



- (51) **International Patent Classification:**
C10M 107/02 (2006.01) *C10M 111/04* (2006.01)
- (21) **International Application Number:** PCT/US2014/055656
- (22) **International Filing Date:** 15 September 2014 (15.09.2014)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:** 61/886,312 3 October 2013 (03.10.2013) US
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- (81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States** (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,

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(54) **Title:** COMPOSITIONS WITH IMPROVED VARNISH CONTROL PROPERTIES

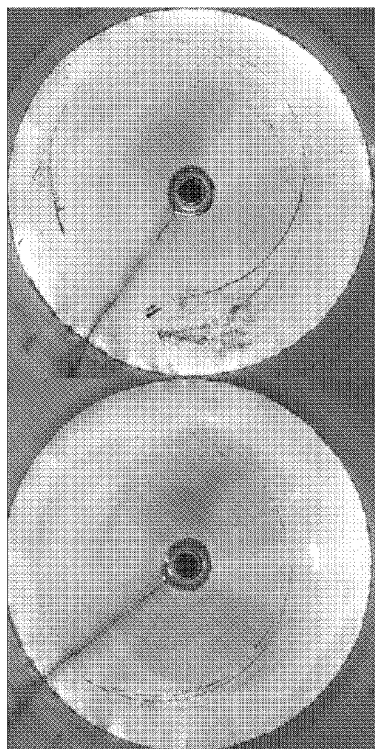


FIG. 1

(57) **Abstract:** A method for improving varnish control in a mechanical device requiring hydraulic fluids, turbine oils, industrial fluids, circulating oils, or combinations thereof. The method involves supplying the mechanical device with a lubricating composition including a Group III lubricating oil base stock. The Group III lubricating oil base stock has a viscosity from 3.8 to 8.5 mm²/s at 100°C, a viscosity index greater than 120, a sulfur content less than 0.0003 weight percent, and an aromatic hydrocarbon content less than 0.2 weight percent, based on the total weight of the Group III lubricating oil base stock. Varnish reduction properties are improved as compared to varnish reduction properties achieved using a lubricating composition containing a different Group III lubricating oil base stock. The disclosure also provides lubricating compositions used in the method.

TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, **Published:**
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, — *with international search report (Art. 21(3))*
LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE,
SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

COMPOSITIONS WITH IMPROVED VARNISH CONTROL
PROPERTIES

FIELD

[0002] This disclosure relates to a method for improving varnish control in a mechanical device requiring hydraulic fluids, turbine oils, industrial fluids, circulating oils, or combinations thereof. This disclosure also provides lubricating compositions used in the method.

BACKGROUND

[0003] The art of formulating lubricating oil compositions has become more complex as a result of increased government and user environmental standards and increased user performance requirements. Lubricants are typically marketed based upon features such as fluid durability, deposit control, antiwear protection, filterability, water tolerance, rust/corrosion protection, and viscosity.

[0004] Deposit or varnish is a growing problem in many hydraulic and sensitive lubrication applications. Varnish formation is usually the result of a complex series of events which come from lubricant degradation. There are three common causes of oil degradation. One cause is oxidation at elevated temperatures leading to the formation of decomposition products, including acids and insoluble particulate, referred to as deposits, varnish, and sludge. The second cause is thermal degradation, such as, pressure induced dieseling or micro-dieseling which occurs when entrained air bubbles are collapsed under high pressure. The third cause, especially for hydraulic fluids, is external contamination of the fluid.

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[0005] It is well known that API Group II and III base stock oils and GTL are typically better than API Group I base oils. The Group II and III base stocks are better because of the oxidation stability of hydroprocessed or hydrocracked base stocks as well as enhanced viscosity and temperature properties compared to conventional solvent refined base stocks. Consequently, many lubricants are being formulated with API Group II and III base stock. A known deficiency of these non-polar, highly saturated API Group II and III base stocks are their lower ability to solubilize or suspend lubricant degradation byproducts in solution once formed. For this reason, API Group II/III based lubricants are more susceptible to deposit formation once oil degradation has begun.

[0006] A large number of failures in hydraulic and other applications have been associated with varnish and sludge formation. Sludge and varnish are insoluble materials formed as a result of either degradation reactions in the oil, contamination of oil or both. Explanations typically include the nature of the base oil, additive instability or degradation, bulk oil oxidation, electrostatic discharge, and low electrical conductivity, among others.

[0007] There is a need to develop hydraulic formulations that use API Group III or other base stocks and that minimize or prevent deposit formation in the device being lubricated.

[0008] The present disclosure provides many advantages, which shall become apparent as described below.

SUMMARY

[0009] This disclosure relates in part to a method for improving varnish control in a mechanical device requiring hydraulic fluids, turbine oils, industrial

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fluids, circulating oils, or combinations thereof. The method comprises supplying the mechanical device with a lubricating composition comprising a Group III lubricating oil base stock. The Group III lubricating oil base stock, e.g., a Gas-to-Liquids (GTL) oil base stock or a Fischer-Tropsch wax derived oil base stock, has a viscosity from 3.8 to 8.5 mm²/s at 100°C, a viscosity index greater than 120, preferably greater than 125, and more preferably greater than 130, a sulfur content less than 0.0003 weight percent, and an aromatic hydrocarbon content less than 0.2 weight percent, based on the total weight of the Group III lubricating oil base stock. Varnish reduction properties are improved as compared to varnish reduction properties achieved using a lubricating composition containing a different Group III lubricating oil base stock.

[0010] This disclosure also relates in part to a lubricating composition that comprises a Group III lubricating oil base stock, and optionally one or more of an antiwear additive, viscosity index improver, antioxidant, dispersant, pour point depressant, corrosion inhibitor, metal deactivator, seal compatibility additive, antifoam agent, co-base stock, pour point depressant, seal compatibility additive, solubility improver, and anti-rust additive. The Group III lubricating oil base stock, e.g., a Gas-to-Liquids (GTL) oil base stock or a Fischer-Tropsch wax derived oil base stock, has a viscosity from 3.8 to 8.5 mm²/s at 100°C, a viscosity index greater than 120, preferably greater than 125, and more preferably greater than 130, a sulfur content less than 0.0003 weight percent, and an aromatic hydrocarbon content less than 0.2 weight percent, based on the total weight of the Group III lubricating oil base stock. In a mechanical device supplied with the lubricating composition, varnish reduction properties are improved as compared to varnish reduction properties achieved using a lubricating composition containing a different Group III lubricating oil base stock.

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[0011] It has been surprisingly found that with lubricating compositions containing a Group III lubricating oil base stock in accordance with this disclosure, varnish reduction properties are improved as compared to varnish reduction properties achieved using a lubricating composition containing a different Group III lubricating oil base stock.

[0012] Further objects, features and advantages of the present disclosure will be understood by reference to the following drawings and detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] Fig. 1 shows photographs taken to determine the extent of varnish deposit in a hydraulic fluid pump test according to the Coordinating Research Council (CRC) rating scale.

[0014] Fig. 2 shows photographs taken to determine the extent of varnish deposit in a turbine oil pump test according to the Coordinating Research Council (CRC) rating scale.

DETAILED DESCRIPTION

[0015] 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.

[0016] In accordance with this disclosure, varnish reduction properties are improved with lubricating compositions containing a Group III lubricating oil base stock in accordance with this disclosure, as compared to varnish reduction

properties achieved using a lubricating composition containing a different Group III lubricating oil base stock.

Lubricating Oil Group III Base Stocks

[0017] The lubricating oil Group III base stocks, e.g., a Gas-to-Liquids (GTL) oil base stock or a Fischer-Tropsch wax derived oil base stock, useful in this disclosure have a viscosity from 3.8 to 8.5 mm²/s at 100°C, a viscosity index greater than 120, preferably greater than 125, and more preferably greater than 130, a sulfur content less than 0.0003 weight percent (determined according to ASTM D2622), and an aromatic hydrocarbon content less than 0.2 weight percent (determined according to ASTM D7419), based on the total weight of the Group III lubricating oil base stock.

[0018] Preferably, the Group III lubricating oil base stocks, e.g., a Gas-to-Liquids (GTL) oil base stock or a Fischer-Tropsch wax derived oil base stock, have a viscosity from 4.0 to 8.3 mm²/s at 100°C, a viscosity index greater than 125, preferably greater than 130, a sulfur content less than 0.0002 weight percent, and an aromatic hydrocarbon content less than 0.18 weight percent, based on the total weight of the Group III lubricating oil base stock.

[0019] More preferably, the Group III lubricating oil base stocks, e.g., a Gas-to-Liquids (GTL) oil base stock or a Fischer-Tropsch wax derived oil base stock, have a viscosity from 4.0 to 8.3 mm²/s at 100°C, a viscosity index greater than 130, a sulfur content less than 0.0002 weight percent, and an aromatic hydrocarbon content less than 0.18 weight percent, based on the total weight of the Group III lubricating oil base stock.

