LUBRICATING OIL COMPOSITIONS HAVING IMPROVED LOW TEMPERATURE PROPERTIES

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

[001] The present invention relates to lubricating oils of improved low temperature properties, especially viscometrics, and low pour points, and to a method for improving the low temperature properties, especially viscometrics, and reducing the pour points of gas-to-liquid (GTL) lubricating oils.

DESCRIPTION OF THE RELATED ART

[002] Lubricating oils and formulated lubricating oils (i.e., lubricating oils comprising mixtures of lubricating oil base stocks/base oils with one or more performance additives) used in most lubrication processes must be capable of delivering lubrication performance at low temperatures, be they low startup temperature or sustained low operating temperature.

[003] To this end, lubricating oils, having better low temperature properties, especially reduced low temperature viscometrics, are desirable. It is important that these lubricant oils can flow at very low temperature to critical machine or engine parts to provide lubrication functions. This flowability of lube base stock or finished product, as measured by pour point measurement, is one of the critical low temperature properties and can be measured easily by a standard pour point method. Base stocks of low pour points are the desirable starting base stocks/base oils for lubricating oils, be they lubricating oils used per se (that is without additives) or lubricating oil compositions (that is, lubricating oils formulated with at least one performance additive), also called formulated lubricating oils.

[004] The pour point of a lubricating oil is traditionally defined as that temperature at which a quantity of lubricating base stock/base oil, or of

formulated lubricating oil does not move from a beaker when the beaker is tilted at angle. Pour point can be measured by standard method ASTM D-97 or similar automated versions. Although pour point of a base stock measures the lowest temperature at which the oil still flows, it is also a good indicator for the low temperature properties. Usually, lower pour point indicates better low temperature properties or better low temperature viscometrics.

[005] Lubricating base stock/base oil pour point is usually a reflection of the wax content of said base stock/base oil. Wax is predominantly a linear paraffin which solidifies at low temperature. The pour point of lubricating base stock/base oil can be reduced, therefore, by removing wax from the base stock/base oil. For certain specially synthesized lube base stocks, such as polyalphaolefins, which contain no crystallizable wax, the pour point of the base stock is usually determined by the viscosity of the fluid at low temperature. At very low temperature when the viscosity of the base stock increases to so high a level that it stops flowing within the D97 test time frame, this temperature is recorded as the pour point even though there is no wax formation in the base stock.

[006] Historically and traditionally wax is removed from lubricating base stock/base oil by dewaxing processes which are identified as being either solvent dewaxing process or catalytic dewaxing process.

[007] In solvent dewaxing processes the lubricating base stock/base oil containing wax, hereinafter "waxy lube base stock" is contacted with a solvent such as methyl ethyl ketone (MEK) and/or methyl isobutyl ketone (MIBK) and/or toluene, etc., the temperature being reduced in the course of the contacting step to precipitate out the wax as a solid. The solid wax is then removed from the cold oil/solvent mixture by decantation, centrifugation or filtration through a filter, the oil/solvent passing through the filter and the wax being deposited on the filter as a filter cake which is subsequently removed from the

filter element material such as by scraping. The recovered wax is known as slack wax.

[008] Alternatively a solvent known as an autorefrigerative solvent can be used. Such solvent(s) is/are liquefied propane and/or propylene and/or butane and/or butylene which is/are mixed with the waxy lube oil under pressure, the pressure subsequently being reduced which causes a reduction in temperature of the entire mixture and a precipitation of solid wax which is then separated from the oil, again by, e.g., decantation, centrifugation or filtration.

[009] Solvent dewaxing constitutes the physical removal of wax from the waxy oil with subsequent recovery of the wax as a separated stream or product.

[010] Catalytic dewaxing removes wax from waxy oil by the conversion of wax into smaller hydrocarbon materials. The substantially linear long chain paraffins (n-paraffins) which constitute the wax are cracked into shorter chain paraffins which have lower pour points or into paraffins which have so short a chain length as to be gases or non-lubricating oil range hydrocarbons.

[011] Catalytic dewaxing physically changes the wax into shorter chain length molecules.

[012] Other dewaxing process, which also involves the use of a catalyst, are hydrodewaxing or hydroisomerization. Either is a process whereby linear long chain paraffins or long chain paraffins containing some branching (i.e., isoparaffins) are converted into more heavily branched isoparaffins by rearrangement, i.e., by isomerization accompanied by some limited cracking. In this way the wax is not actually removed from the oil but is converted into another form of paraffins (i.e., into isoparaffins) which have pour points lower than the substantially linear long chain wax paraffins. This type of fluids is sometimes called "chemically modified mineral oils".

[013] In some instances, depending on the isomerization catalyst employed the hydroisomerized lubricating oil may be subjected to a subsequent solvent or catalytic dewaxing step to remove the residual long chain n-paraffins and the only slightly branched iso-paraffins so as to further reduce the pour point.

[014] Another way to reduce the pour point of lubricating base stock/base oil is the use of one or more pour point depressing (PPD) performance additives.

[015] Pour point depressing additives are themselves large molecular which function by interfering with the coagulation/solidification of the linear long chain paraffins in the waxy lube oil as temperature is reduced.

[016] PPDs are used in low concentrations, usually 0.01 to about 3.0 wt% of the lubricating base stock/base oil.

[017] PPDs are typically polymeric materials of high molecular weight and include polymethacrylate, polyalkylmethacrylate, alkylated naphthalene, vinyl acetate-fumarate copolymers, polyarylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymer, and terpolymers of dialkylfumarates, vinyl esters of fatty acids and allyl vinyl ethers.

[018] Limited amounts of such pour point depressants are used because the addition of too much of the pour point depressant can have detrimental effects on the oil being treated, e.g., the pour point can go up or the oil solidifies.

[019] USP 3,396,114 teaches a dual purpose lubricant comprising a quantity of tricresyl phosphate, a neutral calcium sulfonate, a poly (C_{4-20} alkyl) methacrylate viscosity index improver (about 10,000 to 30,000 molecular weight), a hindered phenol antioxidant, about 0.5 to 2.0 volume percent of a paraffin wax alkylated naphthalene lubricating oil pour point depressant, an alkyl ester of a chlorinated fatty acid, an anti foamant and a petroleum lubricating base oil.

[020] The pour point depressant is a wax alkylated naphthalene which is identified as a well known PPD for lubricating oil, generally prepared by chlorinating paraffin wax and condensing the chlorowax with naphthalene (see also USP 1,815,022 and USP 2,015,748).

[021] USP 2,671,051 teaches low pour point lubricants made by adding to a waxy hydrocarbon lubricating oil wherein the wax is predominantly normal aliphatic hydrocarbon waxes, a pour point depressant in an amount in the range of 75 to 150% based on the weight of said waxes of at least one extraneous hydrocarbon wax bearing a cyclic end group on an aliphatic hydrocarbon chain, the chain differing from the average normal aliphatic hydrocarbon wax chain length by no more than about 4 carbon atoms. The pour point depressant can be at least one extraneous naphthenic wax bearing a naphthenic end group having an aliphatic hydrocarbon side chain or an extraneous aromatic wax bearing an aromatic end group having an aliphatic hydrocarbon side chain, the aromatic end group being a dicyclic aromatic group, e.g., naphthalene.

[022] USP 4,753,745 teaches methylene linked aromatic pour point depressant of the general formula

$$Ar\,(R) — [\,Ar'\,(R')\,]_n — Ar''$$

wherein Ar, Ar' and Ar'' are independently an aromatic moiety containing 1 to 3 aromatic rings and each aromatic moiety is substituted with zero to 3 substituents, (R) and (R') are independently an alkylene group containing about 1 to 100 carbon atoms with the proviso that at least one of (R) or (R') is CH_2 and n is zero to about 1000. The material has a molecular weight varying from about 271 to about 300,000.

[023] WO 2004/081157 teaches a lubricant composition based on Fischer-Tropsch (F-T) derived base oils having a pour point from -15 to -31°C obtained by a catalytic dewaxing step and containing a pour point depressant additive, and 15 wt% or greater of a Detergent Inhibitor (DI) additive package. Suitable pour

point depressants are alkylated naphthalene, and phenolic polymers, polymethacrylates, maleate/fumarate copolymer esters, methacrylate vinyl pyrrolidone copolymer or vinyl acetate-fumarate copolymer. Preferred amounts used range from 0.1 wt% to preferably not more than 0.3 wt%.

[024] WO 02/04578 teaches compositions comprising blends of API Group II and/or Group III base stocks and alkylated fused and/or polyfused aromatic compositions, such as alkylated naphthalenes which exhibit excellent additive solvency, thermo-oxidative stability, hydrolytic stability and seal swell characteristics.

[025] USP 6,071,864 is directed to catalystic methods for the preparation of arylated polyolefins for use as synthetic lubricants. The aryl moiety can be benzene, naphthalene, furan, thiophene, anthracene, phenanthrene, etc.

