and a third having a TBN of less than 100.

20. The composition of Claim 14 further comprising a Group IV base stock wherein the Group IV base stock is at least 4 and less than 10 weight percent of the composition.

21. The composition of Claim 14 further comprising a PAO.

22. The use of at least one alkylated earth metal as a pour point depressant.

23. The use according to claim 22, wherein the alkylated earth metal is used in a lubricant wherein at least one base stock of the lubricant is chosen form the group consisting of Group III, GTL, and any combination thereof.

24. The use according to claim 23 wherein the alkylated earth metal is a calcium salicylate.

25. The composition of claim 8 wherein an alkyl group on an aromatic ring of the alkaline earth metal detergent is linear and comprises of C8 to C30 more preferably from C12 to C18 carbon atoms.