[0020] The Group III lubricating oil base stock preferably contains consecutive carbon numbers, and is highly isoparaffinic in nature. The Group III

lubricating oil base stock is preferably produced from natural gas and subsequent wax isomerization.

[0021] Illustrative Group III lubricating oil base stocks useful in this disclosure include, for example, Shell QHVI 4, Shell QHVI 8, and the like.

[0022] The lubricating compositions of this disclosure may also have a so-called multigrade rating such as SAE 75W-80, 75W-90, 75W-140, 80W-90, 80W-140, 85W-90, or 85W-140. Multigrade lubricants may include a viscosity improver which is formulated with the base oil of lubricating viscosity to provide the above lubricant grades. Useful viscosity improvers include but are not limited to polyolefins, such as ethylene-propylene copolymers, or polybutylene rubbers, including hydrogenated rubbers, such as styrene-butadiene or styrene-isoprene rubbers; or polyacrylates, including polymethacrylates. In one embodiment, the viscosity improver is a polyolefin or polymethacrylate. These additives, as well as additional additives which may be used in the compositions of the disclosure, are described in more detail herein.

[0023] In one embodiment, the lubricating composition of this disclosure further comprises a Group II co-base stock. The Group II co-base stock preferably has a viscosity from 6.5 to 11.0 mm²/s at 40°C, is isoparaffinic, and is produced from natural gas and subsequent wax isomerization. Illustrative Group II co-base stocks include, for example, Shell QHVI 3, and the like.

[0024] In another embodiment, the lubricating composition of this disclosure further comprises a heavy Group II co-base stock. The heavy Group II co-base stock preferably has a viscosity from 10.0 to 13.0 mm²/s at 100°C, a viscosity index greater than 90, a sulfur content less than 0.001 weight percent, and saturates content greater than 99%. Illustrative Group II co-base stocks include, for example, EHC 110 and Flint Hills 600-HC.

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[0025] The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the lubricating composition of the present disclosure is in the form of a concentrate (which may be combined with additional oil to form, in whole or in part, a finished lubricant), the ratio of the additives to the base oil of lubricating viscosity and/or to diluent oil include the ranges of 1:99 to 99:1 by weight, or from 80:20 to 10:90 by weight.

[0026] The base oil constitutes the major component of the lubricant composition of the present disclosure and typically is present in an amount ranging from 50 to 99 weight percent, preferably from 80 to 99 weight percent, more preferably from 70 to 95 weight percent, and even more preferably from 85 to 95 weight percent, based on the total weight of the composition. Mixtures of synthetic and natural base oils may be used if desired. Bi-modal mixtures of Group I, II, III, IV, and/or V base stocks may be used if desired.

Lubricating Oil Co-Base Stocks

[0027] A wide range of lubricating co-base oils useful in this disclosure is known in the art. Lubricating co-base oils that are useful in the present disclosure are both natural oils, and synthetic oils, and unconventional oils (or mixtures thereof) can be used unrefined, refined, or rerefined (the latter is also known as reclaimed or reprocessed oil). Unrefined oils are those obtained directly from a natural or synthetic source and used without added purification. These include shale oil obtained directly from retorting operations, petroleum oil obtained directly from primary distillation, and ester oil obtained directly from an esterification process. Refined oils are similar to the oils discussed for unrefined oils except refined oils are subjected to one or more purification steps to improve at least one lubricating oil property. One skilled in the art is familiar with many purification processes. These processes include solvent extraction,

secondary distillation, acid extraction, base extraction, filtration, and percolation. Rerefined oils are obtained by processes analogous to refined oils but using an oil that has been previously used as a feed stock.

[0028] Groups I, II, III, IV and V are broad base oil stock categories developed and defined by the American Petroleum Institute (API Publication 1509; www.API.org) to create guidelines for lubricant base oils. Group I base stocks have a viscosity index of between 80 to 120 and contain greater than 0.03% sulfur and/or less than 90% saturates. Group II base stocks 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 stocks have a viscosity index greater than 120 and contain less than or equal to 0.03 % sulfur and greater than 90% saturates. Group IV includes polyalphaolefins (PAO). Group V base stock includes base stocks not included in Groups I-IV. Table 1 below summarizes properties of each of these five groups.

Table 1

| | Base Oil Properties | | |
|-----------|---|------------|-----------------|
| | Saturates | Sulfur | Viscosity Index |
| Group I | <90 and/or | >0.03% and | ≥80 and <120 |
| Group II | ≥90 and | ≤0.03% and | ≥80 and <120 |
| Group III | ≥90 and | ≤0.03% and | ≥120 |
| Group IV | Includes polyalphaolefins (PAO) and GTL products | | |
| Group V | All other base oil stocks not included in Groups I, II, III or IV | | |

[0029] Natural oils include animal oils, vegetable oils (castor oil and lard oil, for example), and mineral oils. Animal and vegetable oils possessing favorable thermal oxidative stability can be used. Of the natural oils, mineral oils are preferred. Mineral oils vary widely as to their crude source, for example, as to

whether they are paraffinic, naphthenic, or mixed paraffinic-naphthenic. Oils derived from coal or shale are also useful. Natural oils vary also as to the method used for their production and purification, for example, their distillation range and whether they are straight run or cracked, hydrorefined, or solvent extracted.

[0030] Group II and/or Group III hydroprocessed or hydrocracked basestocks, including synthetic oils such as polyalphaolefins, alkyl aromatics and synthetic esters are also well known basestock oils.

[0031] Synthetic oils include hydrocarbon oil. Hydrocarbon oils include oils such as polymerized and interpolymerized olefins (polybutylenes, polypropylenes, propylene isobutylene copolymers, ethylene-olefin copolymers, and ethylene-alphaolefin copolymers, for example). Polyalphaolefin (PAO) oil base stocks are commonly used synthetic hydrocarbon oil. By way of example, PAOs derived from C₈, C₁₀, C₁₂, C₁₄ olefins or mixtures thereof may be utilized. See U.S. Patent Nos. 4,956,122; 4,827,064; and 4,827,073.

[0032] The number average molecular weights of the PAOs, which are known materials and generally available on a major commercial scale from suppliers such as ExxonMobil Chemical Company, Chevron Phillips Chemical Company, BP, and others, typically vary from 250 to 3,000, although PAO's may be made in viscosities up to 100 cSt (100°C). The PAOs are typically comprised of relatively low molecular weight hydrogenated polymers or oligomers of alphaolefins which include, but are not limited to, C₂ to C₃₂ alphaolefins with the C₈ to C₁₆ alphaolefins, such as 1-octene, 1-decene, 1-dodecene and the like, being preferred. The preferred polyalphaolefins are poly-1-octene, poly-1-decene and poly-1-dodecene and mixtures thereof and mixed olefin-derived polyolefins. However, the dimers of higher olefins in the

range of C₁₄ to C₁₈ may be used to provide low viscosity base stocks of acceptably low volatility. Depending on the viscosity grade and the starting oligomer, the PAOs may be predominantly trimers and tetramers of the starting olefins, with minor amounts of the higher oligomers, having a viscosity range of 1.5 to 12 cSt. PAO fluids of particular use may include 3.0 cSt, 3.4 cSt, and/or 3.6 cSt and combinations thereof. Bi-modal mixtures of PAO fluids having a viscosity range of 1.5 to 100 cSt may be used if desired.

[0033] The PAO fluids may be conveniently made by the polymerization of an alphaolefin in the presence of a polymerization catalyst such as the Friedel-Crafts catalysts including, for example, aluminum trichloride, boron trifluoride or complexes of boron trifluoride with water, alcohols such as ethanol, propanol or butanol, carboxylic acids or esters such as ethyl acetate or ethyl propionate. For example the methods disclosed by U.S. Patent Nos. 4,149,178 or 3,382,291 may be conveniently used herein. Other descriptions of PAO synthesis are found in the following U.S. Patent Nos. 3,742,082; 3,769,363; 3,876,720; 4,239,930; 4,367,352; 4,413,156; 4,434,408; 4,910,355; 4,956,122; and 5,068,487. The dimers of the C₁₄ to C₁₈ olefins are described in U.S. Patent No. 4,218,330.

