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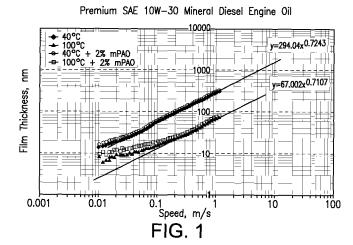
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(54) Title: LUBRICATING COMPOSITION PROVIDING HIGH WEAR RESISTANCE



(57) Abstract: Disclosed are lubricating compositions comprised of a mineral oil base stock including one or more components selected from the group consisting a Group I base oil component, a Group II base oil component, and a Group III base oil component; and a minimal amount of a particular polyalphaolefm component. The lubricating compositions provide improved film thickness and wear properties relative to conventional mineral oil lubricants. In particular, the lubricating compositions provide improved film thickness and wear properties relative to conventional mineral oil lubricants, without the need of having to include additional polar additives to enhance wear and film thickness characteristics.



LUBRICATING COMPOSITION PROVIDING HIGH WEAR RESISTANCE

FIELD

This disclosure is directed to a lubricating composition comprised of a mineral oil base stock and a particular polyalphaolefin component. In particular, the lubricating composition includes one or more components selected from the group consisting of a Group I base oil component, a Group II base oil component, and a Group III base oil component; and a polyalphaolefin component having characteristics that enhance film thickness and wear protection of the mineral oil.

BACKGROUND

One purpose of a lubricant is to provide a film of lubrication between two metal surfaces, reducing friction, wear and heat and ensuring a long life span for the equipment being lubricated. In other words, a particular function of a lubricant is to lubricate moving metal parts to reduce friction and wear.

[0003] Metal to metal contact of moving parts creates tremendous heat and frictional forces and causes wear in the form of minute particles of metal. A relatively high quality motor oil reduces friction and provides wear protection by bonding to metal surfaces to form a protective layer, particularly for optimum performance for a cold-start.

[0004] Mineral oil based lubricating compositions, i.e., lubricating oil compositions containing mineral oil base stocks at a concentration of 60 wt % or more of the total weight of the lubricant, have been extensively used for lubricating an wide variety of moving metal parts. However, many mineral oil lubricating compositions have been or are being replaced by synthetic based lubricating compositions to further reduce friction and wear problems. These

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synthetic compositions generally contain at least 60 wt % polyalphaolefins (PAOs).

ExxonMobil Chemical discloses in "High-Performance Synthetic Basestocks Solve Lubrication Challenges," Tribology and Lubrication Technology, Nov. 2008, Vol. 64, pp. 36-38, a range of PAOs including SpectraSynTM, SpectraSyn PlusTM, SpectraSyn UltraTM. SpectraSyn PlusTM PAO blended with Group III base stocks is shown to be effective in enhancing volatility and low-temperature characteristics relative to those base stocks without the SpectraSyn PlusTM PAO. SpectraSyn Ultra 150TM blended with a low viscosity PAO, ISO 22 synthetic lubricant, is shown to be effective in enhancing film thickness at low speeds.

[0006] Mobil Oil Corp. discloses in "Mobil Releases SuperSyn PAOs," Lubrication Engineering, 1999, Vol. 55(8), p. 45, a range of SuperSyn PAOs having viscosities of 150, 300, 1000 and 3000 cSt at 100°C. The PAOs are used at low treat rates to balance viscometrics and/or improve various qualities of the finished product.

[0007] Although, the PAO synthetic compositions have been found to provide enhanced performance characteristics, these compositions are nevertheless costly, and may not necessarily be the performance choice for certain engines and/or gears. It would, therefore, be of particular benefit to return to or stay with mineral oil based lubricants, if performance levels of mineral oil based lubricants can be boosted to higher levels, without significantly increasing the cost of the lubricant. In particular, it would be beneficial to provide mineral oil based lubricating compositions that provide improved film thickness and wear properties relative to conventional mineral oil lubricants that often include a substantial concentration of detergents and/or dispersants. In many cases, detergent and/or dispersant concentrations can negate effectiveness of additives that have been shown to be effective in enhancing film thickness

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and anti-wear properties. Therefore, it would be especially beneficial to provide mineral oil based lubricating compositions that provide improved anti-wear properties and increased film thickness relative to conventional mineral oil lubricants that could work at a higher performance level using standard additives, such as detergents and/or dispersants. It would also be beneficial to provide mineral oil bases lubricating compositions that provide improved performance levels without having to rely on additional polar additives to enhance wear and film thickness characteristics.

SUMMARY

[0008] This disclosure provides lubricating compositions comprised of a mineral oil base stock including one or more components selected from the group consisting a Group I base oil component, a Group II base oil component, and a Group III base oil component; and a minimal amount of a particular polyalphaolefin component. The lubricating compositions provide improved film thickness and wear properties relative to conventional mineral oil lubricants.

[0009] In a particular embodiment, the lubricating compositions provide enhanced improved film thickness and wear properties relative to conventional mineral oil lubricants, by including effective amounts of detergents and/or dispersants common to engine oils (e.g., gasoline and/or diesel engines). The use of such additives can result in higher performance levels with only minimal addition of the particular polyalphaolefin, especially a particular high viscosity polyalphaolefin, as described below.

[0010] In another embodiment, the lubricating compositions of this disclosure provide enhanced improved film thickness and wear properties relative to conventional mineral oil lubricants, without the need of having to include additional polar additives to enhance wear and film thickness

characteristics as described below. For example, addition of polar type base stock materials such as naphthalenes is not necessary to obtain increased mixing properties and enhanced performance.

[0011] According to one aspect of the disclosure, there is provided a lubricating composition, comprising a mixture of at least 60 wt. % of a mineral oil base stock including one or more components selected from the group consisting a Group I base oil component, a Group II base oil component, and a Group III base oil component, based on the total weight of the lubricating composition; and from 2 wt. % to 5 wt. % of a polyalphaolefin component, based on the total weight of the lubricating composition, wherein the polyalphaolefin component contains not more than 5.0 wt. % of a polymer having a molecular weight of greater than 45,000 Daltons.

DETAILED DESCRIPTION

[0012] All numerical values within the detailed description and the claims herein are modified by "about" or "approximately" the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

I. Lubricating Composition Provides Improved Film Thickness and Wear Properties

[0013] This disclosure provides a mineral oil lubricating composition having improved film thickness and wear properties relative to conventional mineral oil lubricants, without the need of having to include additional polar additives such as polar anti-wear additives. The provided mineral oil lubricating composition is particularly useful for industrial applications such as industrial gear applications, pumps and hydraulic systems. The composition is further useful for automotive gear applications such as light duty (e.g., cars) and heavy

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duty (e.g., Class 5 and Class 8 trucks) axles. The axles can be rear axle or front-wheel transaxle configurations (e.g., light duty) or rear axle and tandem-axle configurations (e.g., heavy duty). In addition, the composition can be used in automotive engine oil applications such as gasoline and diesel (e.g., light duty/passenger car and heavy duty/commercial truck) engine applications, having particular benefit on piston ring wear, cam lobe wear and valve/lifter wear.

[0014] The lubricating composition of this disclosure is comprised of a mixture of a mineral oil base stock and a particular polyalphaolefin component. In particular, the lubricating oil composition is comprised of at least 60 wt. % of a mineral oil base stock including one or more components selected from the group consisting a Group I base oil component, a Group II base oil component, and a Group III base oil component, based on the total weight of the lubricating composition. The lubricating composition further comprises from 2 wt. % to 5 wt. % of a polyalphaolefin component, based on the total weight of the lubricating composition, wherein the polyalphaolefin component contains not more than 5.0 wt. % of a polymer having a molecular weight of greater than 45,000 Daltons.

II. Mineral Oil Base Stock Component

[0015] The lubricating compositions comprise at least one mineral oil base stock selected from Group I, Group II and Group III base oil stocks. The terms "base oil" and "base stock" as referred to herein are to be considered consistent with the definitions as also stated in APPENDIX E—API BASE OIL INTERCHANGEABILITY GUIDELINES FOR PASSENGER CAR MOTOR OILS AND DIESEL ENGINE OILS, July 2009 Version. According to Appendix E, base oil is the base stock or blend of base stocks used in an API-licensed oil. Base stock is a lubricant component that is produced by a single

manufacturer to the same specifications (independent of feed source or manufacturer's location); that meets the same manufacturer's specification; and that is identified by a unique formula, product identification number, or both.

[0016] Useful Group I-III base stocks have a Kv_{100} (kinetic viscosity at 100° C) of greater than 2 cSt to 25 cSt. Group I base stocks can be considered to have a viscosity index of between 80 to 120 and contain greater than 0.03% sulfur and less than 90% saturates. Group II base stocks can be considered to have a viscosity index of between 80 to 120, and contain less than or equal to 0.03% sulfur and greater than or equal to 90% saturates. Group III base stocks can be considered to have a viscosity index greater than 120 and contains less than or equal to 0.03% sulfur and greater than 90% saturates. The following Table summarizes the properties of the Groups I-III base stocks.

TABLE 1

Base Stock	Saturates	Sulfur	Viscosity Index
	(wt. %)	(wt. %)	
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

[0017] Manufacturing plants that make Group I base stocks typically use solvents to extract the lower viscosity index (VI) components and increase the VI of the crude to the desired specifications. These solvents are typically phenol or furfural. Solvent extraction gives a product with less than 90% saturates and more than 300 ppm sulfur. The majority of lube production in the world is in the Group I category.