[026] USP 5,132,478 is directed to alkylaromatic lubricant fluids. Aromatic compounds are alkylated with C_{20}-C_{1300} olefinic oligomers using an acidic alkylation catalyst to produce alkylated aromatic products exhibiting high viscosity index and low pour point. They are described as also being useful as additives such as dispersants, detergents, VI improvers, extreme pressure/antiwear additives, antioxidants, pour point depressants, emulsifiers, demulsifiers, corrosion inhibitors, anti-rust inhibitors, anti-staining additives, friction modifiers and the like.

[027] USP 5,602,086 teaches lubricant compositions comprising mixtures of polyalphaolefins and alkylated aromatic fluids. The alkyl aromatic can be alkylated naphthalene having a kinematic viscosity at 100°C ranging from about 4 mm^2/s to about 30 mm^2/s. The mixture is characterized by improved oxidation resistance.

[028] USP 4,714,794 teaches mixture of specific mono-alkylated naphthalenes as synthetic oil having excellent oxidation stability and useful as a thermal

medium oil or as the main component of a synthetic lubricating oil. The mixture of specific mono-alkylated naphthalenes can be incorporated with mineral oils and/or known lubricating oils in amounts which do not impair their high oxidation stability. The mineral oils and/or known lubricating oils may be added in amounts up to 75% by weight, preferably up to 50% by weight, more preferably up to 25% by weight.

[029] USP 4,604,491 teaches mixtures of monoalkylated naphthalene and polyalkylated naphthalenes having a viscosity at 210°F between 61 and 88 SUS, a viscosity index between 105 and 136 and a flash point (COC = Cleveland Open Cup) of between 508°F and 560°F, useful as a synthetic oil for functional fluids and greases.

[030] Publication No. US 2005/0077209 is directed to a process for producing lubricant base oils with optimized branching.

[031] The lubricants are characterized as having low pour points and extremely high viscosity indexes. The lubricants are produced by hydroisomerization dewaxing of waxy feed using a shape selective intermediate pore size molecular sieve to produce an intermediate oil isomerate in which the extent of branching is less than 7 alkyl branches per 100 carbons and solvent dewaxing the intermediate oil isomerate to produce a lube oil wherein the extent of branching is less than 8 alkyl branches per 100 carbon atoms and less than 20 wt% of the alkyl branches are at the 2 position, the lube base oil having a pour point of less than -8 °C, a kinematic viscosity at 100°C of about 3.2 mm^2/s or greater, a VI greater than a Target VT as calculated as follows:

$$\text{Target VI} = 22 \times \ln(\text{kinematic viscosity at } 100°C)$$

[032] It is stated that this base oil can be blended with preferably less than 95 wt% of conventional Group I, Group II and Group III base stocks, isomerized petroleum wax oils, polyalpha olefins, poly internal olefins, diesters, polyol

esters, phosphate esters, alkylated aromatics and mixtures thereof. Alkylated aromatics are identified as synthetic lubricants produced from the alkylation of aromatics with haloalkanes, alcohols or olefins in the presence of a Lewis or Bionstead acid catalyst. Useful examples include alkylated benzene and alkylated naphthalene which have good low temperature properties and may provide improved additive solubility.

[033] USP 6,627,779 teaches an improved method for preparing a blended lube base oil comprising at least one highly paraffinic Fischer-Tropsch (F-T) lube base stock and at least one base stock composed of alkyl aromatic, alkylcyclo-paraffins or mixtures thereof to improve the yield of lube base oils from F-T facilities. The alkyl aromatics, alkylcycloparaffins or mixtures thereof are present in an amount of from about 1 wt% to about 50 wt%. The alkylaromatic are alkyl aromatics boiling in the lube oil boiling ranges and are alkyl benzene, alkylnaphthalene, alkyltetralines of alkyl polynuclear aromatics. Preferably the alkyl aromatic is alkyl benzene. Fischer-Tropsch synthesis process product is fractionally distilled to produce a C_{20}+ fraction, a light aromatics fraction and a light Fischer-Tropsch products fraction containing olefins, alcohols and mixtures thereof. The light aromatics fraction is alkylated with the light Fischer-Tropsch product fraction to yield the alkyl aromatics.

[034] The blended lube base oils are described as having excellent viscosity and viscosity index properties. Only blends with alkyl benzene or alkyl cyclohexane are exemplified. There is no mention about the pour points or low temperature viscometrics for the blends containing alkylbenzene.

[035] Gas-to-liquids base stocks usually have pour points ranging from 0°C to -25°C. If one tries to produce GTL derived base stocks with pour points much below -25°C, the process lube yield will be decreased significantly, which is undesirable. Therefore, it would be a significant technical advance if a way

could be found to reduce the pour point of GTL base stock/base oil by ways other than through conventional solvent dewaxing or catalytic dewaxing, or through an increase in the intensity of the hydrodewaxing or hydroisomerization procedure.

DESCRIPTION OF THE FIGURE

[036] Figure 1 graphically presents pour points of blend fluids vs. wt% alkylnaphthalene fluid (AN), ester, a low pour point alkylbenzene fluid (Ar PAO) and a C_{20}-C_{24} alkylbenzene (C_{2024}AB) prepared according to prior art, all in a 6 cSt GTL base stock (GTL 6). This graph demonstrates the effects alkylated naphthalene fluid and the low pour point alkylbenzene (Ar PAO) have on lowering the pour point of GTL base stock.

DESCRIPTION OF THE INVENTION

[037] A method is disclosed for reducing the pour point of gas-to-liquids (GTL) lube base stocks/base oils or hydrodewaxed or hydroisomerized/catalytic (or solvent) dewaxed wax derived base stocks/base oil(s) by adding to such base stocks/base oils from about 1 to 95 wt% preferably 5 to 80 wt%, more preferably 5 to 60 wt% of an alkylated aromatic synthetic fluid. When the alkyl aromatic synthetic fluid is alkyl naphthalene, said alkylated naphthalene synthetic fluid, has a kinematic viscosity at 100°C falling in the range from about 1.5 mm^2/s to about 600 mm^2/s, preferably from about 2 mm^2/s to about 300 mm^2/s, more preferably from about 2 mm^2/s to about 100 mm^2/s, a pour point of 0°C or less, preferably -15°C or less, more preferably -25°C or less, still more preferably -35°C or less, a viscosity index in the range of from about 0 to 200, preferably about 50 to 150, more preferably about 50 to 145.

[038] When the synthetic alkyl aromatic fluid is alkyl benzene said alkyl benzene synthetic fluid has a kinematic viscosity falling in the range from about 1.5 mm^2/s to 600 mm^2/s, preferably from about 2 mm^2/s to about 300 mm^2/s, more preferably about 2 mm^2/s to 100 mm^2/s, a pour point of 0°C or less,

preferably -15°C or less, more preferably -25°C or less, still more preferably -35°C or less, most preferably -60°C or less, a viscosity index in the range of from about 0 to 200, preferably about 70 to 200, more preferably about 80 to 180.

[039] Kinematic Viscosity (KV) is determined by ASTM D 445. Pour point is determined by ASTM D 97. Viscosity Index (VI) is determined by ASTM D 2270.

[040] Base stock means a lubricating oil produced by a single manufacturer to a particular specification regardless of feed stock source, manufacturer's location or process used, and identified by a specific identification formula or number or code. Base oil is one or a mixture of base stocks meeting the particular oil component requirement of a specific lubricating oil product specification, e.g., specific engine oil, turbine oil, etc., finished product performance requirements.

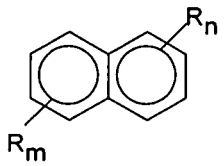
[041] Gas-to-liquids (GTL) base stocks/base oils, and hydrodewaxed or hydroisomerized/catalytic (and/or solvent) dewaxed wax derived base stock(s)/base oil(s) defined in greater detail below, have many outstanding lubricant properties. However, they are known to be highly paraffinic in nature and non-polar, resulting in their having poor solubility for polar additives used in many high quality, high performance lubricating oil formulations. They also have poor solvency and dispersancy for degradation products or sludges formed in the lubricant over long service times. Esters have been used to improve solvency and dispersivity but esters are expensive and have performance deficiencies.

[042] It has been discovered that the pour point and low temperature properties of such base stock/base oil especially GTL base stock/base oil can be improved, as can be the base stock/base oil solvency and dispersancy by combining into said base stock/base oil a particular alkylated aromatic selected from alkylated

naphthalenes and/or low pour point alkylated benzene or their hydrogenated analogues.

[043] The alkylated naphthalene used in the present method differs from the alkylated naphthalene pour point depressants disclosed in the prior art. The alkylated naphthalenes used in the present invention are alkyl naphthalene fluids having kinematic viscosity at 100°C falling in the range of from 1.5 to 600 mm^2/s and having pour points of 0°C or less and VI in the range of 0 to 200. They are flowable liquids at room temperature.

[044] The fluid alkylated naphthalenes used in the present invention have the following general formula:



wherein n + m = 1 to 8, preferably 1 to 6, more preferably 1 to 5, and R is C_1-C_{30}, preferably C_1-C_{20} linear alkyl group, C_3-C_{300} , preferably C_3-C_{100}, more preferably C_3-C_{30} branched alkyl group or mixtures of such groups with the total number of carbons in R_m and R_n, preferably being at least 4.