[0034] Other useful lubricant oil base stocks include wax isomerate base stocks and base oils, comprising hydroisomerized waxy stocks (e.g. waxy stocks such as gas oils, slack waxes, fuels hydrocracker bottoms, etc.), hydroisomerized Fischer-Tropsch waxes, Gas-to-Liquids (GTL) base stocks and base oils, and other wax isomerate hydroisomerized base stocks and base oils, or mixtures thereof. Fischer-Tropsch waxes, the high boiling point residues of Fischer-Tropsch synthesis, are highly paraffinic hydrocarbons with very low sulfur content. The hydroprocessing used for the production of such base stocks may use an amorphous hydrocracking/hydroisomerization catalyst, such as one

of the specialized lube hydrocracking (LHDC) catalysts or a crystalline hydrocracking/hydroisomerization catalyst, preferably a zeolitic catalyst. For example, one useful catalyst is ZSM-48 as described in U.S. Patent No. 5,075,269, the disclosure of which is incorporated herein by reference in its entirety. Processes for making hydrocracked/hydroisomerized distillates and hydrocracked/hydroisomerized waxes are described, for example, in U.S. Patent Nos. 2,817,693; 4,975,177; 4,921,594 and 4,897,178 as well as in British Patent Nos. 1,429,494; 1,350,257; 1,440,230 and 1,390,359. Each of the aforementioned patents is incorporated herein in their entirety. Particularly favorable processes are described in European Patent Application Nos. 464546 and 464547, also incorporated herein by reference. Processes using Fischer-Tropsch wax feeds are described in U.S. Patent Nos. 4,594,172 and 4,943,672, the disclosures of which are incorporated herein by reference in their entirety.

[0035] Gas-to-Liquids (GTL) base oils, Fischer-Tropsch wax derived base oils, and other wax-derived hydroisomerized (wax isomerate) base oils can be advantageously used in the instant disclosure, and may have useful kinematic viscosities at 100°C of 3 cSt to 50 cSt, preferably 3 cSt to 30 cSt, more preferably 3.5 cSt to 25 cSt, as exemplified by GTL 4 with kinematic viscosity of 4.0 cSt at 100°C and a viscosity index of 131. These Gas-to-Liquids (GTL) base oils, Fischer-Tropsch wax derived base oils, and other wax-derived hydroisomerized base oils may have useful pour points of -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. Useful compositions of Gas-to-Liquids (GTL) base oils, Fischer-Tropsch wax derived base oils, and wax-derived hydroisomerized base oils are recited in U.S. Patent Nos. 6,080,301; 6,090,989, and 6,165,949 for example, and are incorporated herein in their entirety by reference.

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[0036] The hydrocarbyl aromatics can be used as base oil or base oil component and can be any hydrocarbyl molecule that contains at least 5% of its weight derived from an aromatic moiety such as a benzenoid moiety or naphthenoid moiety, or their derivatives. These hydrocarbyl aromatics include alkyl benzenes, alkyl naphthalenes, alkyl diphenyl oxides, alkyl naphthols, alkyl diphenyl sulfides, alkylated bis-phenol A, alkylated thiodiphenol, and the like. The aromatic can be mono-alkylated, dialkylated, polyalkylated, and the like. The aromatic can be mono- or poly-functionalized. The hydrocarbyl groups can also be comprised of mixtures of alkyl groups, alkenyl groups, alkynyl, cycloalkyl groups, cycloalkenyl groups and other related hydrocarbyl groups. The hydrocarbyl groups can range from C₆ up to C₆₀ with a range of C₈ to C₂₀ often being preferred. A mixture of hydrocarbyl groups is often preferred, and up to three such substituents may be present. The hydrocarbyl group can optionally contain sulfur, oxygen, and/or nitrogen containing substituents. The aromatic group can also be derived from natural (petroleum) sources, provided at least 5% of the molecule is comprised of an above-type aromatic moiety. Viscosities at 100°C of approximately 3 cSt to 50 cSt are preferred, with viscosities of approximately 3.4 cSt to 20 cSt often being more preferred for the hydrocarbyl aromatic component. In one embodiment, an alkyl naphthalene where the alkyl group is primarily comprised of 1-hexadecene is used. Other alkylates of aromatics can be advantageously used. Naphthalene or methyl naphthalene, for example, can be alkylated with olefins such as octene, decene, dodecene, tetradecene or higher, mixtures of similar olefins, and the like. Useful concentrations of hydrocarbyl aromatic in a lubricant oil composition can be 2% to 25%, preferably 4% to 20%, and more preferably 4% to 15%, depending on the application.

[0037] Alkylated aromatics such as the hydrocarbyl aromatics of the present disclosure may be produced by well-known Friedel-Crafts alkylation of aromatic

compounds. See Friedel-Crafts and Related Reactions, Olah, G. A. (ed.), Inter-science Publishers, New York, 1963. For example, an aromatic compound, such as benzene or naphthalene, is alkylated by an olefin, alkyl halide or alcohol in the presence of a Friedel-Crafts catalyst. See Friedel-Crafts and Related Reactions, Vol. 2, part 1, chapters 14, 17, and 18, See Olah, G. A. (ed.), Inter-science Publishers, New York, 1964. Many homogeneous or heterogeneous, solid catalysts are known to one skilled in the art. The choice of catalyst depends on the reactivity of the starting materials and product quality requirements. For example, strong acids such as AlCl_3 , BF_3 , or HF may be used. In some cases, milder catalysts such as FeCl_3 or SnCl_4 are preferred. Newer alkylation technology uses zeolites or solid super acids.

[0038] Esters comprise a useful base stock. Additive solvency and seal compatibility characteristics may be secured by the use of esters such as the esters of dibasic acids with monoalkanols and the polyol esters of 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, didecyl phthalate, dieicosyl sebacate, etc.

[0039] Particularly useful synthetic esters are those 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

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dipentaerythritol) with alkanolic 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, or mixtures of any of these materials.

[0040] 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. These esters are widely available commercially, for example, the Mobil P-41 and P-51 esters of ExxonMobil Chemical Company.

[0041] Also useful are esters derived from renewable material such as coconut, palm, rapeseed, soy, sunflower and the like. These esters may be monoesters, di-esters, polyol esters, complex esters, or mixtures thereof. These esters are widely available commercially, for example, the Mobil P-51 ester of ExxonMobil Chemical Company.

[0042] Hydraulic system formulations containing renewable esters are included in this disclosure. For such formulations, the renewable content of the ester is typically greater than 70 weight percent, preferably more than 80 weight percent and most preferably more than 90 weight percent.

[0043] Other useful fluids of lubricating viscosity include non-conventional or unconventional base stocks that have been processed, preferably catalytically, or synthesized to provide high performance lubrication characteristics.

[0044] Non-conventional or unconventional base stocks/base oils include one or more of a mixture of base stock(s) derived from one or more Gas-to-Liquids

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(GTL) materials, as well as isomerate/isodewaxate base stock(s) derived from natural wax or waxy feeds, mineral and or non-mineral oil waxy feed stocks such as slack waxes, natural waxes, and waxy stocks such as gas oils, waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, or other mineral, mineral oil, or even non-petroleum oil derived waxy materials such as waxy materials received from coal liquefaction or shale oil, and mixtures of such base stocks.

[0045] GTL materials are materials that are derived via one or more synthesis, combination, transformation, rearrangement, and/or degradation/deconstructive processes from gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks such as hydrogen, carbon dioxide, carbon monoxide, water, methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane, butylenes, and butynes. GTL base stocks and/or base oils are GTL materials of lubricating viscosity that are generally derived from hydrocarbons; for example, waxy synthesized hydrocarbons, that are themselves derived from simpler gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks. GTL base stock(s) and/or base oil(s) include oils boiling in the lube oil boiling range (1) separated/fractionated from synthesized GTL materials such as, for example, by distillation and subsequently subjected to a final wax processing step which involves either or both of a catalytic dewaxing process, or a solvent dewaxing process, to produce lube oils of reduced/low pour point; (2) synthesized wax isomerates, comprising, for example, hydrodewaxed or hydroisomerized cat and/or solvent dewaxed synthesized wax or waxy hydrocarbons; (3) hydrodewaxed or hydroisomerized cat and/or solvent dewaxed Fischer-Tropsch (F-T) material (i.e., hydrocarbons, waxy hydrocarbons, waxes and possible analogous oxygenates); preferably hydrodewaxed or hydroisomerized/ followed by cat and/or solvent dewaxing

dewaxed F-T waxy hydrocarbons, or hydrodewaxed or hydroisomerized/ followed by cat (or solvent) dewaxing dewaxed, F-T waxes, or mixtures thereof.

[0046] GTL base stock(s) and/or base oil(s) derived from GTL materials, especially, hydrodewaxed or hydroisomerized/ followed by cat and/or solvent dewaxed wax or waxy feed, preferably F-T material derived base stock(s) and/or base oil(s), are characterized typically as having kinematic viscosities at 100°C of from 2 mm²/s to 50 mm²/s (ASTM D445). They are further characterized typically as having pour points of -5°C to -40°C or lower (ASTM D97). They are also characterized typically as having viscosity indices of 80 to 140 or greater (ASTM D2270).