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[0018] Manufacturing plants that make Group II base stocks typically employ hydroprocessing such as hydrocracking or severe hydrotreating to increase the VI of the crude oil to the specifications value. The use of hydroprocessing typically increases the saturate content above 90% and reduces the sulfur below 300 ppm. Approximately 10% of the lube base oil production in the world is in the Group II category, and 30% of U.S. production is Group II.

Group III base stocks are usually produced using a three-stage process involving hydrocracking an oil feed stock, such as vacuum gas oil, to remove impurities and to saturate all aromatics which might be present to produce highly paraffinic lube oil stock of very high viscosity index, subjecting the hydrocracked stock to selective catalytic hydrodewaxing which converts normal paraffins into branched paraffins by isomerization followed by hydrofinishing to remove any residual aromatics, sulfur, nitrogen or oxygenates.

[0020] Group III base stocks include non-conventional or unconventional base stocks and/or base oils which include one or a mixture of base stock(s) and/or base oil(s) derived from: (1) one or more Gas-to-Liquids (GTL) materials; as well as (2) hydrodewaxed, or hydroisomerized/cat (and/or solvent) dewaxed base stock(s) and/or base oil(s) derived from synthetic wax, natural wax or waxy feeds, waxy feeds including feeds such as mineral and/or non-mineral oil waxy feed stocks, for example gas oils, slack waxes (derived from the solvent dewaxing of natural oils, mineral oils or synthetic; e.g., Fischer-Tropsch feed stocks) and waxy stocks such as waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, foots oil or other natural, mineral oil, or even non-petroleum oil derived waxy materials such as waxy materials recovered from coal liquefaction or shale oil, linear or branched hydrocarbyl compounds with carbon number of 20 or greater, preferably 30 or greater, and mixtures of such base stocks and/or base oils.

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[0021] 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 are GTL materials of lubricating viscosity that are generally derived from hydrocarbons, for example waxy synthesized hydrocarbons, that are themselves derived from simpler gaseous carboncontaining compounds, hydrogen-containing compounds and/or elements as feedstocks. GTL base stock(s) include oils boiling in the lube oil boiling range separated/fractionated from GTL materials such as by, for example, distillation or thermal diffusion, and subsequently subjected to well-known catalytic or solvent dewaxing processes to produce lube oils of reduced/low pour point; wax isomerates, comprising, for example, hydroisomerized or isodewaxed synthesized hydrocarbons; hydroisomerized or isodewaxed Fischer-Tropsch ("F-T") material (i.e., hydrocarbons, waxy hydrocarbons, waxes and possible analogous oxygenates); preferably hydroisomerized or isodewaxed F-T hydrocarbons or hydroisomerized or isodewaxed F-T waxes, hydroisomerized or isodewaxed synthesized waxes, or mixtures thereof.

[0022] GTL base stock(s) derived from GTL materials, especially, hydroisomerized/isodewaxed F-T material derived base stock(s), and other hydroisomerized/isodewaxed wax derived base stock(s) are characterized typically as having kinematic viscosities at 100°C of from 2 mm²/s to 50 mm²/s, preferably from 3 mm²/s to 50 mm²/s, more preferably from 3.5 mm²/s to 30 mm²/s, as exemplified by a GTL base stock derived by the isodewaxing of F-T wax, which has a kinematic viscosity of 4 mm²/s at 100°C and a viscosity index of 130 or greater. The term GTL base oil/base stock and/or wax isomerate base oil/base stock as used herein and in the claims is to be understood

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as embracing individual fractions of GTL base stock/base oil or wax isomerate base stock/base oil as recovered in the production process, mixtures of two or more GTL base stocks/base oil fractions and/or wax isomerate base stocks/base oil fractions, as well as mixtures of one or two or more low viscosity GTL base stock(s)/base oil fraction(s) and/or wax isomerate base stock(s)/base oil fraction(s) with one, two or more high viscosity GTL base stock(s)/base oil fraction(s) and/or wax isomerate base stock(s)/base oil fraction(s) to produce a bi-modal blend wherein the blend exhibits a viscosity within the aforesaid recited range. Reference herein to Kinematic Viscosity refers to a measurement made according to ASTM method D445.

[0023] GTL base stocks derived from GTL materials, especially hydroisomerized/isodewaxed F-T material derived base stock(s), and other hydroisomerized/isodewaxed wax-derived base stock(s), such as wax hydroisomerates/isodewaxates, which can be used as base stock components of this disclosure are further characterized typically as having pour points of -5° C or lower, preferably -10° C or lower, more preferably -15° C or lower, still more preferably -20° C or lower, and under some conditions may have advantageous pour points of -25° C or lower, with useful pour points of -30° C to -40° C or lower. A separate dewaxing step may be practiced to achieve the desired pour point. References herein to pour point refer to measurement made according to ASTM D97 and similar automated versions.

[0024] The GTL base stock(s) derived from GTL materials, especially hydroisomerized/isodewaxed F-T material derived base stock(s), and other hydroisomerized/isodewaxed wax-derived base stock(s), which are base stock components that can be used in this disclosure, can also be characterized as having viscosity indices of 80 or greater, preferably 100 or greater, and more preferably 120 or greater. The viscosity index of these base stocks may be 130 or greater, or 135 or greater, or 140 or greater. For example, GTL base stock(s)

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that derive from GTL materials, preferably F-T materials especially F-T wax, can have a viscosity index of 130 or greater. References herein to viscosity index refer to ASTM method D2270.

[0025] In addition, the GTL base stock(s) are typically highly paraffinic (e.g., greater than 90 percent saturates) and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stocks have relatively low sulfur and nitrogen content, generally containing less than 10 ppm, and more typically less than 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock obtained by the hydroisomerization/isodewaxing of F-T material, especially F-T wax is essentially nil.

[0026] GTL base stock(s) can comprise paraffinic materials, which can be comprised of a majority of of non-cyclic isoparaffins and minor amounts of cycloparaffins. These GTL base stock(s) can comprise paraffinic materials comprised of greater than 60 wt % non-cyclic isoparaffins, preferably greater than 80 wt % non-cyclic isoparaffins, more preferably greater than 85 wt % non-cyclic isoparaffins, and most preferably greater than 90 wt % non-cyclic isoparaffins.

Useful compositions of GTL base stock(s), hydroisomerized or [0027] F-T isodewaxed derived material base stock(s), and wax-derived hydroisomerized/isodewaxed base stock(s), such as isomerates/isodewaxates, are recited in U.S. Pat. Nos. 6,080,301; 6,090,989, and 6,165,949, for example.

[0028] Base stock(s) derived from waxy feeds, which are also suitable for use as the Group III stocks in this disclosure, are paraffinic fluids of lubricating

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

[0029] Slack wax is considered wax recovered from any waxy hydrocarbon oil including synthetic oil such as F-T waxy oil or petroleum oils by solvent or auto-refrigerative dewaxing. Solvent dewaxing employs chilled solvent such as methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), mixtures of MEK/MIBK, mixtures of MEK and toluene, while auto refrigerative dewaxing employs pressurized, liquefied low boiling hydrocarbons such as propane or butane.

Slack waxes secured from synthetic waxy oils such as F-T waxy [0030] 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.

[0031] The process of making the lubricant oil base stocks from wax or waxy stocks, e.g. slack wax, F-T wax or waxy feed, may be characterized as an isomerization process. As previously indicated, if slack waxes are used as the feed, they may need to be subjected to a preliminary hydrotreating step under

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conditions already well known to those skilled in the art to reduce (to levels that would effectively avoid poisoning or deactivating the isomerization catalyst) or to remove sulfur- and nitrogen-containing compounds which would otherwise deactivate the hydroisomerization or hydrodewaxing catalyst used in subsequent steps. If F-T waxes are used, such preliminary treatment is not required because such waxes have only trace amounts (less than 10 ppm, or more typically less than 5 ppm to nil each) of sulfur and/or nitrogen compound content. However, waxes hydrodewaxing catalyst feed F-T may benefit some prehydrotreatment for the removal of oxygenates while others may benefit from oxygenates treatment. The hydroisomerization or hydrodewaxing process may be conducted over a combination of catalysts, or over a single catalyst.

[0032] Following hydrodenitrogenation or hydrosulfurization, the hydroprocessing used for the production of base stocks from such waxy feeds may use an amorphous hydrocracking/hydroisomerization catalyst, such as a lube hydrocracking (LHDC) catalysts, for example catalysts containing Co, Mo, Ni, W, Mo, etc., on oxide supports, e.g., alumina, silica, silica/alumina, or a crystalline hydrocracking/hydroisomerization catalyst, preferably a zeolitic catalyst.

[0033] Hydrocarbon conversion catalysts useful in the conversion of the n-paraffin waxy feedstocks disclosed herein to form the isoparaffinic hydrocarbon base oil are zeolite catalysts, such as ZSM-5, ZSM-11, ZSM-23, ZSM-35, ZSM-12, ZSM-38, ZSM-48, offretite, ferrierite, zeolite beta, zeolite theta, and zeolite alpha, as disclosed in U.S. Pat. No. 4,906,350. These catalysts are used in combination with Group VIII metals, in particular palladium or platinum. The Group VIII metals may be incorporated into the zeolite catalysts by conventional techniques, such as ion exchange.