[045] Examples of typical alkyl naphthalenes are mono-, di-, tri-, tetra-, or penta-C_3 alkyl naphthalene, C_4 alkyl naphthalene, C_5 alkylnaphthalene, C_6 alkyl naphthalene, C_8 alkyl naphthalene, C_{10} alkyl naphthalene, C_{12} alkyl naphthalene, C_{14} alkyl naphthalene, C_{16} alkyl naphthalene, C_{18} alkyl naphthalene, etc., C_{10}-C_{14} mixed alkyl naphthalene, C_6-C_{18} mixed alkyl naphthalene, or the mono-, di-, tri-, tetra-, or penta C_3, C_4, C_5, C_6, C_8, C_{10}, C_{12}, C_{14}, C_{16}, C_{18} or mixture thereof alkyl monomethyl, dimethyl, ethyl, diethyl, or methylethyl naphthalene, or mixtures thereof. The alkyl group can also be branched alkyl group with C_{10} to C_{300}, e.g., C_{24}-C_{56} branched alkyl naphthalene, C_{24}-C_{56} branched alkyl mono-, di-, tri-, tetra- or penta- C_1-C_4 naphthalene. These branched alkyl group substituted naphthalenes or branched alkyl group substituted mono-, di-, tri-, tetra- or penta

C_1-C_4 naphthalene can also be used as mixtures with the previously recited materials. These branched alkyl group can be prepared from oligomerization of small olefins, such as C_5 to C_{24} alpha- or internal-olefins. When the branched alkyl group is very large (that is 8 to 300 carbons), usually only one or two of such alkyl groups are attached to the naphthalene core. The alkyl groups on the naphthalene ring can also be mixtures of the above alkyl groups. Sometimes mixed alkyl groups are advantageous because they provide more improvement of pour points and low temperature fluid properties. The fully hydrogenated fluid alkylnaphthalenes can also be used for blending with GTL base stock/base oil, but the alkyl naphthalenes are preferred.

[046] Typically the alkyl naphthalenes are prepared by alkylation of naphthalene or short chain alkyl naphthalene, such as methyl or di-methyl naphthalene, with olefins, alcohols or alkylchlorides of 6 to 24 carbons over acidic catalyst inducing typical Friedel Crafts catalysts. Typical Friedel-Crafts catalysts are $AlCl_3$, BF_3, HT, zeolites, amorphous alumniosilicates, acid clays, acidic metal oxides or metal salts, USY, etc.

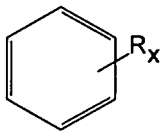
[047] Methods for the production of alkylnaphthalenes suitable for use in the present invention are described in USP 5,034,563, USP 5,516,954, USP 6,436,882 as well as in references cited in those patents as well as taught elsewhere in the literature. Because alkylated naphthalene synthesis techniques are well known to those skilled in the art as well as being well documented in the literature such techniques will not be further addressed herein.

[048] The naphthalene or mono- or di-substituted short chain alkyl naphthalenes can be derived from any conventional naphthalene-producing process from petroleum, petrochemical process or coal process or source stream. Naphthalene-containing feeds can be made from aromaticization of suitable streams available from the F-T process. For example, aromatization of olefins or paraffins can produce naphthalene or naphthalene-containing component (DE84-

3414705, US20060138024 A1). Many medium or light cycle oils from petroleum refining processes contain significant amounts of naphthalene, substituted naphthalenes or naphthalene derivatives. Indeed, substituted naphthalenes recovered from whatever source, if possessing up to about three alkyl carbons can be used as raw material to produce alkylnaphthalene for this invention. Furthermore, alkylated naphtahlenes recovered from whatever source or processing can be used in the present method, provided they possess kinematic viscosities, VI, pour point, etc., as previously recited.

[049] Suitable alkylated naphthalenes are available commercially from ExxonMobil Chemical Company under the tradename Synesstic AN or from King Industries under the tradename NA-Lube naphthalene-containing fluids.

[050] As previously indicated, alkylated benzene of the following structure with viscosity at 100°C of 1.5 to 600 cS, VI of 0 to 200 and pour point of 0°C or less, preferably -15°C or less, more preferably -25°C or less, still more preferably -35°C or less, most preferably -60°C or less are useful for this invention.



In this structure, x = 1 to 6, preferably 1 to 5, more preferably 1 to 4. When it is monoalkylated benzene, the R can be linear C_{10} to C_{30} alkyl group or a C_{10}-C_{300} branched alkyl group preferably C_{10}-C_{100} branched alkyl group, more preferably C_{15}-C_{50} branched alkyl group. When n is 2 or greater than 2, one or two of the alkyl group can be small alkyl radical of C_1 to C_5 alkyl group, preferably C_1-C_2 alkyl group. The other alkyl group or groups can be any combination of linear C_{10}-C_{30} alkyl group, or branched C_{10} and higher up to C_{300} alkyl group, preferably C_{15}-C_{50} branched alkyl group. These branched large alkyl radicals can be prepared from the oligomerization or polymerization of C_3 to C_{20} internal

or alpha-olefins or mixture of these olefins. The total number of carbons in the alkyl subsitutents ranged from C_{10} to C_{300}. Preferred alkyl benzene fluids can be prepared according to USP 6,071,864 or USP 6,491,809 or EP 0,168,534.

[051] In accordance with the present invention the alkylated benzene is preferably prepared by the method comprising the steps of:

(a) oligomerizing one or more alpha olefins or internal olefins to form olefin dimers and some higher oligomers; and

(b) arylating the olefin oligomers with benzene or a short alkyl chain (C_1-C_5 alkyl group) mono or poly substituted benzene to yield the alkylated benzene product.

[052] An α-olefin or internal olefins is oligomerized in the presence of promoted catalyst to give predominantly olefin dimer and higher oligomers. Once the reaction has gone to completion, an aromatic composition containing one or more aromatic compounds is reacted with the oligomers, in the presence of the same catalyst, to give alkylated aromatic lube base stocks in high yield.

[053] In preferred embodiments, the α-olefin has from 6 to about 20 carbon atoms. In more preferred embodiments, the α-olefin has from about 8 to about 16 carbon atoms. In especially preferred embodiments the α-olefin has from about 8 to about 14 carbon atoms.

[054] In accordance with the present invention, one or more α-olefins are oligomerized to form predominantly olefin dimer, with some trimer or higher oligomers. In preferred embodiments the olefin dimer has from about 20 to about 36 carbon atoms, more preferably from about 20 to about 28 carbon atoms. In another embodiment, one or more internal olefins, by themselves or mixed with a-olefins are oligomerized to form oligomers, which can further be alkylated with an aromatic compound. The preferred internal olefins starting

material are C8 to C30 internal olefins, preferably C10 to C20, more preferably C12 to C18.

[055] The aromatic moiety is benzene or a short chain (C_1-C_5 alkyl group) or hydroxy, alkoxy, aroxy alkylthio, or arylthio mono or poly substituted benzene, preferably C_1-C_5 alkyl group mono or poly substituted benzene, more preferably toluene, o-, m- or p-xylene, ethylene benzene, di-ethyl benzene, n- or iso-propyl benzene, di-n- or di-isoparopyl benzene, n-iso or tert-butyl benzene, di- no- or di-iso or di-tert butyl benzene.

[056] The catalysts used include a Lewis acid catalyst such as BF_3, AlCl, triflic acid, BCl_3, $AlBr_3$, $SnCl_4$, $GaCl_3$, an acid clay catalyst, or an acidic zeolite, for example zeolite Beta, USY, Mordenite, Montmorillonite, or other acidic layered, open-structure zeolites, such as MCM-22, MCM-56 or solid superacids, such as sulfated zirconia, and activated Wo_x/ZrO_2. In particularly preferred embodiments, the catalyst is BF_3 or $AlCl_3$ or their promoted versions.

[057] It is known that catalysts such as those described herein are advantageously employed in conjunction with a promoter. Suitable promoters for use with the catalysts in the present invention include those known in the art, for example water, alcohols, or esters, or acids.

[058] A preferred catalyst is MCM-56. MCM-56 is a member of the MCM-22 group useful in the invention which includes MCM-22, MCM-36, MCM-49 and MCM-56. MCM-22 is described in U.S. Pat. No. 4, 954, 325. MCM-36 is described in U.S. Pat. No. 5,250,277 and MCM-36 (bound) is described in U.S. Pat. No. 5,292,698. MCM-49 is described in U.S. Pat. No. 5,236, 575 and MCM-56 is described in U.S. Pat. No. 5,362,697.

[059] The catalysts as mixed metal oxide super acids comprise an oxide of a Group IVB metal, preferably zirconia or titania. The Group IVB metal oxide is

modified with an oxyanion of a Group VIB metal, such as an oxyanion of tungsten, such as tungstate. The modification of the Group IVB metal oxide with the oxyanion of the Group VIB metal imparts acid functionality to the material. The combination of Group IVB metal oxide with an oxyanion of a Group VIB metal is believed to enter into an actual chemical interaction which, in any event, provides a composition with more acidity than a simple mixture of separately formed Group IVB metal oxide mixed with a separately formed Group VIB metal oxide or oxyanion.