[0047] In addition, the GTL base stock(s) and/or base oil(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stock(s) and/or base oil(s) typically have very low sulfur and nitrogen content, generally containing less than 10 ppm, and more typically less than 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock(s) and/or base oil(s) obtained from F-T material, especially F-T wax, is essentially nil. In addition, the absence of phosphorous and aromatics make this materially especially suitable for the formulation of low SAP products.

[0048] The term GTL base stock and/or base oil and/or wax isomerate base stock and/or base oil is to be understood as embracing individual fractions of such materials of wide viscosity range as recovered in the production process, mixtures of two or more of such fractions, as well as mixtures of one or two or

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more low viscosity fractions with one, two or more higher viscosity fractions to produce a blend wherein the blend exhibits a target kinematic viscosity.

[0049] The GTL material, from which the GTL base stock(s) and/or base oil(s) is/are derived is preferably an F-T material (i.e., hydrocarbons, waxy hydrocarbons, wax).

[0050] In addition, the GTL base stock(s) and/or base oil(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stock(s) and/or base oil(s) and hydrodewaxed, or hydroisomerized/cat (and/or solvent) dewaxed base stock(s) and/or base oil(s) typically have very low sulfur and nitrogen content, generally containing less than 10 ppm, and more typically less than 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock(s) and/or base oil(s) obtained from F-T material, especially F-T wax, is essentially nil. In addition, the absence of phosphorous and aromatics make this material especially suitable for the formulation of low sulfur, sulfated ash, and phosphorus (low SAP) products.

[0051] Co-base oils for use in the formulated lubricating compositions of the present disclosure are any of the variety of oils corresponding to API Group I, Group II, Group III, Group IV, and Group V oils and mixtures thereof, preferably API Group II, Group III, Group IV, and Group V oils and mixtures thereof, more preferably the Group III to Group V base oils due to their exceptional volatility, stability, viscometric and cleanliness features. Minor quantities of Group I stock, such as the amount used to dilute additives for blending into formulated lube oil products, can be tolerated but should be kept to

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a minimum, i.e. amounts only associated with their use as diluent/carrier oil for additives used on an “as-received” basis. Even in regard to the Group II stocks, it is preferred that the Group II stock be in the higher quality range associated with that stock, i.e., a Group II stock having a viscosity index in the range $100 < VI < 120$.

[0052] As described herein, the lubricating composition of this disclosure preferably comprises a Group II co-base stock. The Group II co-base stock preferably has a viscosity from 6.5 to 11.0 mm²/s at 40°C, is isoparaffinic, and is produced from natural gas and subsequent wax isomerization. Illustrative Group II co-base stocks include, for example, Shell QHVI 3, and the like.

[0053] Also, as described herein, the lubricating composition of this disclosure preferably comprises a heavy Group II co-base stock. The heavy Group II co-base stock preferably has a viscosity from 10.0 to 13.0 mm²/s at 100°C, a viscosity index greater than 90, a sulfur content less than 0.001 weight percent, and saturates content greater than 99%. Illustrative Group II co-base stocks include, for example, EHC 110 and Flint Hills 600-HC.

[0054] The co-base oil constitutes the minor component of the lubricant composition of the present disclosure and typically is present in an amount ranging from 0.1 to 20 weight percent, preferably from 0.5 to 15 weight percent, and more preferably from 1.0 to 10.0 weight percent, based on the total weight of the lubricant composition. The co-base oil may be selected from any of the synthetic or natural oils typically used in hydraulic systems. Mixtures of synthetic and natural base oils may be used if desired. Bi-modal mixtures of Group I, II, III, IV, and/or V base stocks may be used if desired.

Other Additives

[0055] The lubricating compositions useful in the present disclosure may additionally contain one or more of the other commonly used lubricating oil performance additives including but not limited to antiwear agents, dispersants, corrosion inhibitors, rust inhibitors, metal deactivators, extreme pressure additives, anti-seizure agents, wax modifiers, viscosity index improvers, viscosity modifiers, fluid-loss additives, seal compatibility agents, lubricity agents, solubility improvers, anti-staining agents, chromophoric agents, defoamants, demulsifiers, emulsifiers, densifiers, wetting agents, gelling agents, tackiness agents, colorants, and others. For a review of many commonly used additives, see Klamann in *Lubricants and Related Products*, Verlag Chemie, Deerfield Beach, FL; ISBN 0-89573-177-0. Reference is also made to "Lubricant Additives" by M. W. Ranney, published by Noyes Data Corporation of Parkridge, NJ (1973); see also U.S. Patent No. 7,704,930, the disclosure of which is incorporated herein in its entirety.

[0056] Many of the additives which may be used are described in greater detail below and these additives may be added separately or as an additive package. Additive packages may contain one or more of the additives described herein and may also contain some amount of diluent oil and/or solvent. An additive package may be added to the compositions of the disclosure such that they are present at 0.2 to 4.0 wt %, 0.5 to 3.0 wt%, or 0.6 to 2.0 wt %. The types and quantities of performance additives used in combination with the instant disclosure in lubricant compositions are not limited by the examples shown herein as illustrations.

Antiwear Additive

[0057] A metal alkylthiophosphate and more particularly a metal dialkyl dithio phosphate in which the metal constituent is zinc, or zinc dialkyl dithio phosphate (ZDDP) is a useful component of the lubricating compositions of this disclosure. ZDDP can be derived from primary alcohols, secondary alcohols or mixtures thereof. 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. Alkyl aryl groups may also be used.

[0058] Preferable zinc dithiophosphates which are commercially available include secondary zinc dithiophosphates such as those available from for example, The Lubrizol Corporation under the trade designations "LZ 1095", "LZ 677A" and "LZ 1371", from for example Chevron Oronite under the trade designation "OLOA 262" and from for example Afton Chemical under the trade designation "HITEC 7169".

[0059] The ZDDP is typically used in amounts of from 0.4 weight percent to 1.2 weight percent, preferably from 0.5 weight percent to 1.0 weight percent, and more preferably from 0.6 weight percent to 0.8 weight percent, based on the total weight of the lubricating composition, although more or less can often be used advantageously. Preferably, the ZDDP is a secondary ZDDP and present in an amount of from 0.6 to 1.0 weight percent of the total weight of the lubricating composition.

[0060] Low phosphorus formulations are included in this disclosure. For such formulations, the phosphorus content is typically less than 0.12 weight percent preferably less than 0.10 weight percent and most preferably less than 0.085 weight percent.

[0061] Metal-free phosphorus-containing compounds are also useful antiwear additives in accordance with this disclosure. A phosphate ester or salt may be a monohydrocarbyl, dihydrocarbyl or a trihydrocarbyl phosphate, wherein each hydrocarbyl group is saturated. In one embodiment, each hydrocarbyl group independently contains from 8 to 30, or from 12 up to 28, or from 14 up to 24, or from 14 up to 18 carbon atoms. In one embodiment, the hydrocarbyl groups are alkyl groups. Examples of hydrocarbyl groups include tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl groups and mixtures thereof.

[0062] A phosphate ester or salt is a phosphorus acid ester can be prepared by reacting one or more phosphorus acid or anhydride with a saturated alcohol. The phosphorus acid or anhydride is generally an inorganic phosphorus reagent, such as phosphorus pentoxide, phosphorus trioxide, phosphorus tetroxide, phosphorous acid, phosphoric acid, phosphorus halide, lower phosphorus esters, or a phosphorus sulfide, including phosphorus pentasulfide, and the like. Lower phosphorus acid esters generally contain from 1 to 7 carbon atoms in each ester group. The alcohols used to prepare the phosphorus acid esters or salts include, for example, commercially available alcohols and alcohol mixtures including Alfol 1218 (a mixture of synthetic, primary, straight-chain alcohols containing 12 to 18 carbon atoms); Alibi 20+ alcohols (mixtures of C₁₈-C₂₈ primary alcohols having mostly C₂₀ alcohols as determined by GLC (gas-liquid-chromatography)); and Alfol22+ alcohols (C₁₈-C₂₈ primary alcohols containing primarily C₂₂ alcohols). Alfol alcohols are available from Continental Oil Company. Another example of a commercially available alcohol mixture is Adol 60 (75% by weight of a straight chain C₂₂ primary alcohol, 15% of a C₂₀ primary alcohol and 8% of C₁₈ and C₂₄ alcohols). The Adol alcohols are marketed by Ashland Chemical.