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[0034] Conversion of the waxy feed stock may be conducted over a combination of Pt/zeolite beta and Pt/ZSM-23 catalysts or over such catalysts used in series in the presence of hydrogen. In another embodiment, the process of producing the lubricant oil base stocks comprises hydroisomerization and dewaxing over a single catalyst, such as Pt/ZSM-35. In yet another embodiment, the waxy feed can be fed over a catalyst comprising Group VII metal loaded ZSM-48, preferably Group VIII noble metal loaded ZSM-48, more preferably Pt/ZSM-48 in either one stage or two stages. In any case, useful hydrocarbon base oil products may be obtained. Catalyst ZSM-48 is described in U.S. Pat. No. 5,075,269.

[0035] A dewaxing step, when needed, may be accomplished using one or more of solvent dewaxing, catalytic dewaxing or hydrodewaxing processes or combinations of such processes in any sequence.

[0036] In solvent dewaxing, the hydroisomerate may be contacted with chilled solvents such as acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), mixtures of ME/MIBK, or mixtures of MEK/toluene and the like, and further chilled to precipitate out the higher pour point material as a waxy solid which is then separated from the solvent-containing lube oil fraction which is the raffinate. The raffinate is typically further chilled in scraped surface chillers to remove more wax solids. Auto-refrigerative dewaxing using low molecular weight hydrocarbons, such as propane, can also be used in which the hydroisomerate is mixed with, e.g., liquid propane, at least a portion of which is flashed off to chill down the hydroisomerate to precipitate out the wax. The wax is separated from the raffinate by filtration, membrane separation or centrifugation. The solvent is then stripped out of the raffinate, which is then fractionated to produce the preferred base stocks useful in the present disclosure.

[0037] In catalytic dewaxing the hydroisomerate is reacted with hydrogen in the presence of a suitable dewaxing catalyst at conditions effective to lower

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

[0038] Any dewaxing catalyst which will reduce the pour point of the hydroisomerate and preferably those which provide a large yield of lube oil base stock from the hydroisomerate may be used. These include shape selective molecular sieves which, when combined with at least one catalytic metal component, have been demonstrated as useful for dewaxing petroleum oil fractions and include, for example, ferrierite, mordenite, ZSM-5, ZSM-11, ZSM-23, ZSM-35, ZSM-22 also known as theta one or TON, and the silicoaluminophosphates known as SAPOs. A dewaxing catalyst which has been found to be unexpectedly particularly effective comprises a noble metal, preferably Pt, composited with H-mordenite. The dewaxing may be accomplished with the catalyst in a fixed, fluid or slurry bed. Typical dewaxing conditions include a temperature in the range of from 400 to 600°F, a pressure of 500 to 900 psig, H₂ treat rate of 1500 to 3500 SCF/B for flow-through reactors and LHSV of 0.1 to 10, preferably 0.2 to 2.0. The dewaxing is typically conducted to convert no more than 40 wt. % and preferably no more than 30 wt. % of the hydroisomerate having an initial boiling point in the range of 650 to 750°F to material boiling below its initial boiling point.

III. Polyalphaolefin Component

[0039] The polyalphaolefin (PAO) component that is included in the lubricating composition of this disclosure can be obtained by polymerizing at least one monomer, e.g., 1-olefin, in the presence of hydrogen and a catalyst

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composition. Alpha-olefins suitable for use in the preparation of the PAOs can contain from 2 to 30, preferably from 2 to 20, carbon atoms, and more preferably from 6 to 12 carbon atoms. Non-limiting examples of such alpha-olefins include ethylene, propylene, 2-methylpropene, 1-butene, 3-methyl-1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, and 1-eicosene, including mixtures of at least two of the alpha-olefins. Preferred alpha-olefins for use herein are 1-octene, 1-decene and 1-dodecene, including mixtures thereof.

[0040] The PAOs that can be used according to this disclosure can be produced by a variety of polymerization processes. However, the PAO component that is mixed with the base stock component to produce the lubricating composition of this disclosure does not contain a significant amount of very heavy fraction, alternatively a very light fraction, or both. These types of non-desirable fractions can contribute to high volatility, unstable viscosity, and poor oxidative and thermal stability. They can be removed in the final product or, preferably, they can be minimized during production using metallocene catalysis.

In general, the polyalphaolefin component that is mixed with the base stock component is comprised of less than 5 wt % of polyalphaolefin having C_{20} or lower carbon numbers, more preferably less than 10 wt % of polyalphaolefin having C_{24} or lower carbon numbers or more preferably less than 15 wt % of polyalphaolefin have C_{26} or lower carbon numbers. It is preferable that the polyalphaolefin component comprise less than 3 wt % of polyalphaolefin having C_{20} or lower carbon numbers, more preferably less than 5 wt % of polyalphaolefin having C_{24} or lower carbon numbers or more preferably less than 8 wt % of polyalphaolefin having C_{26} or lower carbon numbers. It is

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preferable that the polyalphaolefin component comprise less than 2 wt % of polyalphaolefin having C_{20} or lower carbon numbers, more preferably less than 3 wt % of polyalphaolefin having C_{24} or lower carbon numbers or more preferably less than 5 wt % of polyalphaolefin having C_{26} or lower carbon numbers. Also, the lower the amount of any of these light hydrocarbons, the better the fluid property of the polyalphaolefin component as can be determined by Noack volatility testing (ASTM D5800).

In another embodiment, it is preferable that the PAO base oil does not contain a significant amount of a high molecular weight fraction. Such PAOs can be made by removing the high MW fraction or by using preferred metallocene catalysts (referred to as mPAO). Preferably, the PAO component mixed with the mineral oil base stock has not more than 5.0 wt. % of polymer having a molecular weight of greater than 45,000 Daltons. Additionally or alternately, the amount of the PAO component that has a molecular weight greater than 45,000 Daltons is not more than 1.5 wt %, or not more than 0.10 wt %. Additionally or alternately, the amount of the PAO component that has a molecular weight greater than 60,000 Daltons is not more than 0.5 wt %, or not more than 0.20 wt %, or not more than 0.1 wt % of the PAO component. The mass fractions at molecular weights of 45,000 and 60,000 can be determined by GPC, as described above.

In general, Noack volatility is a strong function of fluid viscosity. Lower viscosity fluid usually has higher volatility and higher viscosity fluid has lower volatility. Preferably, the polyalphaolefin component has a Noack volatility of not greater than 10% weight loss, as determined by a modified ASTM D5800, alternatively not greater than 5% weight loss, or not greater than 2% weight loss, as determined by a modified ASTM D5800.

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[0044] Certain PAO components useful according to this disclosure can be produced by the polymerization of olefin feed in the presence of a catalyst such as AlCl₃, BF₃, or promoted AlCl₃, BF₃. Processes for the production of such PAOs are disclosed, for example, in the following patents: U.S. Pat. Nos. 3,149,178; 3,382,291; 3,742,082; 3,769,363; 3,780,128; 4,172,855 and 4,956,122, which are fully incorporated by reference. Additional PAOs are also discussed in: Will, J. G. *Lubrication Fundamentals*, Marcel Dekker: New York, 1980. Subsequent to polymerization, the PAO lubricant range products are typically hydrogenated in order to reduce the residual unsaturation, generally to a level of greater than 90% of hydrogenation. These PAOs may be further processed to remove any significant amount of an undesirable fraction as described above.

[0045] PAOs that can be used according to the disclosure can also be produced by polymerization of an alpha-olefin in the presence of a polymerization catalyst such as Friedel-Crafts catalysts. These include, for example, boron trichloride, aluminum trichloride, or boron trifluoride, promoted with water, with alcohols such as ethanol, propanol, or butanol, with carboxylic acids, or with esters such as ethyl acetate or ethyl propionate or ether such as diethyl ether, diisopropyl ether, etc. (See for example, the methods disclosed by U.S. Pat. No. 4,149,178 or 3,382,291.) Other descriptions of PAO synthesis are found in the following patents: U.S. Pat. No. 3,742,082 (Brennan); U.S. Pat. No. 3,769,363 (Brennan); U.S. Pat. No. 3,876,720 (Heilman); U.S. Pat. No. 4,239,930 (Allphin); U.S. Pat. No. 4,367,352 (Watts); U.S. Pat. No. 4,413,156 (Watts); U.S. Pat. No. 4,434,408 (Larkin); U.S. Pat. No. 4,910,355 (Shubkin); U.S. Pat. No. 4,956,122 (Watts); and U.S. Pat. No. 5,068,487 (Theriot). These PAOs may be further processed to remove any significant amount of an undesirable fraction as described above.

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Another class of PAO components that can be incorporated as a part of this disclosure can be prepared by the action of a supported, reduced chromium catalyst with an alpha-olefin monomer. Such PAOs are described in U.S. Pat. No. 4,827,073 (Wu); U.S. Pat. No. 4,827,064 (Wu); U.S. Pat. No. 4,967,032 (Ho et al.); U.S. Pat. No. 4,926,004 (Pelrine et al.); and U.S. Pat. No. 4,914,254 (Pelrine). Commercially available PAOs of this type can include the higher viscosity SpectraSynTM oils. (ExxonMobil Chemical Company, Houston, Tex.). However, these PAOs may be further processed to remove any significant amount of an undesirable fraction as described above.