[060] The acidic solid materials useful as a catalyst are described in U.S. Pat. Nos. 5,510,539 and 5,563,310. These solid materials comprise an oxide of a Group IVB metal, preferably zirconia or titania. The Group IVB metal oxide is modified with an oxyanion of a Group VIB metal, such as an oxyanion of tungsten, such as tungstate. The modification of the Group IVB metal oxide with the oxyanion of the Group VIB metal imparts acid functionality to the material. The modification of a Group IVB metal oxide, particularly, zirconia, with a Group VIB metal oxyanion, particularly tungstate, is described in U.S. Pat. No. 5,113,034; in Japanese Kokai Patent Application No. Hei 1 [1989]-288339; and in an article by K. Arata and M. Hino in Proceeding 9th International Congress on Catalysis, Volume 4, pages 1727-1735 (1988). According to these publications, tungstate is impregnated onto a preformed solid zirconia material. This chemical interaction is discussed in the aforementioned article by K. Arata and M. Hino which also suggests that solid superacids are formed when sulfates are reacted with hydroxides or oxides of certain metals, e.g., Zr. These superacids are said to have the structure of a bidentate sulfate ion coordinated to the metal, e.g., Zr. The article suggests further that a superacid can also be formed when tungstates are reacted with hydroxides or oxides of Zr. The resulting tungstate modified zirconia materials are theorized to have an analogous structure to the aforementioned superacids comprising sulfate and

zirconium, wherein tungsten atoms replace sulfur atoms in the bidentate structure. It is further suggested that the tungsten oxide combines with zirconium oxide compounds to create superacid sites at the time the tetragonal phase is formed.

[061] Although it is believed that the present catalysts may comprise the bidentate structure suggested in the aforementioned article by Arata and Hino, the particular structure of the catalytically active site in the present Group IVB metal oxide modified with an oxyanion of a Group VIB metal has not yet been confirmed, and it is not intended that this catalyst component should be limited to any particular structure.

[062] Suitable sources of the Group IVB metal oxide, used for preparing the catalyst, include compounds capable of generating such oxides, such as oxychlorides, chlorides, nitrates, oxynitrates, etc., particularly of zirconium or titanium. Alkoxides of such metals may also be used as precursors or sources of the Group IVB metal oxides. Examples of such alkoxides include zirconium n-propoxide and titanium i-propoxide. These sources of a Group IVB metal oxide, particularly zirconia, may form zirconium hydroxide, i.e., $Zr(OH)_4$, or hydrated zirconia as intermediate species upon precipitation from an aqueous medium in the absence of a reactive source of tungstate. The expression, hydrated zirconia, is intended to connote materials comprising zirconium atoms covalently linked to other zirconium atoms via bridging oxygen atoms, i. e., Zr-O-Zr, further comprising available surface hydroxy groups. When hydrated zirconia is impregnated with a suitable source of tungstate under sufficient conditions, these available surface hydroxyl groups are believed to react with the source of tungstate to form an acidic catalyst. As suggested in the article by K. Arata and M. Hino, precalcination of $Zr(OH)_4$ at a temperature of from about 100°C to about 400°C results in a species which interacts more favorably with tungstate upon impregnation therewith. This precalcination is believed to result in the

condensation of ZrOH groups to form a polymeric zirconia species with surface hydroxyl groups which may be referred to as a form of a hydrated zirconia.

[063] Suitable sources for the oxyanion of the Group VIB metal, preferably molybdenum or tungsten, include, but are not limited to, ammonium metatungstate or metamolybdate, tungsten or molybdenum chloride, tungsten or molybdenum carbonyl, tungstic or molybdic acid and sodium tungstate or molybdate.

[064] The ratio of aromatic compound to α-olefin oligomers preferably is from about 0.05:1 to about 20:1. In more preferred embodiments the ratio of aromatic compound to α-olefin oligomers is from about 0.1:1 to about 8:1.

[065] The methods provide arylated poly α-olefins in higher yield than the conventional alkylbenzene fluid synthesis, where 2 moles of α-olefin and one mole of aromatic compound are mixed together with a catalyst.

[066] Reaction temperatures typically range from about 20 to 100°C.

[067] The alkylbenzene fluids used in this invention have good low temperature properties, including good pour points. Their pour points are usually 0°C or less. A preferred alkyl methyl benzene fluid and the one used in all experiments was prepared according to procedures described in USP 6,071,864, starting from the oligomerization of a mixture of C_8, C_{10} and C_{12} linear alpha olefins, over a promoted BF_3 catalyst to produce a product which is reacted with toluene over the same catalyst at same reaction temperature. The product was isolated to yield a lube base stock with viscometrics and pour point meeting the requirement for this invention (>1.5 cS and less than 0°C pour point). It has been discovered that this alkylbenzene unexpectedly reduces the pour point of GTL fluids synergistically.

[068] A dialkylbenzene (DAB) as described in US6491809 can also be used with GTL lube to give similar benefit. These types of DAB can be prepared by repeated alkylation of benzene e.g., alkylation of benzene to give mono-alkylbenzene, followed by further alkylation of this mono-alkylbenzene in the same reactor or in a separate reactor. Alkylbenzenes meeting the requirement for this invention can also be obtained from many detergent alkylbenzene processes. In these processes, linear alkylbenzene (LAB) is produced by alkylation of benzene over alkylation catalyst. The mono-alkyl LAB is used as raw material for detergent production. This detergent LAB process also produces some heavier by-product streams, which contain mixtures of di-alkylbenzene and high alkylbenzenes or oligomerized alkylated benzene. These higher fractions often have properties meeting the description of this invention and are suitable to blend with GTL base stocks .

[069] In contrast, the conventional C_{20}-C_{24} alkylbenzene fluids, prepared by isomerizing C_{20}-C_{24} linear alpha-olefins resulting in the rearrangement of the double bond from the alpha to an internal position and then alkylating benzene with such C_{20}-C_{24} linear olefins (USP 6,627,779), have pour points above 0°C. These types of fluids have no effect on GTL pour point or in fact raise the pour point.

[070] Further, it has been found that the hydrogenated analogues of the alkylated naphthalene or alkylated benzene described above are also effective pour point depressant fluids for GTL base stocks, and hydrodewaxed or hydroisomerized/catalytic (and/or solvent) dewaxed wax derived base stocks/base oils. Further, it has been found that the alkylated naphthalene or alkylated benzene fluids can provide un-expected improvement of oxidation stability of the blends with GTL fluids. This oxidative stability improvement can be demonstrated by longer RBOT (ASTM D2272 method) or other oxidation test methods. Further, it has been found that the alkylated naphthalene

or alkylated benzene fluids can improve the polarity of the blends with GTL fluids. This higher polarity of the blend indicates a better solubility of additives and other polar components formed during oil service. Thus, the blend of GTL with these alkylated aromatic fluids can provide higher level of finished lubricant performance.

[071] The base stocks and/or base oils employed in the present invention include one or more of a mixture of base stock(s) and/or base oil(s) derived from one or more Gas-to-Liquids (GTL) materials, as well as hydrodewaxed, or hydroisomerized/conventional cat (and/or solvent) dewaxed base stock(s) and/or base oils derived from natural wax or waxy feeds, mineral and or non-mineral oil waxy feed stocks such as slack waxes (derived from the solvent dewaxing of natural oils, mineral oils or synthetic, e.g. Fischer-Tropsch feed stocks), natural waxes, and waxy stocks such as gas oils, waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, foots oil or other mineral, mineral oil, or even non-petroleum oil derived waxy materials such as waxy materials received from coal liquefaction or shale oil, linear or branched hydrocarbyl compounds with carbon numbers of about 20 or greater, preferably about 30 or greater, and mixtures of such base stocks and/or base oils.

[072] Base stock(s) and/or base oil(s) derived from waxy feeds, which are also suitable for use in this invention, are paraffinic fluids of lubricating viscosity derived from hydrodewaxed, or hydroisomerized/cat (and/or solvent) dewaxed 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 stock(s) and/or base oil(s).

[073] 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/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 stock(s) and/or base oil(s) include oils boiling in the lube oil boiling range (1) separated/fractionated from synthesized GTL materials such as for example, by distillation and subsequently subjected to a final wax processing step which involves either or both of a catalytic dewaxing process, or a solvent dewaxing process, to produce lube oils of reduced/low pour point; (2) synthesized wax isomerates, comprising, for example, hydrodewaxed, or hydroisomerized/followed by cat and/or solvent dewaxed synthesized wax or waxy hydrocarbons; (3) hydrodewaxed, or hydroisomerized/followed by cat and/or solvent dewaxed Fischer-Tropsch (F-T) material (i.e., hydrocarbons, waxy hydrocarbons, waxes and possible analogous oxygenates); preferably hydrodewaxed, or hydroisomerized/followed by cat and/or solvent dewaxing dewaxed F-T waxy hydrocarbons, or hydrodewaxed or hydroisomerized/followed by cat (or solvent) dewaxing dewaxed, F-T waxes, or mixtures thereof.