[0063] A variety of mixtures of monohydric fatty alcohols derived from naturally occurring triglycerides and ranging in chain length from C₈-C₁₈ are available from Procter & Gamble Company. These mixtures contain various amounts of fatty alcohols containing 12, 14, 16, or 18 carbon atoms. For example, CO-1214 is a fatty alcohol mixture containing 0.5% of C₁₀ alcohol, 66.0% of C₁₂ alcohol, 26.0% of C₁₄ alcohol and 6.5% of C₁₆ alcohol.

[0064] Another group of commercially available mixtures include the "Neodol" products available from Shell Chemical Co. For example, Neodol 23 is a mixture of C₁₂ and C₁₃ alcohols; Neodol 25 is a mixture of C₁₂-C₁₅ alcohols; and Neodol 45 is a mixture of C₁₄-C₁₅ linear alcohols. The phosphate contains from 14 to 18 carbon atoms in each hydrocarbyl group. The hydrocarbyl groups of the phosphate are generally derived from a mixture of fatty alcohols having from 14 up to 18 carbon atoms. The hydrocarbyl phosphate may also be derived from a fatty vicinal diol. Fatty vicinal diols include those available from Ashland Oil under the general trade designation Adol 114 and Adol 158. The former is derived from a straight chain alpha olefin fraction of C₁₁-C₁₄, and the latter is derived from a C₁₅-C₁₈ fraction.

[0065] The phosphate salts may be prepared by reacting an acidic phosphate ester with an amine compound or a metallic base to form an amine or a metal salt. The amines may be monoamines or polyamines. Useful amines include those amines disclosed in U.S. Pat. No. 4,234,435.

[0066] The monoamines generally contain a hydrocarbyl group which contains from 1 to 30 carbon atoms, or from 1 to 12, or from 1 to 6. Examples of primary monoamines useful in the present disclosure include methylamine, ethylamine, propylamine, butylamine, cyclopentylamine, cyclohexylamine, octylamine, dodecylamine, allylamine, cocoamine, stearylamine, and lauryl

amine. Examples of secondary monoamines include dimethylamine, diethylamine, dipropylamine, dibutylamine, dicyclopentylamine, dicyclohexylamine, methylbutylamine, ethylhexylamine, etc.

[0067] An amine is a fatty (C₈-C₃₀) amine which includes n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine, oleylamine, etc. Also useful fatty amines include commercially available fatty amines such as "Armeen" amines (products available from Akzo Chemicals, Chicago, Ill.), such Armeen C, Armeen O, Armeen OL, Armeen T, Armeen HT, Armeen S and Armeen SD, wherein the letter designation relates to the fatty group, such as coco, oleyl, tallow, or stearyl groups.

[0068] Other useful amines include primary ether amines, such as those represented by the formula, R''(OR') x NH₂, wherein R' is a divalent alkylene group having 2 to 6 carbon atoms; x is a number from one to 150, or from one to five, or one; and R'' is a hydrocarbyl group of 5 to 150 carbon atoms. An example of an ether amine is available under the name SURFAM® amines produced and marketed by Mars is Chemical Company, Atlanta, Ga. Preferred etheramines are exemplified by those identified as SURFAM P14B (decyloxypropylamine), SURFAM P16A (linear C₁₆), SURFAM P17B (tridecyloxypropylamine). The carbon chain lengths (i.e., C₁₄, etc.) of the SURFAMS described above and used hereinafter are approximate and include the oxygen ether linkage.

[0069] An amine is a tertiary-aliphatic primary amine. Generally, the aliphatic group, preferably an alkyl group, contains from 4 to 30, or from 6 to 24, or from 8 to 22 carbon atoms. Usually the tertiary alkyl primary amines are monoamines the alkyl group is a hydrocarbyl group containing from one to 27

carbon atoms and R6 is a hydrocarbonyl group containing from 1 to 12 carbon atoms. Such amines are illustrated by tert-butylamine, tert-hexylamine, 1-methyl-1-amino-cyclohexane, tert-octylamine, tert-decylamine, tert-dodecylamine, tert-tetradecylamine, tert-hexadecylamine, tert-octadecylamine, tert-tetracosylamine, and tert-octacosylamine. Mixtures of tertiary aliphatic amines may also be used in preparing the phosphate salt. Illustrative of amine mixtures of this type are "Primene 81R" which is a mixture of C₁₁-C₁₄ tertiary alkyl primary amines and "Primene JMT" which is a similar mixture of C₁₈-C₂₂ tertiary alkyl primary amines (both are available from Rohm and Haas Company). The tertiary aliphatic primary amines and methods for their preparation are known to those of ordinary skill in the art. An amine can be a heterocyclic polyamine. The heterocyclic polyamines include aziridines, azetidines, azolidines, tetra- and dihydropyridines, pyrroles, indoles, piperidines, imidazoles, di- and tetra-hydroimidazoles, piperazines, isoindoles, purines, morpholines, thiomorpholines, N-aminoalkylmorpholines, N-aminoalkylthiomorpholines, N-aminoalkyl-piperazines, N,N'-diaminoalkylpiperazines, azepines, azocines, azonines, azecines and tetra-, di- and perhydro derivatives of each of the above and mixtures of two or more of these heterocyclic amines. Preferred heterocyclic amines are the saturated 5- and 6-membered heterocyclic amines containing only nitrogen, oxygen and/or sulfur in the hetero ring, especially the piperidines, piperazines, thiomorpholines, morpholines, pyrrolidines, and the like. Piperidine, aminoalkyl substituted piperidines, piperazine, aminoalkyl substituted piperazines, morpholine, aminoalkyl substituted morpholines, pyrrolidine, and aminoalkyl-substituted pyrrolidines, are especially preferred. Usually the aminoalkyl substituents are substituted on a nitrogen atom forming part of the hetero ring. Specific examples of such heterocyclic amines include N-aminopropylmorpholine, N-aminoethylpiperazine, and N,N'-diaminoethylpiperazine. Hydroxy heterocyclic polyamines are also useful.

Examples include N-(2-hydroxyethyl)cyclohexylamine, 3-hydroxycyclopentylamine, parahydroxyaniline, N-hydroxyethylpiperazine, and the like.

[0070] The metal free phosphorus containing compounds are typically used in amounts of from 0.4 weight percent to 1.2 weight percent, preferably from 0.5 weight percent to 1.0 weight percent, and more preferably from 0.6 weight percent to 0.8 weight percent, based on the total weight of the lubricating composition, although more or less can often be used advantageously.

Viscosity Index Improvers

[0071] Viscosity index improvers (also known as VI improvers, viscosity modifiers, and viscosity improvers) can be included in the lubricant compositions of this disclosure.

[0072] Viscosity index improvers provide lubricants with high and low temperature operability. These additives impart shear stability at elevated temperatures and acceptable viscosity at low temperatures. Suitable viscosity index improvers include high molecular weight hydrocarbons, polyesters and viscosity index improver dispersants that function as both a viscosity index improver and a dispersant. Typical molecular weights of these polymers are between 10,000 to 1,500,000, more typically 20,000 to 1,200,000, even more typically between 50,000 and 1,000,000, and yet even more typically between 50,000 and 200,000. Viscosity index improvers may also be considered multifunctional. For example multifunctional viscosity index improvers can also function as dispersants. Examples of such viscosity index improvers are polyisobutylene, copolymers of ethylene and propylene and higher alpha-olefins, polymethacrylates, polyalkylmethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, inter

polymers of styrene and acrylic esters, and partially hydrogenated copolymers of styrene/isoprene, styrene/butadiene, and isoprene/butadiene, as well as the partially hydrogenated homopolymers of butadiene and isoprene and isoprene/divinylbenzene.

[0073] Other examples of suitable viscosity index improvers are linear or star-shaped 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.

[0074] Suitable polyalkyl methacrylate viscosity index improvers include, for example, homopolymers prepared from methacrylic acid such as poly methyl methacrylate, poly ethyl methacrylate, poly propyl methacrylate, poly butyl methacrylate, poly hexyl methacrylate, poly octyl methacrylate, poly 2-ethylhexyl methacrylate, poly decyl methacrylate, poly undecyl methacrylate, poly dodecyl methacrylate, poly tridecyl methacrylate, poly tetradecyl methacrylate, poly pentadecyl methacrylate, poly hexadecyl methacrylate, or mixtures thereof.

[0075] Other suitable polyalkyl methacrylate viscosity index improvers include, for example, copolymers (typically an interpolymers) of (i) a vinyl aromatic monomer; and (ii) an unsaturated carboxylic acid, anhydride, or

derivatives thereof, (c) an interpolymer of (i) an alpha-olefin; and (ii) an unsaturated carboxylic acid, anhydride, or derivatives thereof, or (d) mixtures thereof. The unsaturated carboxylic acid, anhydride or derivatives thereof, include in addition to methacrylic acid, others such as acrylic acid, butenoic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, or mixtures thereof. In one embodiment the unsaturated carboxylic acid or derivatives thereof includes methacrylic acid and at least one of maleic acid, maleic anhydride, fumaric acid, itaconic acid, or mixtures thereof. In another embodiment, the unsaturated carboxylic acid or derivatives thereof includes methacrylic acid and at least one of maleic acid or maleic anhydride.