[0047] The PAO component that is particularly useful in this disclosure is made by metallocene catalysis. The metallocene-catalyzed PAO (mPAO) can be a copolymer made from at least two or more different alphaolefins, or a homopolymer made from a single alphaolefin feed employing a metallocene catalyst system.

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

[0049] The copolymer mPAO composition is made from at least two alphaolefins of C_3 to C_{30} range and having monomers randomly distributed in the polymers. It is preferred that the average carbon number is at least 4.1. Advantageously, ethylene and propylene, if present in the feed, are present in the amount of less than 50 wt % individually or preferably less than 50 wt % combined. The copolymers can be isotactic, atactic, syndiotactic polymers or any other form of appropriate taciticity.

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[0050] mPAO can also be made from mixed feed Linear Alpha Olefins (LAOs) comprising at least two and up to 26 different linear alphaolefins selected from C_3 to C_{30} linear alphaolefins. The mixed feed LAO can be obtained, for example, from an ethylene growth processing using an aluminum catalyst or a metallocene catalyst. The growth olefins comprise mostly C_6 to C_{18} LAO. LAOs from other processes can also be used.

[0051] The homo-polymer mPAO composition can be made from single alphaolefin chosen from alphaolefins in the C_3 to C_{30} range, preferably C_3 to C_{16} , most preferably C_3 to C_{14} or C_3 to C_{12} . The homo-polymers can be isotactic, atactic, syndiotactic polymers or any other form of appropriate taciticity. The taciticity can be carefully tailored by the polymerization catalyst and polymerization reaction condition chosen or by the hydrogenation condition chosen.

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

[0053] The product obtained is an essentially random liquid copolymer comprising the at least two alphaolefins. By "essentially random" is meant that one of ordinary skill in the art would consider the products to be random copolymer. Likewise the term "liquid" will be understood by one of ordinary

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skill in the art as meaning liquid under ordinary conditions of temperature and pressure, such as ambient temperature and pressure.

[0054] The process for producing mPAO employs a catalyst system comprising a metallocene compound (Formula 1, below) together with an activator such as a non-coordinating anion (NCA) (Formula 2, below) or methylaluminoxane (MAO) 1111 (Formula 3, below):

Formula 1

A
$$L_2$$
 MX_2

Formula 2

 $B(C_6F_5)_4$
 $N-Me$
 Me
 NCA
 NCA
 CH_3
 MAO

[0055] The term "catalyst system" is defined herein to mean a catalyst precursor/activator pair, such as a metallocene/activator pair. When "catalyst system" is used to describe such a pair before activation, it means the unactivated catalyst (precatalyst) together with an activator and, optionally, a co-activator (such as a trialkyl aluminum compound). When it is used to describe such a pair after activation, it means the activated catalyst and the activator or other charge-balancing moiety. Furthermore, this activated "catalyst system" may optionally comprise the co-activator and/or other charge-balancing moiety. Optionally and often, the co-activator, such as trialkyl aluminum compound, is also used as an impurity scavenger.

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The metallocene is selected from one or more compounds according to Formula 1 above. In Formula 1, M is selected from Group 4 transition metals, preferably zirconium (Zr), hafnium (Hf) and titanium (Ti), L1 and L2 are independently selected from cyclopentadienyl ("Cp"), indenyl, and fluorenyl, which may be substituted or unsubstituted, and which may be partially hydrogenated. A is an optional bridging group which, if present, can be selected from dialkylsilyl, dialkylmethyl, diphenylsilyl or diphenylmethyl, ethylenyl (-CH₂—CH₂), alkylethylenyl (—CR₂—CR₂), where alkyl can be independently C₁ to C₁₆ alkyl radical or phenyl, tolyl, xylyl radical and the like, and wherein each of the two X groups, Xa and Xb, are independently selected from halides OR(R is an n alkyl group, preferably selected from C₁ to C₅ straight or branched chain alkyl groups), hydrogen, C₁ to C₁₆ alkyl or aryl groups, haloalkyl, and the like. Usually relatively more highly substituted metallocenes give higher catalyst productivity and wider product viscosity ranges.

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

[0058] The mPAOs described herein may have monomer units represented by Formula 4 in addition to the all regular 1,2-connection:

$$C_f$$
 Formula 4

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

[0059] Any of the mpolyalphaolefins (mPAO) described herein may have a Mw (weight average molecular weight) of 100,000 or less, preferably between 100 and 80,000, preferably between 250 and 60,000, preferably between 280 and 50,000, preferably between 336 and 40,000 g/mol.

[0060] Any of the mpolyalphaolefins (mPAO) described herein may have a Mn (number average molecular weight) of 50,000 or less, preferably between 200 and 40,000, preferably between 250 and 30,000, preferably between 500 and 20,000 g/mol.

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

[0062] Molecular weight distribution (MWD), defined as the ratio of weight-averaged MW to number-averaged MW (=Mw/Mn), can be determined by gel permeation chromatography (GPC) using polystyrene standards, as described in p. 115 to 144, Chapter 6, The Molecular Weight of Polymers in "Principles of Polymer Systems" (by Ferdinand Rodrigues, McGraw-Hill Book, 1970). The GPC solvent was HPLC Grade tetrahydrofuran, uninhibited, with a column temperature of 30° C., a flow rate of 1 ml/min, and a sample concentration of 1 wt %, and the Column Set is a Phenogel 500 A, Linear, 10E6A.

[0063] Any mPAO described herein may have a pour point of less than 0° C (as measured by ASTM D97), preferably less than -10° C, preferably less than -20° C, preferably less than -30° C, preferably less than -30° C, preferably less than -30° C, preferably from -10° C to -80° C, preferably from -15° C to -70° C.

The polyalphaolefin component used in the production of the lubricating composition is preferably a high viscosity PAO. For example, the polyalphaolefin component can have a kinematic viscosity at 100°C of at least 100 cSt (mm²/s), or at least 120 cSt (mm²/s) or at least 140 cSt (mm²/s). As an alternative example, the polyalphaolefin component can have a kinematic viscosity at 100°C in a range of from 100 cSt (mm²/s) to 500 cSt (mm²/s), or from 110 cSt (mm²/s) to 300 cSt (mm²/s), or from 120 cSt (mm²/s) to 200 cSt (mm²/s), or from 135 cSt (mm²/s) to 170 cSt (mm²/s).

IV. Additional Additives

[0065] The lubricating compositions of this disclosure optionally contain one or more additional components or additives. In certain embodiments, performance characteristics of a blend of mineral oil base stock and high viscosity PAO can be particularly enhanced by adding nominal levels of detergents and/or dispersants, as described below.

[0066] In another embodiment, the lubricating compositions of this disclosure can also provide an advantage that little if any polar additives need be included in the compositions. Polar additives can be indirectly described accorded to aniline point, measured according to ASTM D611-7. In general, the higher the polarity, the lower the aniline point. High concentrations of low aniline point additives are not necessary to achieve the benefits of this disclosure.

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[0067] In one aspect, the lubricating composition of this disclosure contains, or is produced by mixing into the overall composition, less than 2 wt. % of any additional component having an aniline point of greater than 25°C, or having an aniline point of greater than 15°C, measured according to ASTM D611-07. In another aspect, the lubricating composition of this disclosure contains, or is produced by mixing into the overall composition, less than 1 wt. % of any additional component having an aniline point of greater than 25°C, or having an aniline point of greater than 15°C, measured according to ASTM D611-07.

[0068] Additional components that can be included in the lubricating composition of this disclosure are described below. If polar additives as described above are used, they should be included in limited quantity based on the aniline point of the particular additive. For example, any additional component such as a component selected from the group consisting of naphthenics (such as alkylated naphthalenes), polyalkylene glycols, VI improvers, friction modifiers, anti-wear agents, detergents and anti-oxidants should be additionally limited based on aniline point of the particular additive.

A. Friction Modifiers

[0069] 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, 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 disclosure if desired. Friction modifiers that lower the coefficient of friction are particularly advantageous in combination with the base oils and lube compositions of this disclosure. Friction

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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. 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, imides, thiophosphates, dithiophosphates, amides. 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 Mo-dithiocarbamates, for example Mo(DTC), as Mo-dithiophosphates, Mo(DTP), Mo-amines, Mo (Am), Mo-alcoholates, Mo-alcohol-amides, etc. See U.S. Pat. No. 5,824,627; U.S. Pat. No. 6,232,276; U.S. Pat. No. 6,153,564; U.S. Pat. No. 6,143,701; U.S. Pat. No. 6,110,878; U.S. Pat. No. 5,837,657; U.S. Pat. No. 6,010,987; U.S. Pat. No. 5,906,968; U.S. Pat. No. 6,734,150; U.S. Pat. No. 6,730,638; U.S. Pat. No. 6,689,725; U.S. Pat. No. 6,569,820; WO 99/66013; WO 99/47629; WO 98/26030.

[0070] Ashless friction modifiers may 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.