[074] GTL base stock(s) and/or base oil(s) derived from GTL materials, especially, hydrodewaxed, or hydroisomerized/followed by cat and/or solvent

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

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

[076] Base stock(s) and/or base oil(s) derived from waxy feeds, which are also suitable for use in this invention, are paraffinic fluids of lubricating viscosity derived from hydrodewaxed, or hydroisomerized/cat (and/or solvent) dewaxed 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 stock(s) and/or base oil(s).

[077] Slack wax is the wax recovered from any waxy hydrocarbon oil including synthetic oil such as F-T waxy oil or petroleum oils by solvent or 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.

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

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

[080] In the present invention mixtures of hydrodewaxate, or hydroisomerate/cat (or solvent) dewaxate base stock(s) and/or base oil(s), mixtures of the GTL base stock(s) and/or base oil(s), or mixtures thereof,

preferably mixtures of GTL base stock(s) and/or base oil(s), can constitute all or part of the base oil.

[081] 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).

[082] 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

[083] Internal combustion engine lubricating oils require the presence of antiwear and/or extreme pressure (EP) additives in order to provide adequate antiwear protection for the engine. Increasingly specifications for 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.

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

[085] 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.

[086] 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

$$R^3R^4C{=}CR^5R^6$$

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.

[087] 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 diisopropyl-phosphorodithioate 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-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. Each of the aforementioned patents is incorporated by reference herein in its entirety.

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

[089] 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. Each of the aforementioned patents is incorporated herein by reference in its entirety.

[090] 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.

Antioxidants

[091] 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, each of which is incorporated by reference herein in its entirety.

[092] Useful antioxidants include hindered phenols. These phenolic antioxidants may be ashless (metal-free) phenolic compounds or neutral or basic metal salts of certain phenolic compounds. Typical phenolic antioxidant compounds are the hindered phenolics which are the ones which contain a sterically hindered hydroxyl group, and these include those derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or p-position to each other. Typical phenolic antioxidants include the hindered phenols substituted with C_6+ 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 proprionic 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).

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

[094] 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.

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

[096] 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 know to be particularly useful.

[097] 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

[098] 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.

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

[0100] 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.

[0101] Preferred detergents include the alkali or alkaline earth metal salts of sulfonates, phenates, carboxylates, phosphates, and salicylates.

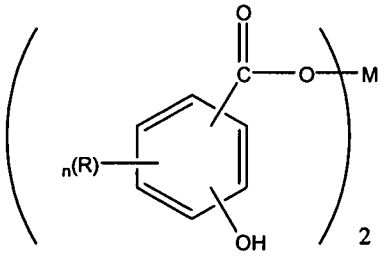
[0102] Sulfonates may be prepared from sulfonic acids that are typically obtained by sulfonation of alkyl substituted aromatic hydrocarbons. Hydrocarbon examples include those obtained by alkylating benzene, toluene, xylene, naphthalene, biphenyl and their halogenated derivatives (chlorobenzene, chlorotoluene, and chloronaphthalene, for example). The alkylating agents typically have about 3 to 70 carbon atoms. The alkaryl sulfonates typically contain about 9 to about 80 carbon or more carbon atoms, more typically from about 16 to 60 carbon atoms.

[0103] 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.

[0104] Alkaline earth phenates are another useful class of detergent. These detergents can be made by reacting alkaline earth metal hydroxide or oxide (CaO, $Ca(OH)_2$, BaO, $Ba(OH)_2$, MgO, $Mg(OH)_2$, for example) with an alkyl phenol or sulfurized alkylphenol. Useful alkyl groups include straight chain or branched C_1-C_{30} alkyl groups, preferably, C_4-C_{20}. Examples of suitable phenols include isobutylphenol, 2-ethylhexylphenol, nonylphenol, dodecyl phenol, and the like. It should be noted that starting alkylphenols may contain more than one

alkyl substituent that are each independently straight chain or branched. When a non-sulfurized alkylphenol is used, the sulfurized product may be obtained by methods well known in the art. These methods include heating a mixture of alkylphenol and sulfurizing agent (including elemental sulfur, sulfur halides such as sulfur dichloride, and the like) and then reacting the sulfurized phenol with an alkaline earth metal base.

[0105] Metal salts of carboxylic acids are also useful as detergents. These carboxylic acid detergents may be prepared by reacting a basic metal compound with at least one carboxylic acid and removing free water from the reaction product. These compounds may be overbased to produce the desired TBN level. Detergents made from salicylic acid are one preferred class of detergents derived from carboxylic acids. Useful salicylates include long chain alkyl salicylates. One useful family of compositions is of the formula



where R is a hydrogen atom or an alkyl group having 1 to about 30 carbon atoms, n is an integer from 1 to 4, and M is an alkaline earth metal. Preferred R groups are alkyl chains of at least C_{11}, preferably C_{13} 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.

[0106] Hydrocarbyl-substituted salicylic acids may be prepared from phenols by the Kolbe reaction. See USP 3,595,791 for additional information on synthesis of these compounds. The metal salts of the hydrocarbyl-substituted salicylic acids may be prepared by double decomposition of a metal salt in a polar solvent such as water or alcohol.

[0107] Alkaline earth metal phosphates are also used as detergents.

[0108] 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.

[0109] Preferred detergents include calcium phenates, calcium sulfonates, calcium salicylates, magnesium phenates, magnesium sulfonates, magnesium salicylates and other related components (including borated detergents). Typically, the total detergent concentration is about 0.01 to about 6.0 wt%, preferably, about 0.1 to 0.4 wt%.

Dispersant

[0110] 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.

[0111] 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.

[0112] 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; 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.

[0113] 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.

[0114] Succinimides are formed by the condensation reaction between alkenyl succinic anhydrides and amines. Molar ratios can vary depending on the poly-amine. 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.

[0115] 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.

[0116] 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.

[0117] 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.

[0118] 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.

[0119] 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.

[0120] 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.

[0121] Examples of $HN(R)_2$ group-containing reactants are alkylene polyamines, principally polyethylene polyamines. Other representative organic compounds containing at least one $HN(R)_2$ group suitable for use in the preparation of Mannich condensation products are well known and include the mono- and di-amino alkanes and their substituted analogs, e.g., ethylamine and diethanol amine; aromatic diamines, e.g., phenylene diamine, diamino naphthalenes; heterocyclic amines, e.g., morpholine, pyrrole, pyrrolidine, imidazole, imidazolidine, and piperidine; melamine and their substituted analogs.

[0122] 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 $H_2N\text{-}(Z\text{-}NH\text{-})_nH$, mentioned before, Z is a divalent ethylene and n is 1 to 10 of the foregoing formula. Corresponding propylene polyamines such as propylene diamine and di-, tri-, tetra-, pentapropylene tri-, tetra-, penta- and hexaamines are also suitable reactants. The alkylene polyamines are usually obtained by the reaction of ammonia and dihalo alkanes, such as dichloro alkanes. Thus the alkylene polyamines obtained from the reaction of 2 to 11 moles of ammonia with 1 to 10 moles of dichloroalkanes

having 2 to 6 carbon atoms and the chlorines on different carbons are suitable alkylene polyamine reactants.

[0123] 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.

[0124] Hydrocarbyl substituted amine ashless dispersant additives are well known to one skilled in the art; see, for example, USP Nos. 3,275,554; 3,438,757; 3,565,804; 3,755,433; 3,822,209 and 5,084,197.

[0125] 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%.

Supplemental Pour Point Depressants

[0126] 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 poly-methacrylates, 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 0.00 to 5 wt%, preferably about 0.01 to 1.5 wt%.

Corrosion Inhibitors

[0127] 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; 2,719,126; and 3,087,932. Such additives may be used in an amount of about 0.01 to 5 wt%, preferably about 0.01 to 1.5 wt%.

Seal Compatibility Additives

[0128] 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

[0129] 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

[0130] 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.

[0131] One type of antirust additive is a polar compound that wets the metal surface preferentially, protecting it with a film of oil. Another type of antirust additive absorbs water by incorporating it in a water-in-oil emulsion so that only the oil touches the metal surface. Yet another type of antirust additive chemically adheres to the metal to produce a non-reactive surface. Examples of suitable additives include zinc dithiophosphates, metal phenolates, basic metal sulfonates, fatty acids and amines. Such additives may be used in an amount of about 0.01 to 5 wt%, preferably about 0.01 to 1.5 wt%.

Friction Modifiers

[0132] 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 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.

[0133] 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.

[0134] 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.