[0076] Olefin copolymers, are commercially available from Chevron Oronite Company LLC under the trade designation "PARATONE®" (such as "PARATONE® 8921" and "PARATONE® 8941"); from Afton Chemical Corporation under the trade designation "HiTEC®" (such as "HiTEC® 5850B"; and from The Lubrizol Corporation under the trade designation "Lubrizol® 7067C". Polyisoprene polymers are commercially available from Infineum International Limited, e.g. under the trade designation "SV200"; diene-styrene copolymers are commercially available from Infineum International Limited, e.g. under the trade designation "SV 260". Polyalkyl methacrylates (PAMA) are commercially available from Evonik Oil Additives, Inc. USA under the trade designation VISCOPLEX® 8-219. Other examples of commercially available viscosity index improvers, such as polymethacrylates are the Viscoplex TM series from Evonik, Lz77XXTM series from Lubrizol, the Hitec 57XXTM series from Afton. Other commercially available viscosity index improvers Lz 7702, 7720, 7727, 7773, 7725, and 7789; Viscoplex 8-890, 8-219, and 4-708, and Hitec 6708 and 5789.

[0077] In an embodiment of this disclosure, the viscosity index improvers may be used in an amount of less than 15 weight percent, preferably less than 10 weight percent, based on the total weight of the formulated oil or lubricating composition.

[0078] In another embodiment of this disclosure, the viscosity index improvers may be used in an amount of from 0.25 to 15.0 weight percent, preferably 0.15 to 10.0 weight percent, and more preferably 0.05 to 8.0 weight percent, based on the total weight of the formulated oil or lubricating composition.

Dispersants

[0079] During operation of a hydraulic system, oil-insoluble oxidation byproducts are produced. Dispersants help keep these byproducts in solution, thus diminishing their deposition on metal surfaces. Dispersants used in the formulation of the lubricating composition may be ashless or ash-forming in nature. Preferably, the dispersant is ashless. So-called ashless dispersants are organic materials that form substantially no ash upon combustion. For example, non-metal-containing or borated metal-free dispersants are considered ashless. In contrast, metal-containing detergents form ash upon combustion.

[0080] Suitable dispersants typically contain a polar group attached to a relatively high molecular weight hydrocarbon chain. The polar group typically contains at least one element of nitrogen, oxygen, or phosphorus. Typical hydrocarbon chains contain 50 to 400 carbon atoms.

[0081] Chemically, many dispersants may be characterized as phenates, sulfonates, sulfurized phenates, salicylates, naphthenates, stearates, carbamates, thiocarbamates, phosphorus derivatives. A particularly useful class of

dispersants are the alkenylsuccinic derivatives, typically produced by the reaction of a long chain hydrocarbyl substituted succinic compound, usually a hydrocarbyl substituted succinic anhydride, with a polyhydroxy or polyamino compound. The long chain hydrocarbyl group constituting the oleophilic portion of the molecule which confers solubility in the oil, is normally a polyisobutylene group. Many examples of this type of dispersant are well known commercially and in the literature. Exemplary U.S. patents describing such dispersants are U.S. Patent 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 dispersant are described in U.S. Patent 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 dispersants may be found, for example, in European Patent Application No. 471 071, to which reference is made for this purpose.

[0082] Hydrocarbyl-substituted succinic acid and hydrocarbyl-substituted succinic anhydride derivatives are useful 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.

[0083] Succinimides are formed by the condensation reaction between hydrocarbyl substituted succinic anhydrides and amines. Molar ratios can vary depending on the polyamine. For example, the molar ratio of hydrocarbyl substituted succinic anhydride to TEPA can vary from 1:1 to 5:1. Representative examples are shown in U.S. Patent 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 Patent No. 1,094,044.

[0084] Succinate esters are formed by the condensation reaction between hydrocarbyl substituted succinic anhydrides and alcohols or polyols. Molar ratios can vary depending on the alcohol or polyol used. For example, the condensation product of a hydrocarbyl substituted succinic anhydride and pentaerythritol is a useful dispersant.

[0085] Succinate ester amides are formed by condensation reaction between hydrocarbyl substituted succinic anhydrides and alkanol amines. For example, suitable alkanol amines include ethoxylated polyalkylpolyamines, propoxylated polyalkylpolyamines and polyalkenylpolyamines such as polyethylene polyamines. One example is propoxylated hexamethylenediamine. Representative examples are shown in U.S. Patent No. 4,426,305.

[0086] The molecular weight of the hydrocarbyl substituted succinic anhydrides used in the preceding paragraphs will typically range between 800 and 2,500 or more. The above products can be post-reacted with various reagents such as sulfur, oxygen, formaldehyde, carboxylic acids such as oleic acid. The above products can also be post reacted with boron compounds such as boric acid, borate esters or highly borated dispersants, to form borated dispersants generally having from 0.1 to 5 moles of boron per mole of dispersant reaction product.

[0087] Mannich base dispersants are made from the reaction of alkylphenols, formaldehyde, and amines. See U.S. Patent No. 4,767,551, which is incorporated herein by reference. Process aids and catalysts, such as oleic acid and sulfonic acids, can also be part of the reaction mixture. Molecular weights of the alkylphenols range from 800 to 2,500. Representative examples are

shown in U.S. Patent Nos. 3,697,574; 3,703,536; 3,704,308; 3,751,365; 3,756,953; 3,798,165; and 3,803,039.

[0088] 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[®]₂ group-containing reactants.

[0089] Hydrocarbyl substituted amine ashless dispersant additives are well known to one skilled in the art; see, for example, U.S. Patent Nos. 3,275,554; 3,438,757; 3,565,804; 3,755,433, 3,822,209, and 5,084,197.

[0090] Preferred dispersants include borated and non-borated succinimides, including those derivatives from mono-succinimides, bis-succinimides, and/or mixtures of mono- and bis-succinimides, wherein the hydrocarbyl succinimide is derived from a hydrocarbylene group such as polyisobutylene having a Mn of from 500 to 5000 or a mixture of such hydrocarbylene groups, often with high terminal vinylic 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 0.1 to 20 weight percent, preferably 0.5 to 8 weight percent.

[0091] As used herein, the dispersant concentrations are given on an “as delivered” basis. Typically, the active dispersant is delivered with a process oil. The “as delivered” dispersant typically contains from 20 weight percent to 80 weight percent, or from 40 weight percent to 60 weight percent, of active dispersant in the “as delivered” dispersant product.

Antioxidants

[0092] Antioxidants retard the oxidative degradation of base oils during service. Such degradation may result in deposits on metal surfaces, the presence of sludge, or a viscosity increase in the lubricant. One skilled in the art knows a wide variety of oxidation inhibitors that are useful in lubricating compositions. See, Klamann in *Lubricants and Related Products*, op cite, and U.S. Patent Nos. 4,798,684 and 5,084,197, for example.

[0093] 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 C₆+ alkyl groups and the alkylene coupled derivatives of these hindered phenols. Examples of phenolic materials of this type 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-t-butyl-4-heptyl phenol; and 2-methyl-6-t-butyl-4-dodecyl phenol. Other useful hindered mono-phenolic antioxidants may include for example hindered 2,6-di-alkyl-phenolic propionic ester derivatives. Bis-phenolic antioxidants may also be advantageously used in combination with the instant 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).

[0094] Non-phenolic oxidation inhibitors which may be used include aromatic amine antioxidants and these may be used either as such or in combination with phenolics. Typical examples of non-phenolic antioxidants include: alkylated and non-alkylated aromatic amines such as aromatic monoamines of the formula $R^8R^9R^{10}N$ where R^8 is an aliphatic, aromatic or substituted aromatic group, R^9 is an aromatic or a substituted aromatic group, and R^{10} is H, alkyl, aryl or $R^{11}S(O)_xR^{12}$ where R^{11} is an alkylene, alkenylene, or aralkylene group, R^{12} is a higher alkyl group, or an alkenyl, aryl, or alkaryl group, and x is 0, 1 or 2. The aliphatic group R^8 may contain from 1 to 20 carbon atoms, and preferably contains from 6 to 12 carbon atoms. The aliphatic group is a saturated aliphatic group. Preferably, both R^8 and R^9 are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring aromatic group such as naphthyl. Aromatic groups R^8 and R^9 may be joined together with other groups such as S.

[0095] 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 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-alpha-naphthylamine; phenyl-alphanaphthylamine; and p-octylphenyl-alpha-naphthylamine.