Useful concentrations of friction modifiers may range from 0.01 wt % to 10-15 wt % or more, often with a preferred range of 0.1 wt % to 5 wt %, unless the friction modifier has a low aniline point as described above. Concentrations of molybdenum-containing materials are often described in terms of Mo metal concentration. Advantageous concentrations of Mo may range from 10 ppm to 3000 ppm or more, and often with a preferred range of 20-2000 ppm, and in some instances a more preferred range of 30-1000 ppm. Mixtures of two or more friction modifiers, or mixtures of friction modifier(s) with alternate surface active material(s) can be used.

B. Antiwear and EP Additives

[0072] Antiwear and/or extreme pressure (EP) additives can be added to the lubricating composition in order to provide additional anti-wear protection for the engine. The particular additives include metal alkylthiophosphate, and more particularly metal dialkyldithiophosphate in which the primary metal constituent is zinc, or zinc dialkyldithiophosphate (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 0.4 to 1.4 wt % of the total lube oil composition, unless the particular additive has a low aniline point as described above.

[0073] Alternatively, some or all of the ZDDP can be replaced with phosphorus-free antiwear additives. A variety of non-phosphorous additives can also be used as antiwear additives. Sulfurized olefins are useful as antiwear and EP additives. Sulfur-containing olefins can be prepared by sulfurization or

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various organic materials including aliphatic, arylaliphatic or alicyclic olefinic hydrocarbons containing from 3 to 30 carbon atoms, preferably 3-20 carbon atoms. The olefinic compounds contain at least one non-aromatic double bond. Such compounds are defined by the formula

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

where each of R³-R⁶ are independently hydrogen or a hydrocarbon radical. Preferred hydrocarbon radicals are alkyl or alkenyl radicals. Any two of R³-R⁶ may be connected so as to form a cyclic ring. Additional information concerning sulfurized olefins and their preparation can be found in U.S. Pat. No. 4,941,984.

[0074] The polysulfides of use of thiophosphorus thiophosphorus acid esters as lubricant additives is disclosed in U.S. Pat. Nos. 2,443,264; 2,471,115; 2,526,497; and 2,591,577. Addition of phosphorothionyl disulfides as an antiwear, antioxidant, and EP additive is disclosed in U.S. Pat. No. 3,770,854. of Use alkylthiocarbamoyl compounds (bis(dibutyl)thiocarbamoyl, for example) in combination with a molybdenum (oxymolybdenum diisopropylphosphorodithioate example) and a phosphorous ester (dibutyl hydrogen phosphite, for example) as antiwear additives in lubricants is disclosed in U.S. Pat. No. 4,501,678. U.S. Pat. No. 4,758,362 discloses use of a carbamate additive to provide improved The use of thiocarbamate as an antiwear and extreme pressure properties. antiwear additive is disclosed U.S. Pat. No. 5,693,598. in Thiocarbamate/molybdenum complexes such moly-sulfur as dithiocarbamate trimer complex (R=C₈-C₁₈ alkyl) are also useful antiwear agents. The use or addition of such materials is preferably kept to a minimum.

[0075] Esters of glycerol may be used as antiwear agents in limited amounts based on aniline point as indicated above. For example, mono-, di-, and tri-oleates, mono-palmitates and mono-myristates may be used.

[0076] ZDDP can be combined with other compositions that provide antiwear properties. U.S. Pat. No. 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. U.S. Pat. No. 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.

[0077] Particular 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 0.01 to 2 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.

C. Viscosity Improvers

[0078] Viscosity improvers (also known as Viscosity Index modifiers, and VI improvers) provide lubricants with high and low temperature operability. These additives increase the viscosity of the oil composition at elevated

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temperatures which increases film thickness, while having limited effect on viscosity at low temperatures.

[0079] Suitable viscosity improvers include high molecular weight hydrocarbons, polyesters and viscosity index improver dispersants that function as both a viscosity index improver and a dispersant. Typical molecular weights of these polymers are between 1,000 to 1,000,000, more typically 2,000 to 500,000, and even more typically between 25,000 and 100,000.

[0080] Examples of suitable viscosity improvers are polymers and copolymers of methacrylate, butadiene, olefins, or alkylated styrenes. Polyisobutylene is a commonly used viscosity index improver. Another suitable viscosity index improver is polymethacrylate (copolymers of various chain length alkyl methacrylates, for example), some formulations of which also serve as pour point depressants. Other suitable viscosity index improvers include copolymers of ethylene and propylene, hydrogenated block copolymers of styrene and isoprene, and polyacrylates (copolymers of various chain length acrylates, for example). Specific examples include styrene-isoprene or styrene-butadiene based polymers of 50,000 to 200,000 molecular weight.

[0081] The amount of viscosity modifier may range from 0.01 to 8 wt %, preferably 0.01 to 4 wt %, more preferably 0.01 to 2 wt % based on active ingredient and depending on the specific viscosity modifier used.

D. Detergents

[0082] Detergents can be added to the blend of base stock and polyalphaolefin to enhance film thickness characteristics. This type of additive components can have an effect of enhancing performance to the extent that polyalphaolefin concentration can be kept relatively low.

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[0083] Anionic detergents that contain a long chain hydrophobic portion of the molecule and a smaller anionic or oleophobic hydrophilic portion of the molecule can be used. The anionic portion of the detergent can be derived from an organic acid such as a sulfur acid, carboxylic acid, phosphorous acid, phenol, or mixtures thereof. The counter-ion can be an alkaline earth or alkali metal.

[0084] Salts that contain a substantially stoichiometric amount of the metal, described as neutral salts having a total base number (TBN, as measured by ASTM D2896) of from 0 to 80, can be used. Such compositions can be 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.

[0085] At least some detergent can be overbased. The overbased material can have a ratio of metallic ion to anionic portion of the detergent of 1.05:1 to 50:1 on an equivalent basis. More preferably, the ratio is from 4:1 to 25:1. The resulting detergent is an overbased detergent that will typically have a TBN of 150 or higher, often 250 to 450 or more. The overbasing cation can be sodium, calcium, or magnesium. A mixture of detergents of differing TBN can be used in the present disclosure.

[0086] Examples of particular detergents include the alkali or alkaline earth metal salts of sulfonates, phenates, carboxylates, phosphates, and salicylates.

[0087] Sulfonate detergents can also be used. 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 can have 3 to 70 carbon atoms. The alkaryl sulfonates can contain 9 to 80 carbon or more carbon atoms, more typically from 16 to 60 carbon atoms.

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

[0089] 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:

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[0090] where R is a hydrogen atom or an alkyl group having 1 to 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.

[0091] Hydrocarbyl-substituted salicylic acids can also be used. These acids can be prepared from phenols by the Kolbe reaction. See U.S. Pat. No. 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.

[0092] Alkaline earth metal phosphates can also be used as detergents.

[0093] 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 U.S. Pat. No. 6,034,039 for example.

[0094] Preferred detergents include calcium phenates, calcium sulfonates, calcium salicylates, magnesium phenates, magnesium sulfonates, magnesium salicylates and other related components (including borated detergents). The total detergent concentration is can be 1 to 8 wt %, preferably 2 to 8 wt % or 3 to 6 wt %.

E. Dispersants

[0095] During machinery operation, oil-insoluble oxidation byproducts are produced. Dispersants can keep these byproducts in solution, thus

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diminishing their deposition on metal surfaces, and enhance film thickness in the overall blend using low concentrations of polyalphaolefin.

[0096] Dispersants may be ashless or ash-forming in nature. Preferably, the dispersant is ashless. 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 tend to form ash upon combustion.

[0097] Suitable dispersants can 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.

[0098] Chemically, dispersants can be further characterized as phenates, sulfonates, sulfurized phenates, salicylates, naphthenates, stearates, carbamates, thiocarbamates, phosphorus derivatives. A particularly useful class of dispersants is 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. Examples of such dispersants can be found in U.S. Pat. Nos. 3,172,892; 3,215,707; 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 dispersants that can be used are described in U.S. Pat. Nos. 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 useful dispersants may be found, for example, in European Patent Application No. 471 071.

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[0099] 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.

[00100] Succinimides are formed by the condensation reaction between alkenyl succinic anhydrides and amines. Molar ratios can vary depending on the polyamine. For example, the molar ratio of alkenyl succinic anhydride to TEPA can vary from 1:1 to 5:1. Representative examples are shown in U.S. Pat. Nos. 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.

[00101] 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.

[00102] 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 polyethylene such as polyamines. example hexamethylenediamine. One is propoxylated Representative examples are shown in U.S. Pat. No. 4,426,305.

[00103] The molecular weight of the alkenyl succinic anhydrides used in the preceding paragraphs can 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 WO 2014/158533 PCT/US2014/017917 - 35 -

or highly borated dispersants. In one embodiment, the dispersants can be borated with from 0.1 to 5 moles of boron per mole of dispersant reaction product.

[00104] Mannich base dispersants are made from the reaction of alkylphenols, formaldehyde, and amines. See U.S. Pat. No. 4,767,551. Process aids and catalysts, such as oleic acid and sulfonic acids, can also be part of the reaction mixture. Molecular weights of the alkylphenols range from 800 to 2,500. Representative examples are shown in U.S. Pat. Nos. 3,697,574; 3,703,536; 3,704,308; 3,751,365; 3,756,953; 3,798,165; and 3,803,039.

[00105] Typical high molecular weight aliphatic acid modified Mannich condensation products useful in this disclosure can be prepared from high molecular weight alkyl-substituted hydroxyaromatics or HN(R)₂ groupcontaining reactants.