Cobasestocks

[0135] Cobasestocks include natural oil, synthetic oils, and other unconventional oils and mixtures thereof and they can be used unrefined, refined, or rerefined (the latter is also known as reclaimed or reprocessed oil). Unrefined oils are those obtained directly from a natural, synthetic or unconventional source and used without further purification. These include for example shale oil obtained directly from retorting operations, oils derived from coal, petroleum oil obtained directly from primary distillation, and ester oil obtained directly from an esterification process. Refined oils are similar to the oils discussed for unrefined oils except refined oils are subjected to one or more purification or transformation steps to improve at least one lubricating oil property. One skilled in the art is familiar with many purification or transformation processes. These processes include, for example, solvent extraction, secondary distillation, acid extraction, base extraction, filtration, percolation, hydrogenation, hydrorefining, and hydrofinishing. Rerefined oils are obtained by processes analogous to refined oils, but use an oil that has been previously used.

[0136] Groups I, II, III, IV and V are broad categories of base oil stocks developed and defined by the American Petroleum Institute (API Publication 1509; www.API.org) to create guidelines for lubricant base oils. Group I base stocks generally have a viscosity index of between about 80 to 120 and contain greater than about 0.03% sulfur and less than about 90% saturates. Group II

base stocks generally have a viscosity index of between about 80 to 120, and contain less than or equal to about 0.03% sulfur and greater than or equal to about 90% saturates. Group III stock generally has a viscosity index greater than about 120 and contains less than or equal to about 0.03% sulfur and greater than about 90% saturates. Group IV includes polyalphaolefins (PAO). Group V base stocks include base stocks not included in Groups I-IV. Table A summarizes properties of each of these five groups.

TABLE A: Base Stock Properties

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

[0137] Natural oils include animal oils, vegetable oils (castor oil and lard oil, for example), and mineral oils. Animal and vegetable oils possessing favorable thermal oxidative stability can be used. Of the natural oils, mineral oils are preferred. Mineral oils vary widely as to their crude source, for example, as to whether they are paraffinic, naphthenic, or mixed paraffinic-naphthenic. Oils derived from coal or shale are also useful in the present invention. Natural oils vary also as to the method used for their production and purification, for example, their distillation range and whether they are straight run or cracked, hydrorefined, or solvent extracted.

[0138] Synthetic oils include hydrocarbon oils as well as non hydrocarbon oils. Synthetic oils can be derived from processes such as chemical combination (for example, polymerization, oligomerization, condensation, alkylation, acylation, etc.), where materials consisting of smaller, simpler molecular species are built up (i.e., synthesized) into materials consisting of larger, more complex molecular species. Synthetic oils include hydrocarbon oils such as polymerized and

interpolymerized olefins (polybutylenes, polypropylenes, polyisobutylene (see: "Polybutenes" J. D. Fotheringham, Synthetic Lubricants and High-Performance Functional Fluids" 2nd Edition, ed. L. R. Rudnick and R. L. Shubkin, published by Marcel Dekker Inc., N.Y. 1999, p. 357-391), propylene isobutylene copolymers, ethylene-olefin copolymers, ethylene-butene copolymer (see: WO 2003/076555A1) and ethylene-alphaolefin copolymers, for example). Polyalphaolefin (PAO) oil base stock is a commonly used synthetic hydrocarbon oil. By way of example, PAO's derived from C_8, C_{10}, C_{12}, C_{14} olefins or mixtures thereof may be utilized. See U.S. Patents 4,956,122; 4,827,064; and 4,827,073.

[0139] The number average molecular weights of the PAO's, which are known materials and generally available on a major commercial scale from suppliers such as ExxonMobil Chemical Company, Chevron, Ineos, and others, typically vary from about 250 to about 3000, or higher, and PAO's may be made in viscosities up to about 100 mm^2/s (100°C), or higher. In addition, higher viscosity PAO's are commercially available, and may be made in viscosities up to about 3000 mm^2/s (100°C), or higher. The PAO's are typically comprised of relatively low molecular weight hydrogenated polymers or oligomers of alpha-olefins which include, but are not limited to, about C_2 to about C_{32} alphaolefins with about C_8 to about C_{16} alphaolefins, such as 1-octene, 1-decene, 1-dodecene and the like, being preferred. The preferred polyalphaolefins are poly-1-octene, poly-1-decene and poly-1-dodecene and mixtures thereof and mixed olefin-derived polyolefins. However, the dimers of higher olefins in the range of about C_{14} to C_{18} may be used to provide low viscosity base stocks of acceptably low volatility. 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, having a viscosity range of about 1.5 to 12 mm^2/s.

[0140] PAO fluids may be conveniently made by the polymerization of an alpha-olefin 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; 4,910,355; 4,956,122; and 5,068,487. The dimers of the C_{14} to C_{18} olefins are described in USP 4,218,330.

[0141] Other useful synthetic lubricating base stock oils such as silicon-based oil or esters of phosphorus containing acids may also be utilized. For examples of other synthetic lubricating base stocks are the seminal work "Synthetic Lubricants", Gunderson and Hart, Reinhold Publ. Corp., NY 1962.

[0142] Alkylene oxide polymers and interpolymers and their derivatives containing modified terminal hydroxyl groups obtained by, for example, esterification or etherification are useful synthetic lubricating oils. By way of example, these oils may be obtained by polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (methyl-polypropylene glycol ether having an average molecular weight of about 1000, diphenyl ether of polyethylene glycol having a molecular weight of about 500-1000, and the diethyl ether of polypropylene glycol having a molecular weight of about 1000 to 1500, for example) or mono- and poly-carboxylic esters thereof (the acidic acid esters, mixed C_{3-8} fatty acid esters, or the C_{13}Oxo acid diester of tetraethylene glycol, for example).

[0143] Esters comprise a useful base stock. Additive solvency and seal compatibility characteristics may be secured by the use of esters such as the esters of dibasic acids with monoalkanols and the polyol esters of mono-

carboxylic acids. Esters of the former type include, for example, the esters of dicarboxylic acids such as phthalic acid, succinic acid, alkyl succinic acid, alkenyl succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acid, alkenyl malonic acid, etc., with a variety of alcohols such as butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, etc. Specific examples of these types of esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, etc.

[0144] Particularly useful synthetic esters are those full or partial esters which are obtained by reacting one or more polyhydric alcohols (preferably the hindered polyols such as the neopentyl polyols e.g. neopentyl glycol, trimethylol ethane, 2-methyl-2-propyl-1,3-propanediol, trimethylol propane, pentaerythritol and dipentaerythritol) with alkanoic acids containing at least about 4 carbon atoms (preferably C_5 to C_{30} acids such as saturated straight chain fatty acids including caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, and behenic acid, or the corresponding branched chain fatty acids or unsaturated fatty acids such as oleic acid).

[0145] Suitable synthetic ester components include the esters of trimethylol propane, trimethylol butane, trimethylol ethane, pentaerythritol and/or dipentaerythritol with one or more monocarboxylic acids containing from about 5 to about 10 carbon atoms.

[0146] Silicon-based oils are another class of useful synthetic lubricating oils. These oils include polyalkyl-, polyaryl-, polyalkoxy-, and polyaryloxy-siloxane oils and silicate oils. Examples of suitable silicon-based oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methylhexyl) silicate, tetra-(p-tert-butylphenyl) silicate, hexyl-(4-methyl-2-pentoxy) disiloxane, poly(methyl) siloxanes, and poly-(methyl-2-methylphenyl) siloxanes.

[0147] Another class of synthetic lubricating oil is esters of phosphorous-containing acids. These include, for example, tricresyl phosphate, trioctyl phosphate, diethyl ester of decanephosphonic acid.

[0148] Another class of synthetic oils includes polymeric tetrahydrofurans, their derivatives, and the like.

[0149] Other useful fluids of lubricating viscosity include non-conventional or unconventional base stocks that have been processed, preferably catalytically, or synthesized to provide high performance lubrication characteristics.

Typical Additive Amounts

[0150] 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.

[0151] 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 text, unless otherwise indicated are directed to the amount of active ingredient (that is the non-solvent portion of the ingredient). The wt% indicated below are based on the total weight of the lubricating oil composition.

TABLE 1

Typical Amounts of Various Lubricant Oil Components

Compound	Approximate wt% (useful)	Approximate wt% (preferred)
Detergent	0.01-6	0.01-4
Dispersant	0.1-20	0.1-8
Friction Reducer	0.01-5	0.01-1.5
Antioxidant	0.0-5	0.0-1.5
Corrosion Inhibitor	0.01-5	0.01-1.5
Anti-wear Additive	0.01-6	0.01-4
Supplemental Pour Point Depressant	0.0-5	0.01-1.5
Anti-foam Agent	0.001-3	0.001-0.15
Co-basestock	0-90	0-50
Base Oil	Balance	Balance

EXAMPLES

[0152] In the Examples, the fluid properties were measured according to standard ASTM methods:

(a) Kinematic viscosity at 40°C and 100°C in cSt (mm^2/s) by ASTM 445 method. In this text, all fluid viscosities are the to their 100°C viscosities unless specified differently.

(b) Pour point by ASTM D97 method or equivalent automated method.

(c) Aniline point by ASTM D611 method.

(d) Rotary Bomb Oxidation of Turbine Oil at 150°C by ASTM D2272 method.

(e) Oxidation test was conducted by purging oil sample with air at 325°C for 40 hours in the presence of copper, iron and lead metal. The oxidation stability was measured by the percent of viscosity increase, change of total acid number, sludge rating and amount of lead loss.