[0096] Sulfurized alkyl phenols and alkali or alkaline earth metal salts thereof also are useful antioxidants.

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[0097] 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 weight percent, preferably 0.01 to 1.5 weight percent, more preferably zero to less than 1.5 weight percent, most preferably zero.

Pour Point Depressants (PPDs)

[0098] Conventional pour point depressants (also known as lube oil flow improvers) may be added to the compositions of the present disclosure if desired. These pour point depressant may be added to lubricating compositions of the present disclosure to lower the minimum temperature at which the fluid will flow or can be poured. Examples of suitable pour point depressants include polymethacrylates, polyacrylates, polyarylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, and terpolymers of dialkylfumarates, vinyl esters of fatty acids and allyl vinyl ethers. U.S. Patent 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 weight percent, preferably 0.01 to 1.5 weight percent.

Antifoam Agents

[0099] Antifoam agents may advantageously be added to lubricant compositions. These agents retard the formation of stable foams. Silicones and organic polymers are typical antifoam agents. For example, polysiloxanes, such as silicon oil or polydimethyl siloxane, provide antifoam properties. Antifoam agents are commercially available and may be used in conventional minor amounts along with other additives such as demulsifiers; usually the amount of

these additives combined is less than 1 weight percent and often less than 0.1 weight percent.

Corrosion Inhibitors and Antirust Additives

[00100] 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.

[00101] 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 weight percent, preferably 0.01 to 1.5 weight percent.

Solubility Improvers

[00102] Solubility improvers are additives that confer solubility to the oil. A wide variety of these additives are commercially available. Solubility improvers are liquid with aniline points less than 115°C, preferably less than 110°C, and more preferably less than 105°C, compatible with lubricating base oils. Examples of solubility improvers include mineral oils and synthetic lubricants such as alkylated aromatics, organic esters, naphthenics, and the like. The solubility improvers can be used in an amount of from 0 to 20 weight percent, preferably from 0 to 15 weight percent, and more preferably from 0 to 10 weight percent.

[00103] When lubricating compositions contain one or more of the additives discussed above, the additive(s) are blended into the composition in an amount sufficient for it to perform its intended function. Typical amounts of such additives useful in the present disclosure are shown in Table 2 below.

[00104] It is noted that many of the additives are shipped from the additive manufacturer as a concentrate, containing one or more additives together, with a certain amount of base oil diluents. Accordingly, the weight amounts in the table below, as well as other amounts mentioned herein, are directed to the amount of active ingredient (that is the non-diluent portion of the ingredient). The weight percent (wt%) indicated below is based on the total weight of the lubricating composition.

Table 2
Typical Amounts of Other Lubricating Components

| Compound | Approximate wt% (Useful) | Approximate wt% (Preferred) |
|---|--------------------------------|--------------------------------|
| Dispersant | 0.1-1.0 | 0.1-1.0 |
| Antioxidant | 0.1-5 | 0.1-1.5 |
| Pour Point Depressant (PPD) | 0.0-5 | 0.01-1.5 |
| Antifoam Agent | 0.001-3 | 0.001-0.15 |
| Viscosity Index Improver (solid polymer basis) | 0.1-10.0 | 0.1-8.0 |
| Antiwear | 0.01-1.2 | 0.01-1 |
| Corrosion Inhibitor and Antirust | 0.01-5 | 0.01-1.5 |

[00105] The foregoing additives are all commercially available materials. These additives may be added independently but are usually precombined in packages which can be obtained from suppliers of lubricant oil additives. Additive packages with a variety of ingredients, proportions and characteristics are available and selection of the appropriate package will take the requisite use of the ultimate composition into account.

[00106] The method and lubricating composition of the disclosure may be suitable hydraulic fluids, turbine oils, industrial fluids, circulating oils, or combinations thereof. In different embodiments, the lubricating composition is suitable for various mechanical devices including industrial systems, hydraulic

systems or turbines. In one embodiment the lubricating composition is suitable for a hydraulic system.

[00107] In some embodiments, the methods and compositions of the disclosure are used in a hydraulic pump. In one embodiment, the pump is a hydraulic piston pump. In one embodiment, the pump is a vane pump. In another embodiment, the pump is a hydraulic hybrid piston and vane pump. In other embodiments, the methods and compositions of the disclosure are used in turbines.

[00108] In one set of embodiments, the hydraulic fluid and turbine oil of the disclosure contain a Group III oil as described herein, and an additive package containing a dispersant (optional), at least one antioxidant, at least one antiwear additive (optional), an antifoam agent, a corrosion inhibitor, and a metal deactivator. Such additive packages may be present at any of the ranges described above, or at 0.04 to 3 wt %.

[00109] While we have shown and described several embodiments in accordance with our disclosure, it is to be clearly understood that the same may be susceptible to numerous changes apparent to one skilled in the art. Therefore, we do not wish to be limited to the details shown and described but intend to show all changes and modifications that come within the scope of the appended claims.

EXAMPLES

[00110] Varnish deposits from oxidation byproducts of hydraulic fluids in service severely impacts the performance of the hydraulic system and can reduce the efficiency and productivity of the lubricant end user. Varnish control of a

hydraulic fluid is assessed in a controlled hydraulic system operating at constant temperature and pressure and the presence of metal catalysts and water contamination by rating the cleanliness of the oil reservoir of the system periodically. The time to failure is determined to be the number of hours for the CRC rating of varnish on the reservoir to reach 7.

[00111] The test rig used to evaluate the fluids was a typical hydraulic circuit composed of a reservoir, hydraulic pump, relief valve, heat exchanger, and filter element. The fluid temperature was kept between 170°F and 180°F and exposed to water, debris, airborne particulates, and metal catalyst. Photographs of the reservoirs were taken periodically to determine the extent of varnish according to the CRC rating scale.

[00112] Table 3 shows results from the testing. Improvement was shown in varnish control of Shell QHVI base oil formulated hydraulic oils over other Group I and Group III base oil formulations.

Table 3

| Base Oil | Time to Failure | Result |
|------------------------|-----------------|---|
| Group I | 1800 hours | |
| Group III (Yubase) | 3375 hours | Expected improvement versus Group I |
| Group III (Shell QHVI) | 4625 hours | Unexpected improvement versus another Group III basestock |

[00113] Fig. 1 shows photographs taken to determine the extent of varnish deposit according to the CRC rating scale. The photographs are of the bottom of the fluid reservoir after 3750 hours of testing. The left reservoir contained a hydraulic fluid using API Group III base oil, Shell QHVI. The right reservoir

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contained a hydraulic fluid using API Group III base oil, Yubase. Both fluids used the same additive chemistry.

[00114] A turbine oil formulation was evaluated in a similar pump test as the hydraulic fluid above.

[00115] Fig. 2 shows photographs taken to determine the extent of varnish deposit according to the CRC rating scale. The photographs are of the bottom of the fluid reservoir after 2000 hours of testing. The right reservoir contained a turbine oil using API Group III base oil, Shell QHVI. The left reservoir contained a turbine oil using API Group III base oil, Yubase. Both fluids used the same additive chemistry. The CRC rating for varnish for the turbine oil using API Group III base oil, Shell QHVI, was 9.3, and the CRC rating for varnish for the turbine oil using API Group III base oil, Yubase, was 7.6. For the turbine oil test, a 1-10 CRC rating system was used with 10 being the cleanest. The results are shown in Table 4.

Table 4

| Base Oil | CRC Rating @ 2000 hrs | Result |
|---------------------------|--------------------------|--|
| Group III (Yubase) | 7.6 | |
| Group III (Shell QHVI) | 9.3 | Unexpected improvement versus another Group III basestock |

[00116] All patents and patent applications, test procedures (such as ASTM methods, UL methods, and the like), and other documents cited herein are fully incorporated by reference to the extent such disclosure is not inconsistent with this disclosure and for all jurisdictions in which such incorporation is permitted.

[00117] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated. While the illustrative embodiments of the disclosure 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 examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present disclosure, including all features which would be treated as equivalents thereof by those skilled in the art to which the disclosure pertains.

[00118] The present disclosure has been described above with reference to numerous embodiments and specific examples. Many variations will suggest themselves to those skilled in this art in light of the above detailed description. All such obvious variations are within the full intended scope of the appended claims.

CLAIMS:

1. A method for improving varnish control in a mechanical device requiring hydraulic fluids, turbine oils, industrial fluids, circulating oils, or combinations thereof, said method comprising:

supplying the mechanical device with a lubricating composition comprising a Group III lubricating oil base stock;

wherein the Group III lubricating oil base stock has a viscosity from 3.8 to 8.5 mm²/s at 100°C, a viscosity index greater than 120, a sulfur content less than 0.0003 weight percent, and an aromatic hydrocarbon content less than 0.2 weight percent, based on the total weight of the Group III lubricating oil base stock; and

wherein varnish reduction properties are improved as compared to varnish reduction properties achieved using a lubricating composition containing a different Group III lubricating oil base stock.