[00106] 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 BF₃, of phenol with high molecular weight polypropylene, polybutylene, and other polyalkylene compounds to give alkyl substituents on the benzene ring of phenol having an average 600-100,000 molecular weight.

[00107] 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

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naphthalenes; heterocyclic amines, e.g., morpholine, pyrrole, pyrrolidine, imidazole, imidazolidine, and piperidine; melamine and their substituted analogs.

[00108] Examples of alkylene polyamide include reactants 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 H₂N—(Z—NH—)_nH, mentioned before, Z is a divalent ethylene and n is 1 to 10 of the foregoing formula. Corresponding propylene polyamines such as propylene diamine and di-, tri-, tetra-, pentapropylene tri-, tetra-, penta- and hexaamines are also suitable 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.

[00109] Aldehyde reactants useful in the preparation of the high molecular products useful in this disclosure 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.

[00110] Hydrocarbyl substituted amine ashless dispersant additives can be used. Examples include those shown in U.S. Pat. Nos. 3,275,554; 3,438,757; 3,565,804; 3,755,433; 3,822,209 and 5,084,197.

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non-borated [00111] Preferred dispersants include borated and succinimides, including those derivatives from mono-succinimides, bissuccinimides, 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 500 to 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 1 to 20 wt %, preferably 1 to 10 wt %, or 2 to 10 wt %, or 3 to 8 wt %.

F. Antioxidants

[00112] 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. Examples include those described by Klamann in Lubricants and Related Products, op cit, and U.S. Pat. Nos. 4,798,684 and 5,084,197.

[00113] Particularly 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-

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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 disclosure. 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).

[00114] 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 R⁸R⁹R¹⁰N where R⁸ is an aliphatic, aromatic or substituted aromatic group, R⁹ is an aromatic or a substituted aromatic group, and R¹⁰ is H, alkyl, aryl or R¹¹S(O)_XR¹² where R¹¹ is an alkylene, alkenylene, or aralkylene group, R¹² is a higher alkyl group, or an alkenyl, aryl, or alkaryl group, and x is 0, 1 or 2. The aliphatic group R⁸ may contain from 1 to 20 carbon atoms, and preferably contains from 6 to 12 carbon atoms. The aliphatic group is a saturated aliphatic group. Preferably, both R⁸ and R⁹ are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring aromatic group such as naphthyl. Aromatic groups R⁸ and R⁹ may be joined together with other groups such as S.

[00115] Typical aromatic amines antioxidants have alkyl substituent groups of at least 6 carbon atoms. Examples of aliphatic groups include hexyl, heptyl, octyl, nonyl, and decyl. Generally, the aliphatic groups will not contain more than 14 carbon atoms. The general types of amine antioxidants useful in the present compositions include diphenylamines, phenyl naphthylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of

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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 disclosure include: p,p'-dioctyldiphenylamine; t-octylphenyl-alphanaphthylamine; phenyl-alphanaphthylamine; and p-octylphenyl-alphanaphthylamine.

[00116] Sulfurized alkyl phenols and alkali or alkaline earth metal salts thereof also are useful antioxidants.

[00117] Another class of antioxidant used in lubricating oil compositions is oil-soluble copper compounds. Any oil-soluble suitable copper compound may be blended into the lubricating oil. Examples of suitable copper antioxidants include copper dihydrocarbyl thio- or dithio-phosphates and copper salts of carboxylic acid (naturally occurring or synthetic). Other suitable copper salts include copper dithiacarbamates, sulphonates, phenates, and acetylacetonates. Basic, neutral, or acidic copper Cu(I) and or Cu(II) salts derived from alkenyl succinic acids or anhydrides are known to be particularly useful.

[00118] Preferred antioxidants include hindered phenols, arylamines. These antioxidants may be used individually by type or in combination with one another. Such additives may be used in an amount of 0.01 to 5 wt %, preferably 0.01 to 1.5 wt %, more preferably zero to less than 1.5 wt %, most preferably zero.

G. Pour Point Depressants

[00119] Pour point depressants (also known as lube oil flow improvers) may be added to the compositions of the present disclosure if desired. The pour point depressants may be added to the lubricating compositions of the disclosure to lower the minimum temperature at which the fluid will flow or can be poured.

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Examples of suitable pour point depressants include polymethacrylates, polyacrylates, polyarylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, and terpolymers of dialkylfumarates, vinyl esters of fatty acids and allyl vinyl ethers. U.S. Pat. Nos. 1,815,022; 2,015,748; 2,191,498; 2,387,501; 2,655,479; 2,666,746; 2,721,877; 2,721,878; and 3,250,715 describe useful pour point depressants and/or the preparation thereof. Such additives may be used in an amount of 0.01 to 5 wt %, preferably 0.01 to 1.5 wt %.

H. Anti-Foam Agents

[00120] Anti-foam agents may advantageously be added to the lubricant compositions. These agents can act to retard the formation of stable foams. Silicones and organic polymers can be useful anti-foam agents. For example, polysiloxanes, such as silicon oil or polydimethyl siloxane, can provide antifoam properties. Anti-foam agents are commercially available and may be used in minor amounts along with other additives such as demulsifiers; usually the amount of these additives combined is less than 1 percent, and in certain embodiments less than 0.1 percent.

I. Corrosion Inhibitors

[00121] Corrosion inhibitors can be 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, U.S. Pat. Nos. 2,719,125; 2,719,126; and 3,087,932. Such additives may be used in an amount of 0.01 to 5 wt %, preferably 0.01 to 1.5 wt %.

J. Seal Compatibility Additives

[00122] Seal compatibility agents can be used to help 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 0.01 to 3 wt %, preferably 0.01 to 2 wt %.

K. Inhibitors and Antirust Additives

[00123] 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.

[00124] 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 0.01 to 5 wt %, preferably 0.01 to 1.5 wt %.

L. Co-Basestocks

[00125] In lubricating oil compositions of this disclosure, in which the mineral oil portion is comprised of at least one of a Group I, Group II or Group III base stock, the lubricating oil compositions may also include a limited

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quantity of one or more co-base stocks. The limitation of such co-base stocks is particularly based on aniline point as described above.

[00126] Esters can be includes as a co-basestock. 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 monocarboxylic 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, dieicosyl sebacate, etc.

[00127] 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 4 carbon atoms (preferably C₅ to C₃₀ 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).

[00128] 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 5 to 10 carbon atoms.

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[00129] Alkylated naphthalenes in particularly limited quantities due their relatively low aniline points can also be a useful co-basestock. Examples of the alkylated naphthalenes include, but are not limited to, mono-alkylated, di-alkylated and tri-alkylated naphthalenes, including mixtures thereof. The alkyl groups on the alkylated naphthalene preferably have from 6 to 30 carbon atoms, with particular preference to 12 to 18 carbon atoms. A preferred class of alkylating agents are the olefins with the requisite number of carbon atoms, for example, the hexenes, heptenes, octenes, nonenes, decenes, undecenes, dodecenes. Mixtures of the olefins, e.g. mixtures of C_{12} - C_{20} or C_{14} - C_{18} olefins, are useful. Branched alkylating agents, especially oligomerized olefins such as the trimers, tetramers, pentamers, etc., of light olefins such as ethylene, propylene, the butylenes, etc., are also useful.

M. Typical Additive Amounts

[00130] 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. Concentrations of additives, including co-base stocks, are particularly limited, however, based on aniline point as described above. Typical amounts of such additives useful in the present disclosure are shown in Table 2 below.

[00131] 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 weight percents indicated below are based on the total weight of the lubricating oil composition.

TABLE 2

Additive	Approximate wt % (useful)	Approximate wt % (preferred)
Friction Modifiers	0.01-5	0.01-2
Antiwear Additives	0.01-4	0.01-2
Viscosity Improvers	0.01-10	0.01-8
Detergents	1-8	2-8
Dispersants	1-20	2-10
Antioxidants	0.01-4	0.01-1.5
Pour Point Depressants	0.01-2	0.01-1.5
Anti-foam Agents	0.001-1	0.001-0.1
Corrosion Inhibitors	0.01-5	0.01-1.5

V. Lubricating Compositions and Production

[00132] Lubricating compositions are prepared by blending together or admixing one or more base stocks from the group consisting of Group I, Group II and Group III, one or more polyalphaolefins as described above, and optionally one or more additives.

[00133] The lubricating compositions can be used as automotive engine lubricants, axle and manual transmission lubricants, and industrial lubricants. The lubricating compositions demonstrate superior performance with regard to film thickness, average friction coefficient and wear, when compared to similar compositions that contain high quantities of polyalphaolefins and polar anti-wear additives.

[00134] In the lubricating compositions of this disclosure, the mineral oil component is comprised of at least one base stock selected from a Group I, Group II, and Group III base stock. The lubricating composition can be comprised, in admixture, of at least 60 wt % of the mineral oil component, or at least 70 wt % of the mineral oil component, or at least 80 wt % of the mineral oil component, or at least 95 wt % of the mineral oil component, or at least 95 wt % of the mineral oil component, based on total weight of the lubricating composition.

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[00135] The lubricating compositions of this disclosure are further comprised, in admixture, of from 2 wt % to 5 wt % of the polyalphaolefin, based on total weight of the lubricating composition. Alternatively, lubricating oil compositions of this disclosure are further comprised, in admixture, of from 2 wt % to 4 wt % of the polyalphaolefin, or from 2 wt % to 3 wt % of the polyalphaolefin, based on total weight of the lubricating composition.