(f) Thermal stability test was conducted by heating a small amount of oil sample sealed inside a metal vessel to 300°C or proper test temperature for 24 hours. The thermal stability was measured by the percent of viscosity decrease and weight loss during to thermal cracking into volatile component.

[0153] The alkylated naphthalenes employed in the following examples are described below. AN5 was prepared by reacting naphthalene with a 1-hexadecene olefin over a USY catalyst according to method described in USP 5034563. AN12 was prepared by reacting naphthalene with 1-tetradecene using a catalytic amount of trifluoromethane sulfonic acid. The Alkylmethylbenzene was synthesized according to procedures described in USP 6,071,864, starting with the oligomerization of a mixture of C_8, C_{10} and C_{12} linear alpha olefins over a promoted BF3 catalyst to produce a product which is further reacted with toluene (methylbenzene) over the same catalyst at the same reaction temperature as the olefin oligomerization. The product was isolated to yield a lube base stock fluid with viscometrics and pour point listed in following table, along with the properties of a C_{12} alkylbenzene as produced according to Example 7.

TABLE 1

Fluid	KV @ 100°C mm^2/s	KV @ 40°C mm^2/s	VI	Pour Point, °C
AN5	4.76	28.16	70	-39
AN12	13.20	118.59	97	-39
Alkylmethyl benzene	5.73	37.9	73	< -60
C_{12} Alkylbenzene	1.5	4.2	--	<-60

EXAMPLE 1

[0154] Various base stocks were used for blending with the alkyl naphthalene fluids in the examples and these base stocks are presented below in combination with various amounts of the alkylated naphthalene fluid AN5 showing the effect on pour point (reported in °C).

TABLE 2

Wt% AN5	0	5	20	60	100
Group I	- 21	- 27	- 29	- 32	- 39
Group III	- 25	- 26	- 28	- 32	- 39
GTL-6	- 21	- 27	- 36	- 42	- 39
PAO-6	- 58	- 58	- 50	- 47	- 39

[0155] As is shown, when the alkylated naphthalene (AN5) was blended with API Group I or Group III base stock, there is no synergistic improvement of the pour point. While the pour point of such blends were decreased, the amount of the decrease is never below the pour point of the AN base stock. When combined with PAO, the AN actually degraded pour point performance. However, when AN was blended with GTL-6 (having a pour point of -21°C) the pour point improvements associated with the blends were non-linear (see Figure 1 and Table 3). Data in Table 3 further demonstrated that the oxidative stabilities of the blended oils were also synergistically improved over pure GTL-6. When 5% AN5 was added, the RBOT was improved from 68 minutes to 102 minutes. When 20% AN5 was added, the RBOT was improved to 132 minutes. This further demonstrated the uniqueness of the blends.

Table 3. AN5 + GTL-6

Wt% of AN5	0	5	20	60	100
Wt% of GTL-6	100	95	80	40	0
Kv 100°C, cS	6.02	5.99	5.77	5.17	4.76
Kv 40°C, cS	29.76	29.34	28.86	27.77	28.16
VI	141	143	134	105	64
Pour Point, °C	-21	-27	-36	-42	-39
RBOT, minutes (D2272)	68	102	132	129	192

EXAMPLE 2

[0156] Various amounts of AN5 (described above) were combined with GTL-14 (nominal kinematic viscosity at 100°C of 14 mm^2/s). The results are presented in Table 4 below:

TABLE 4

Wt% of AN5	0	5	20	60	100
Wt% of GTL 14	100	95	80	40	0
Grams of AN5	0	2.5	7.125	30	0
Grams of GLT 14	0	47.5	28.5	20	0
Grams total	0	50	35.625	50	0
Kv 100°C, cS	14.3	13.64	11.72	7.73	4.76
Kv 40°C, cS	94.98	90.29	76.4	47.32	28.16
VI	155	143	137	119	64
Pour point, °C	- 24	- 27	- 36	- 42	- 39

[0157] As is seen the pour point of the GTL was still synergistically improved by the addition of the alkylated naphthelene fluid.

EXAMPLE 3

[0158] Various amounts of AN12 (described above) were combined with GTL-6. The results are presented in Table 5.

TABLE 5

Wt% of AN12	0	20	60	100
Wt% of GTL-6	100	80	40	0
Kv 100°C, cS	6.02	6.78	8.90	13.20
Kv 40°C, cS	29.76	36.72	58.82	118.59
VI	141	133	117	97
Pour point, °C	- 21	- 30	- 39	- 39
RBOT, Minutes (D2272)	68	111	127	128

[0159] Again, it is seen that the addition of alkylated naphthalene, in this instance a high viscosity AN, to a GTL (GTL-6) resulted in a blend which exhibited a non-linear reduction in pour point. Furthermore, the oxidative stabilities of the blends were improved synergistically. The RBOT increased from 68 minutes to 111 minutes, when 20 wt% of AN12 was added.

EXAMPLE 4

[0160] In this example an AN5 was fully hydrogenated in the presence of 800 psi H2 pressure with a 2 wt% nickel on Kieselguhr catalyst for 16 hours to yield a hydrogenated AN5 fluid (an alkyl cycloparaffin fluid). This fluid was blended in varying amounts with GTL-6 and the results are reported in Table 6.

TABLE 6

Wt% (fully hydrogenated AN) (HAN)	0	5	20	60	100
Wt% of GTL	100	95	80	40	0
Kv 100°C, cS	6.02	6.03	5.91	5.56	5.25
Kv 40°C, cS	29.76	29.86	29.65	29.74	30.57
VI	141	141	136	115	89
Pour point, °C	- 21	- 24	- 33	- 39	- 39

[0161] As is seen, the fully hydrogenated alkycycloparaffin fluid derived from an alkyl naphthalene has the same influence on the pour point of the blend, the pour point of the blend being reduced non-linearly.

EXAMPLE 5

[0162] An alkylmethylbenzene fluid (ArPAO) was prepared and combined in various amounts with GTL-6. The alkylmethylbenzene was prepared by first oligomerizing a mixture of C_8, C_{10} and C_{12} linear alpha olefins to give oligomers over promoted BF3 catalyst. The high boiling fraction, > 750°F (398.8°C), was isolated as high quality PAO base stock after hydrogenation at 200°C, 600 psi H2 pressure over a standard hydrogenation catalyst, a nickel on Kieselguhr catalyst. The lighter oligomers with boiling points below 750°F were separated by distillation. This light fraction usually contains olefins with less than 24 carbons. These light olefin oligomers were then further reacted with toluene over a similar promoted BF_3 catalyst as used in the oligomerization step. The resulting alkylmethylbenzene fluid had excellent VI, pour point, thermal and oxidative stability. This alkylmethylbenzene fluid was combined in various amounts with GTL-6. The results are presented in Table 7 and Figure 1.

TABLE 7

Wt% of alkylmethylbenzene	0	20	60	100
Wt% of GTL	100	80	40	0
Kv 100°C, cS	6.02	5.87	5.53	5.22
Kv 40°C, cS	29.76	29.77	30.58	32.33
VI	141	132	107	73
Pour point, °C	- 21	- 27	- 36	<- 60

[0163] As can be seen, the pour point of the GTL-6 was reduced by the addition of the alkylmethylbenzene fluid.

EXAMPLE 6

[0164] The hydrogenated version of the alkylmethylbenzene fluid of Example 5 was prepared by hydrogenation of the fluid using 2 wt% nickel on Kieselguhr catalyst (50 wt% nickel metal content) at 200°C, 800 psi H_2 pressure for 8 hours. The hydrogenated alkylmethylbenzene fluid was combined in various amounts with GTL-6 and the results are presented in Table 8.

TABLE 8

Wt% of hydrogenated alkylmethylbenzene fluid	0	20	60	100
Wt% of GTL	100	80	40	0
Kv 100°C, cS	6.02	5.99	5.82	5.73
Kv 40°C, cS	29.76	30.6	33.42	37.9
VI	141	133	105	73
Pour point, °C	- 21	- 21	- 36	<- 60

[0165] Again, a reduction in the pour point of the GTL is seen.

[0166] Example 7. An alkylbenzene fluid was prepared by alkylation of benzene with 1-dodecene over a zeolite MCM22, according to the general procedures as described in US 4962256. The property of this fluid was

summarized in Table 1. This fluid was blended with GTL 6 and the blend properties were summarized in following Table 9. Again, these data demonstrated that low pour point alkylaromatic fluids recited in this invention improve the pour point of the blend stock when combined with GTL derived base stocks.

TABLE 9

Wt% of Alkylbenzene in GTL6	0	5	20	60	100
Blend Properties					
Kv 100°C, cS	6.02	5.6	4.55	2.61	1.5
Kv 40°C, cS	29.76	25.7	19.45	8.8/2	4.22
VI	141	152	143	145	
Pour Point, °C	-21	-35	-42	-65	-65

COMPARATIVE EXAMPLE 1

[0167] A C_{20}-C_{24} alkyl benzene fluid was prepared according to the teaching of USP 6,627,779. That C_{20}-C_{24} alkyl benzene was blended with GTL-6 and the pour points of the individual fluids and of various blends were reported in Table 10 and Figure 1.