2. The method of clause 1 wherein the Group III lubricating oil base stock has a viscosity from 4.0 to 8.3 mm²/s at 100°C, a viscosity index greater than 125, a sulfur content less than 0.0002 weight percent, and an aromatic hydrocarbon content less than 0.18 weight percent, based on the total weight of the Group III lubricating oil base stock.

3. The method of clauses 1 and 2 wherein the Group III lubricating oil base stock contains consecutive carbon numbers, and is a Gas-to-Liquids (GTL) oil base stock or a Fischer-Tropsch wax derived oil base stock.

4. The method of clauses 1-3 wherein the lubricating composition further comprises (i) a Group II co-base stock; wherein the Group II co-base stock has a viscosity from 6.5 to 11.0 mm²/s at 40°C, is isoparaffinic, and is produced from natural gas and subsequent wax isomerization; or (ii) a heavy Group II base stock

having a viscosity from 10.0 to 13.0 mm²/s at 100°C, a viscosity index greater than 90, a sulfur content less than 0.001 weight percent, and saturates content greater than 99%.

5. The method of clauses 1-4 wherein the Group III lubricating oil base stock is present in an amount from 80 weight percent to 99 weight percent, based on the total weight of the lubricating composition.

6. The method of clauses 1-5 wherein the lubricating composition further comprises at least one of an antiwear additive, viscosity index improver, antioxidant, dispersant, pour point depressant, corrosion inhibitor, metal deactivator, seal compatibility additive, antifoam agent, co-base stock, pour point depressant, seal compatibility additive, solubility improver, and antirust additive.

7. The method of clauses 1-6 wherein the mechanical device is a hydraulic system or a turbine system.

8. A lubricating composition comprising:

a Group III lubricating oil base stock, wherein the Group III lubricating oil base stock has a viscosity from 3.8 to 8.5 mm²/s at 100°C, a viscosity index greater than 120, a sulfur content less than 0.0003 weight percent, and an aromatic hydrocarbon content less than 0.2 weight percent, based on the total weight of the Group III lubricating oil base stock; and

optionally one or more of an additive, viscosity index improver, antioxidant, dispersant, pour point depressant, corrosion inhibitor, metal deactivator, seal compatibility additive, antifoam agent, co-base stock, pour point depressant, seal compatibility additive, solubility improver, and antirust additive;

wherein, in a mechanical device supplied with the lubricating composition, varnish reduction properties are improved as compared to varnish

reduction properties achieved using a lubricating composition containing a different Group III lubricating oil base stock.

9. The lubricating composition of clause 8 which is a hydraulic fluid, turbine oil, industrial fluid, circulating oil, or combination thereof.

10. The lubricating composition of clauses 8 and 9 wherein the Group III lubricating oil base stock has a viscosity from 4.0 to 8.3 mm²/s at 100°C, a viscosity index greater than 125, a sulfur content less than 0.0002 weight percent, and an aromatic hydrocarbon content less than 0.18 weight percent, based on the total weight of the Group III lubricating oil base stock.

11. The lubricating composition of clauses 8-10 wherein the Group III lubricating oil base stock contains consecutive carbon numbers, and is a Gas-to-Liquids (GTL) oil base stock or a Fischer-Tropsch wax derived oil base stock.

12. The lubricating composition of clauses 8-11 wherein the lubricating composition further comprises (i) a Group II co-base stock; wherein the Group II co-base stock has a viscosity from 6.5 to 11.0 mm²/s at 40°C, is isoparaffinic, and is produced from natural gas and subsequent wax isomerization; or (ii) a heavy Group II base stock having a viscosity from 10.0 to 13.0 mm²/s at 100°C, a viscosity index greater than 90, a sulfur content less than 0.001 weight percent, and saturates content greater than 99%.

13. The lubricating composition of clauses 8-12 wherein the Group III lubricating oil base stock is present in an amount from 80 weight percent to 99 weight percent, based on the total weight of the lubricating composition.

14. The lubricating composition of clauses 8-13 wherein the improved varnish reduction properties are rated according to a Coordinating Research Council

(CRC) rating scale, the sulfur content is determined according to ASTM D2622, and the aromatic hydrocarbon content is determined according to ASTM D7419.

15. The lubricating composition of clauses 8-14 wherein the mechanical device is a hydraulic system or a turbine system.

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FIG. 1

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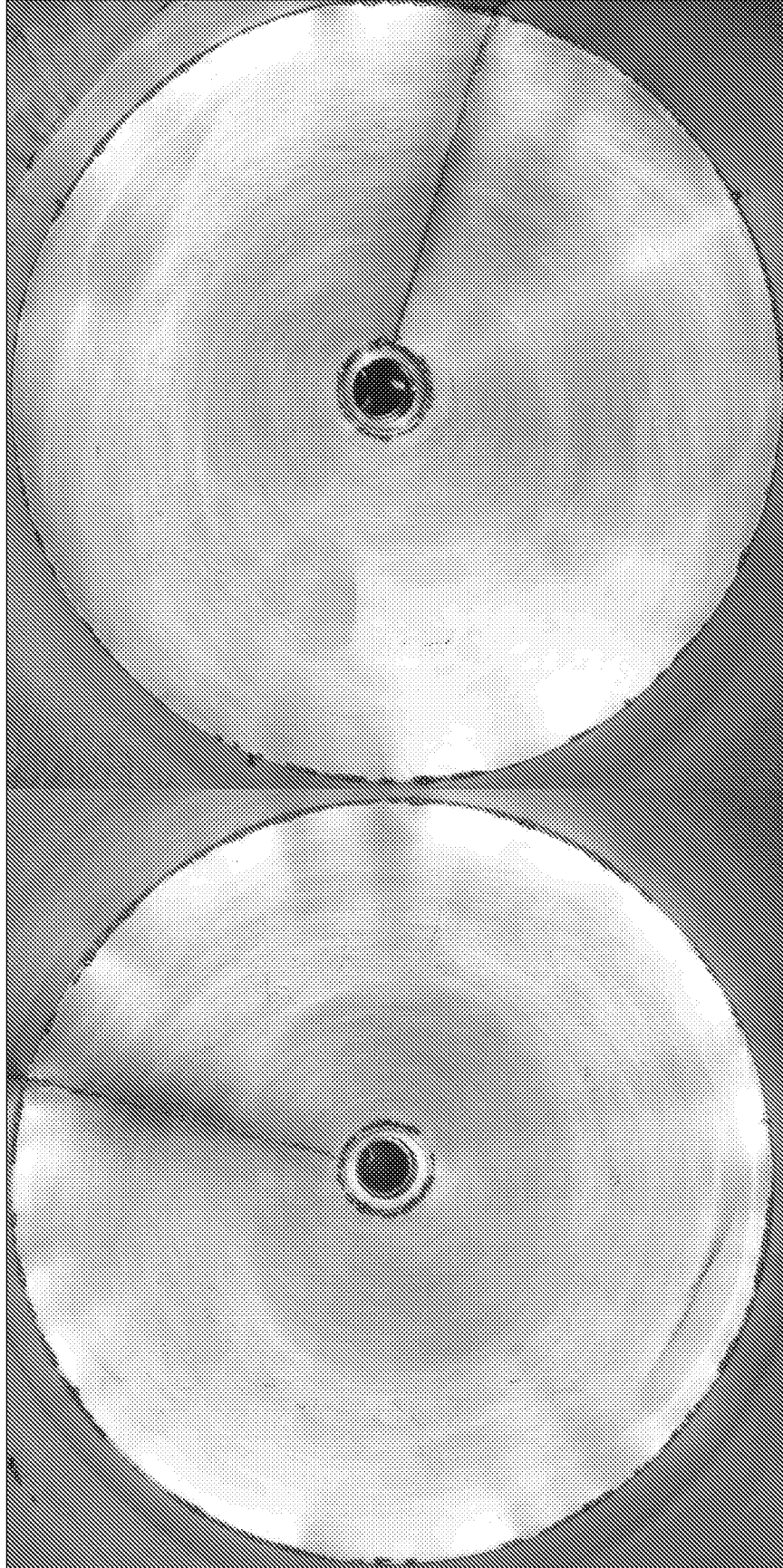


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/055656

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M107/02 C10M111/04
ADD.

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)
C10M C10N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, COMPENDEX, WPI Data

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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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| Date of the actual completion of the international search | Date of mailing of the international search report |
| 21 November 2014 | 05/12/2014 |

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/055656

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