[00136] In one embodiment, the lubricating composition of this disclosure can be identified by viscosity standards of the Society of Automotive Engineers (SAE) for automotive lubricants. As one example, the lubricating composition is identified by the SAE J300 standard, a viscosity classification for engine oils. As another example, the lubricating composition can be identified according to the SAE J306 standard, a standard for axle and manual transmission lubricants.

Table 3. The J300 viscosity grades of this disclosure are summarized in Table 3. The J306 viscosity grades of this disclosure are shown in Table 4. In both of these classifications, the grades denoted with the letter "W" are intended for use in applications operating in low-temperature conditions. At one point, the "W" was originally coined for lubricants that were considered "winter grade." However, these compositions can be referred to as multigrade lubricants, whereas the grades without a "W" are recognized as monograde, or straight grade, lubricants.

TABLE 3

SAE Viscosity Grade	Low-Temp (°C) Cranking Viscosity, cP Max	Low-Temp (°C) Pumping Viscosity, cP Max with no yield stress	Kinematic Viscosity (cSt) at 100°C Max	Kinematic Viscosity (cSt) at 40°C Max	High Shear Viscosity (cP) at 150°C Min
OW	3250 @ -30	60,000 @ -40	3.8	ı	-
5W	3500 @ -25	60,000 @ -35	3.8	ı	-
10W	3500 @ -20	60,000 @ -30	4.1	-	-
15W	3500 @ -15	60,000 @ -25	5.6	-	-
20W	4500 @ -10	60,000 @ -20	5.6	-	-
25W	6000 @ -5	60,000 @ -15	9.3	-	-
20	-	-	5.6	<9.3	2.6
30	-	-	9.3	<12.5	2.9
40	_	-	12.5	<16.3	2.9*
40	-	-	12.5	<16.3	3.7**
50	-	-	16.3	<21.9	3.7
60	-	-	21.9	<26.1	3.7

^{*} For 0W-40, 5W-40 and 10W-40 Grades

TABLE 4

SAE Viscosity Grade	Maximum Temperature for Viscosity of 150,000 cP °C	Viscosity at 100°C cSt Minimum	Viscosity at 100°C cSt Maximum
70W	-55	4.1	-
75W	-40	4.1	-
80W	-26	7.0	-
85W	-12	11.0	-
80	-	7.0	<11.0
85	-	11.0	<13.5
90	-	13.5	<18.5
110	-	18.5	<24.0
140	-	24.0	<32.5
190	-	32.5	<41.0
250			

[00138] Industrial lubricating compositions of this disclosure can be identified according to a viscosity classification jointly developed by ASTM International and the Society of Tribologists and Lubrication Engineers (STLE), and recognized as ASTM D2422. This method originally standardized 18 different viscosity grades measured at 100°F in Saybolt Universal Seconds (SUS). It was later converted to more universally accepted metric system values

^{**} For 15W-40, 20W-40, 25W-40 and 40 Grades

measured at 40°C. The lubricating composition of this disclosure includes viscosity ranges denoted in Table 5. These viscosity ranges can be referred to as "ISO viscosity grade numbers," also as "ISO VG numbers," and classified according to ISO 3448.

TABLE 5

ISO Viscosity Grade	Kinematic Viscosity at 40°C, Min cSt	Kinematic Viscosity at 40°C, Max cSt
2	1.98	2.42
3	2.88	3.52
5	4.14	5.06
7	6.12	7.48
10	9.00	11.0
15	13.5	16.5
22	19.8	24.2
32	28.8	35.2
46	41.4	50.6
68	61.2	74.8
100	90.0	110
150	135	165
220	198	242
320	288	352
460	414	506
680	612	748
1000	900	1100
1500	1350	1650

[00139] The lubricating compositions of this disclosure have a viscosity at any one or more of the grades shown in the above Tables 3-5, depending upon the use of the lubricating composition. For example, the lubricating compositions of this disclosure can have a kinematic viscosity at 100°C from 3.8 cSt to 26.1 cSt, as well as ranges incorporating any variety of ranges in according to SAE J300.

[00140] The lubricating compositions of this disclosure can also have a kinematic viscosity at 100°C of at least 4.1 cSt, for example 4.1 cSt to 50 cSt, as well as ranges incorporating any variety of ranges in according to SAE J306.

[00141] The lubricating compositions of this disclosure can additionally have a kinematic viscosity at 40°C of from 1.98 cSt to 1650 cSt, as well as ranges incorporating any variety of ranges in according to ISO 3448.

The lubricating compositions have improved frictional properties. Average friction coefficients can be measured by a High Frequency Reciprocating Rig (HFRR) test. The HFRR is manufactured by PCS Instruments and identified as model HFR2 (AutoHFRR). The test equipment and procedure are similar to the ASTM D6079 method except the test oil temperature is raised from 32°C to 195°C at 2°C/minute, 400 g load, 60 Hz frequency, and 0.5 mm stroke length.

[00143] The kinematic viscosities at 40°C of the lubricating compositions were measured according to the ASTM D445 standard. The kinematic viscosities at 100°C of the lubricating compositions were also measured according to the ASTM D445 standard.

[00144] The disclosure will now be more particularly described with reference to the following non-limiting Examples, which rely on bench scale tests considered in the industry to be highly predictive of actual engine performance.

EXAMPLES

Example 1

[00145] Film thicknesses of a fully formulated premium diesel engine oil (10W-30 viscosity grade, Group II base stock mineral oil, containing up to 20 wt % Group III) (representing the comparative oil), and a blend of the same fully formulated premium diesel engine oil, as a base stock, with 2 wt % mPAO 150,

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based on total weight of the engine oil blend, were measured in a PCS Instruments EHL Ultra Thin Film Measurement System at 40°C and 100°C at 20 Newtons of load. The measurements were made with a rotating glass disc and (driven) steel ball at speeds from 1.3 to 0.018 m/s and 0% slide/roll ratio. The results are shown in FIG. 1.

[00146] FIG. 1 shows that the blend of the premium diesel engine oil with the 2 wt % mPAO engine oil has a significantly enhanced thickness at lower speed relative to the premium engine oil without mPAO. This indicates that the blend of the premium diesel engine oil and 2 wt % mPAO would be expected to exhibit significantly enhanced wear protection of engine and gear components.

Example 2

[00147] Film thicknesses of the comparative fully formulated diesel engine oil of Example 1 and a blend of the diesel engine oil of the same fully formulated premium diesel engine oil, as a base stock, with 5 wt % mPAO 150, based on total weight of the engine oil blend, were measured in a PCS Instruments EHL Ultra Thin Film Measurement System at 40°C and 100°C at 20 Newtons of load. The measurements were made with a rotating glass disc and (driven) steel ball at speeds from 1.3 to 0.018 m/s and 0% slide/roll ratio. The results are shown in FIG. 2.

[00148] FIG. 2 shows that the blend of the premium diesel engine oil with 5 wt % mPAO is significantly thicker at lower speed relative to the premium diesel engine oil without mPAO. This indicates that the blend of mineral oil base stock and 5 wt % mPAO would be expected to exhibit significantly enhanced wear protection of engine and gear components.

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Example 3

[00149] Film thicknesses of a fully formulated flagship synthetic diesel engine oil (5W-40 viscosity grade; Group IV oil) (representing the comparative oil) and a blend of the same fully formulated flagship synthetic diesel engine oil, as a base stock, with 2 wt % mPAO, based on total weight of the engine oil, were measured in a PCS Instruments EHL Ultra Thin Film Measurement System at 40°C and 100°C at 20 Newtons of load. The measurements were made with a rotating glass disc and (driven) steel ball at speeds from 1.3 to 0.018 m/s and 0% slide/roll ratio. The results are shown in FIG. 3.

[00150] FIG. 3 shows there is no significant difference between the film thickness of the blend of synthetic diesel engine oil with 2 wt % mPAO and the synthetic diesel engine oil without mPAO at any speed. This indicates that the addition of the 2 wt % mPAO to the synthetic diesel engine oil would not be expected to have any apparent effect in protecting engine and gear components against wear.

Example 4

[00151] Film thicknesses of the fully formulated flagship synthetic diesel engine oil of Example 3 and a blend of the fully formulated flagship synthetic diesel engine oil, as a base stock, with 5 wt % mPAO, based on total weight of the engine oil, were measured in a PCS Instruments EHL Ultra Thin Film Measurement System at 40°C and 100°C at 20 Newtons of load. The measurements were made with a rotating glass disc and (driven) steel ball at speeds from 1.3 to 0.018 m/s and 0% slide/roll ratio. The results are shown in FIG. 4.

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[00152] FIG. 4 shows there is a significant difference between the film thickness of the blend of the fully formulated flagship synthetic diesel engine oil with 5 wt % mPAO and the fully formulated flagship synthetic diesel engine oil without mPAO at low speed only at 100°C, with no significant difference at any speed at 40°C. The fact that there is no significant difference using either a 2 wt % or 5 wt % concentration of mPAO in a fully formulated synthetic diesel engine oil, as shown in Examples 3 and 4, is believed to be due to the presence of high concentrations of additives such as detergents and/or dispersants in the fully formulated synthetic diesel engine oil. As shown in Examples 1 and 2, a fully formulated diesel engine oil that is mineral oil-based shows significantly different and positive results. This difference was not predictable or expected.