TABLE 10

C_{20}-C_{24} alkyl benzene	0	5	20	60	100
Wt% of GTL-6	100	95	80	40	0
Kv 100°C, cS	6.02	6.03	5.85	5.44	5
Kv 40°C, cS	29.76	26.69	28.31	25.61	23.24
VI	141	142	143	142	135
Pour point, °C	- 21	- 21	- 6	6	9

[0168] As is seen the C_{20}-C_{24} alkyl benzene of USP 6,627,779 exhibited a high pour point and did not in any way reduce the pour point of the GTL fluid, the

blends all exhibiting either no change or significantly increased pour points as compared to the data presented in Tables 6 and 7.

COMPARATIVE EXAMPLE 2

[0169] An ester of nominal kinematic viscosity at 100°C of 5 mm^2/s (Ester 5) was blended with GTL-6 in various amounts and the results are presented in Table 11 and Figure 1.

TABLE 11

Wt% of ester	0	5	20	60	100
Wt% of GTL-6	100	95	80	40	0
Properties of Blends					
Kv 100°C, cS	6.02	6.04	5.79	5.41	5.27
Kv 40°C, cS	29.76	29.02	27.92	26.25	26.29
VI	141	148	143	135	124
Pour point, °C	- 21	- 24	- 24	- 33	<-61

[0170] As can be seen Ester 5, despite having a pour point of < -61 had substantially no effect on the pour point of the GTL-6 at treat levels of 5 and 20 wt% and only lowered the pour point of GTL from -21 down to -33°C at a treat level of 60 wt% of Ester 5, clearly demonstrative of a lack of any significant pour point reducing capacity and no synergistic impact as is the case when alkylated naphthalene is employed. Merely because a second, added fluid has a low pour point, therefore, does not automatically mean that the addition of such low pour point fluid to a higher pour point fluid will result in a mixture having a pour point significantly lower than that of the high pour point fluid. Thus, the present results secured using the alkylated naphthalene and alkylbenzene synthetic fluids as disclosed herein are truly surprising and unexpected.

CLAIMS:

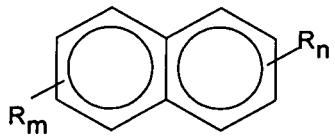
1. A method for reducing the pour point of Gas-to-Liquids (GTL) lube base stocks/base oils, hydrodewaxed or hydroisomerized/catalytic (and/or solvent) dewaxed waxy feed lube base stocks/base oils or mixture thereof by adding to such base stock/base oil from about 1 to 95 wt% of a synthetic alkylated naphthalene fluid having a kinematic viscosity at 100°C in the range of from about 1.5 mm^2/s to about 600 mm^2/s, a pour point of $\leq$ 0°C, a viscosity index in the range of from 0 to 200.

2. The method of claim 1 wherein the base stock/base oil which has its pour point reduced is a GTL base stock/base oil.

3. The method of claim 1 wherein the base stock/base oil which has its pour point reduced is a hydrodewaxed Fischer-Tropsch wax lube base stock/base oil.

4. The method of claim 1 wherein the base stock/base oil which has its pour point reduced is a hydroisomerized/catalytic (and/or solvent) dewaxed Fischer-Tropsch wax lube base stock/base oil.

5. The method of claim 1, 2, 3 or 4 wherein the alkylated naphthalene has the general formula



wherein n + m is an integer ranging from 1 to 8, R is a C_1 to C_{30} linear alkyl group, a C_3 to C_{300} branched alkyl group or mixture thereof, and wherein the total number of carbons in R_n and R_m is at least 4.

6. The method of claim 5 wherein n + m is an integer ranging from 1 to 6.

7. The method of claim 5 wherein R is a C_1 to C_{20} linear alkyl group, C_3 to C_{100} branched alkyl group or mixture thereof.

8. The method of claim 7 wherein R is a branched alkyl group containing at least 4 carbon and n + m is 1 or 2.

9. The method of claim 1, 2, 3 or 4 wherein the alkylated naphthalene is hydrogenated.

10. The method of claim 7 wherein the alkylated naphthalene is selected from the group consisting of mono-, di-, tri-, tetra-, or penta-C_3 alkyl naphthalene, C_4 alkyl naphthalene, C_5 alkyl naphthalene, C_6 alkyl naphthalene, C_8 alkyl naphthalene, C_{10} alkyl naphthalene, C_{12} alkyl naphthalene, C_{14} alkyl naphthalene, C_{16} alkyl naphthalene, C_{18}, alkyl naphthalene, mono-, di-, tri-, tetra-, or penta-C_3 alkyl monomethyl, dimethyl, ethyl, diethyl or methyl ethyl naphthalene, C_4 alkyl monomethyl, dimethyl, ethyl, diethyl or methyl ethyl naphthalene, C_5 alkyl monomethyl, dimethyl, ethyl, diethyl or methyl ethyl naphthalene, C_6 alkyl monomethyl, dimethyl, ethyl, diethyl or methyl ethyl naphthalene, C_8 alkyl monomethyl, dimethyl, ethyl, diethyl or methyl ethyl naphthalene, C_{10} alkyl naphthalene, C_{12} alkyl monomethyl, dimethyl, ethyl, diethyl or methyl ethyl naphthalene, C_{14} alkyl monomethyl, dimethyl, ethyl, diethyl or methyl ethyl naphthalene, C_{16} alkyl monomethyl, dimethyl, ethyl, diethyl or methyl ethyl naphthalene, C_{18}, alkyl monomethyl, dimethyl, ethyl, diethyl or methyl ethyl naphthalene, C_{24}-C_{56} branched alkyl naphthalene, or C_{24}-C_{56} branch alkyl mono, di-, tri- tetra- or penta- C_1-C_4 naphthalene, and mixtures thereof.

11. The method of claim 10 wherein the alkylated naphthalene is hydrogenated.

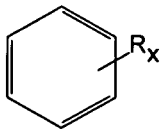
12. A method for reducing the pour point of Gas-to-Liquids (GTL) lube base stocks/base oils, hydrodewaxed or hydroisomerized/catalytic (and/or solvent) dewax waxy feed lube base stock/base oil or mixture thereof by adding to such base stock/base oil from about 1 to 95 wt% of an alkylated benzene synthetic fluid having a kinematic viscosity at 100°C in the range of from about 1.5 mm^2/s to about 600 mm^2/s, a pour point of 0°C or less and a viscosity index of from 0 to 200.

13. The method of claim 12 wherein the base stock/base oil which has to pour point reduced is a GTL base stock/base oil.

14. The method of claim 12 wherein the base stock/base oil which has its pour point reduced is a hydrodewaxed Fischer-Tropsch wax lube base stock/base oil.

15. The method of claim 12 wherein the base stock/base oil which has its pour point reduced is a hydroisomerized/catalytic (and/or solvent) dewaxed Fischer-Tropsch wax lube base stock/base oil.

16. The method of claim 12, 13, 14 or 15 wherein the alkylated benzene has the general formula



wherein x is an integer ranging from 1 to 6, R is a C_{10} to C_{30} linear alkyl group, C_{10} to C_{300} branched alkyl group or mixture thereof wherein when x is 2 or greater than 2 one or more of the R group can be a C_1-C_5 alkyl group provided however that there is one or more additional alkyl groups which is a C_{10} to C_{30} linear alkyl group or a C_{10} to C_{200} branched alkyl group or mixture thereof.

17. The method of claim 16 wherein x is an integer ranging from 1 to 5.

18. The method of claim 16 wherein the alkylated benzene has a pour point of -35°C or less.

19. The method of claim 16 wherein the alkylated benzene is an alkyl methyl benzene prepared by oligomerizing a mixture of C_8, C_{10} and C_{12} linear alpha olefins over a catalyst to produce an oligomerized product which is then arylated with toluene over a catalyst.

20. A base oil for lubricating oil compositions, said base oil comprising one or more lubricating oil stocks selected from Gas-to-Liquids (GTL) lube base stocks/base oils, hydrodewaxed or hydroisomerized/catalytic (and/or solvent) dewaxed waxy feed lube base stocks/base oils and from about 1 to 95 wt% of an alkylated benzene synthetic fluid having a kinematic viscosity at 100°C in the range of from about 1.5 mm^2/s to about 600 mm^2/s, a pour point of 0°C or less and a viscosity index of from 0 to 200.

21. The base oil of claim 20 wherein the lubricating oil stock is GTL base stock/base oil.

22. The base oil of claim 20 wherein the lubricating oil stock is hydrodewaxed Fischer-Tropsch wax lube base stock/base oil.

23. The base oil of claim 20 wherein the alkylated benzene has a pour point of -35°C or less.

24. The base oil of claim 20 or 23 wherein the alkylated benzene is an alkyl methyl benzene prepared by oligomerizing a mixture of C_8, C_{10} and C_{12} linear alpha olefins over a catalyst to produce an oligomerized product which is then arylated with toluene over a catalyst.