[00173] All patents, test procedures, and other documents cited herein, including priority documents, are fully incorporated by reference to the extent such disclosure is not inconsistent and for all jurisdictions in which such incorporation is permitted.

[00174] While the illustrative forms disclosed herein have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the disclosure. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the example and descriptions set forth herein, but rather that the claims be construed as encompassing all the features of patentable novelty which reside herein, including all features which would be treated as equivalents thereof by those skilled in the art to which this disclosure pertains.

[00175] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated.

CLAIMS:

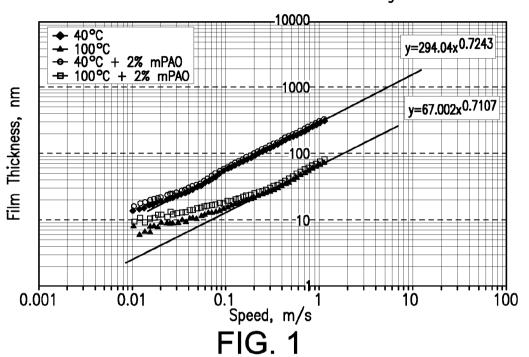
- 1. A lubricating composition, comprising a mixture of: at least 60 wt. % of a mineral oil base stock including one or more components selected from the group consisting of a Group I base oil component, a Group II base oil component, and a Group III base oil component, based on the total weight of the lubricating composition; and from 2 wt. % to 5 wt. % of a polyalphaolefin component, based on the total weight of the lubricating composition, wherein the polyalphaolefin component contains not more than 5.0 wt. % of a polymer having a molecular weight of greater than 45,000 Daltons.
- 2. The lubricating composition of claim 1, wherein the polyalphaolefin component contains not more than 1.5 wt. % of a polymer having a molecular weight of greater than 45,000 Daltons.
- 3. The lubricating composition of claims 1-2, wherein the polyalphaolefin component has a kinematic viscosity of greater than 100 cSt at 100°C.
- 4. The lubricating composition of claims 1-3, wherein the polyalphaolefin component has a viscosity index of greater than 100.
- 5. The lubricating composition of claims 1-4, wherein the polyalphaolefin component is a mPAO.
- 6. The lubricating composition of claims 1-5, wherein the lubricating composition further comprises, in admixture, 1 wt % to 8 wt % of at least one detergent, based on total weight of the lubricating composition.

- 7. The lubricating composition of claims 1-6, wherein the lubricating composition further comprises, in admixture, 1 wt % to 20 wt % of at least one dispersant, based on total weight of the lubricating composition.
- 8. The lubricating composition of claims 1-7, wherein the lubricating composition has a kinematic viscosity at 100°C of from 3.8 cSt to 26.1 cSt.
- 9. The lubricating composition of claims 1-7, wherein the lubricating composition has a kinematic viscosity at 100°C of at least 4.1 cSt.
- 10. The lubricating composition of claims 1-7, wherein the lubricating composition has a kinematic viscosity at 40°C of from 1.98 cSt to 1650 cSt.
- 11. A method for producing a mineral oil lubricating composition having improved film thickness and wear properties, comprising blending together at least the following components: at least 60 wt. % of a mineral oil base stock including one or more components selected from the group consisting of a Group I base oil component, a Group II base oil component, and a Group III base oil component, based on the total weight of the lubricating composition; and from 2 wt. % to 5 wt. % of a polyalphaolefin component, based on the total weight of the lubricating composition, wherein the polyalphaolefin component contains not more than 5.0 wt. % of a polymer having a molecular weight of greater than 45,000 Daltons.
- 12. The method of claim 11, wherein the polyalphaolefin component contains not more than 1.5 wt. % of a polymer having a molecular weight of greater than 45,000 Daltons.
- 13. The method of claims 11-12, wherein the polyalphaolefin component has a kinematic viscosity of greater than 100 cSt at 100°C.

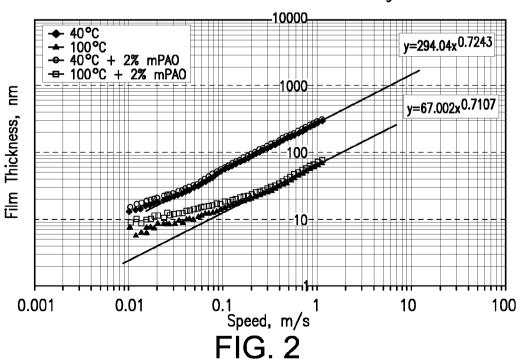
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- 14. The method of claims 11-13, wherein the polyalphaolefin component has a viscosity index of greater than 100.
- 15. The method of claims 11-14, wherein the polyalphaolefin component is a mPAO.
- 16. The method of claims 11-15, wherein the method further comprises blending 1 wt % to 8 wt % of at least one detergent, based on total weight of the lubricating composition.
- 17. The method of claims 11-16, wherein the method further comprises blending 1 wt % to 20 wt % of at least one dispersant, based on total weight of the lubricating composition.
- 18. The method of claims 11-17, wherein the lubricating composition has a kinematic viscosity at 100°C of from 3.8 cSt to 26.1 cSt.
- 19. The method of claims 11-17, wherein the lubricating composition has a kinematic viscosity at 100°C of at least 4.1 cSt.
- 20. The method of claims 11-17, wherein the lubricating composition has a kinematic viscosity at 40°C of from 1.98 cSt to 1650 cSt.

Premium SAE 10W-30 Mineral Diesel Engine Oil

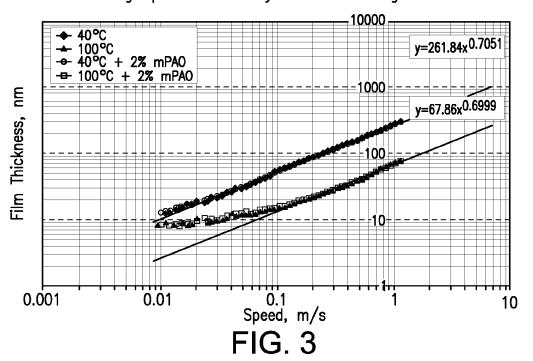


Premium SAE 10W-30 Mineral Diesel Engine Oil

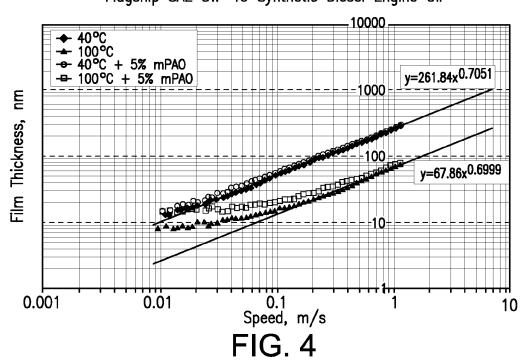


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Flagship SAE 5W-40 Synthetic Diesel Engine Oil



Flagship SAE 5W-40 Synthetic Diesel Engine Oil



INTERNATIONAL SEARCH REPORT

International application No PCT/US2014/017917

A. CLASSIFICATION OF SUBJECT MATTER INV. C10M101/02 ADD.						
According to	According to International Patent Classification (IPC) or to both national classification and IPC					
B. FIELDS	SEARCHED					
	Minimum documentation searched (classification system followed by classification symbols)					
Documenta	tion searched other than minimum documentation to the extent that su	uch documents are included in the fields sea	arched			
Electronic d	ata base consulted during the international search (name of data bas	e and, where practicable, search terms use	ed)			
EPO-In	ternal					
C. DOCUM	ENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where appropriate, of the rele	evant passages	Relevant to claim No.			
X	US 2013/029892 A1 (YAMADA RYOU [JP]) 31 January 2013 (2013-01-31) paragraph [0092] - paragraph [0094]; examples 2,4		1-20			
X	US 2009/312211 A1 (YAMADA RYOU [17 December 2009 (2009-12-17) paragraph [0085] - paragraph [008 examples 1,3,4; table 1	1-20				
Х	WO 03/076555 A1 (EXXONMOBIL RES & ENG CO [US]) 18 September 2003 (2003-09-18) paragraph [0026]; claim 15; examples 5, 6		1-20			
Х	US 2009/088356 A1 (HEE ALLAN G [US] ET AL) 2 April 2009 (2009-04-02) paragraph [0027]; claims 1, 3; figure 2		1-20			
Furti	her documents are listed in the continuation of Box C.	X See patent family annex.				
** Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filling date "C" document of particular relevance; the claimed invent considered novel or cannot be considered to involve step when the document is taken alone "Y" document of particular relevance; the claimed invent considered novel or cannot be considered to involve step when the document is taken alone "Y" document of particular relevance; the claimed invent considered to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other			ation but cited to understand invention laimed invention cannot be ered to involve an inventive e laimed invention cannot be po when the document is a documents, such combination			
means being obvious to a person skilled in the art "P" document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family						
Date of the actual completion of the international search Date of mailing of the international search report			<u> </u>			
2	4 July 2014	06/08/2014				
Name and r	mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Klaes, Daphne				

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Information on patent family members

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PCT/US2014/017917

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