LUBRICANT COMPOSITIONS HAVING IMPROVED RATES OF AIR RELEASE

FIELD OF THE INVENTION

[001] The invention relates to lubricant compositions exhibiting good rates of air release. More particularly, the invention relates to lubricant compositions having low ash, sulfur and phosphorous content and good rates of air release.

BACKGROUND OF THE INVENTION

[002] Lubricating oils, including hydraulic oils and crankcase oils, often are used in environments in which the oil is subject to mechanical agitation in the presence of air. As a consequence, the air becomes entrained in the oil and also forms a foam.

[003] Foam appears on the surface of an oil as air bubbles greater than 1 mm in diameter. Air entrainment generally refers to the dispersion within the oil of air bubbles less than 1 mm in diameter.

[004] Air entrainment and foaming in lubricating compositions are undesirable phenomena. For example, air entrainment reduces the bulk modulus of the fluid resulting in spongy operation and poor control of a hydraulic system's response. It can result in reduced viscosity of a lubricating composition. Both air entrainment and foaming can contribute to fluid deterioration due to enhanced oil oxidation.

[005] Air entrainment, however, is more problematic than foaming. Foaming is typically depressed in lubricating compositions by the use of antifoamant additives. These additives expedite the breakup of a foam, but they do not inhibit air entrainment. Indeed, some antifoamants, such as silicone oils typically used

in diesel and automotive crankcase oils, are known to retard air release. The rate of air release and amount of air entrainment of lubricating compositions may be determined by the test method of ASTM D 3427. Indeed, the rate of air release referred to herein has been determined by that method.

[006] US Patent 6,090,758 discloses that foaming in a lubricant comprising a slack wax isomerate is effectively reduced by use of an antifoamant exhibiting a spreading coefficient of about 2 mN/m without increasing the air release time. While the specified antifoamant does not degrade the air release time, further improvements in enhancing air release characteristics are desirable.

[007] Many modern gasoline and diesel engines are designed to use the crankcase oil to function as a hydraulic fluid to operate fuel injectors, valve train controls and the like. For these functions, low air entrainment and rapid air release are indicative of high performance lubricants. Indeed, it is anticipated that the rate of air release from engine lubricants will become more critical in the future to the proper operation of internal combustion engines as engine designs evolve and become ever more complex.

[008] US Patent 6,713,438 discloses a lubricating oil composition that exhibits improved air release characteristics. The composition comprises a basestock, typically a polyalphaolefin (PAO), and two polymers of different molecular weight. One of the polymers is a viscoelastic fluid having a shear stress greater than ll kPa such as a high VI PAO, and the other preferably is a block copolymer.

[009] US Patent Publication No. US 2006/0116302 describes a detergent additive for lubricating oil compositions that comprises at least two of low, high and medium TBN (total base number) detergents, preferably calcium salicylate detergents. No reference is made to the air release properties of lubricants

formulated with the mixed detergents. Indeed, the claimed benefits of the mixed detergents related to piston cleanliness, film forming tendency and frictional properties.

[010] Various government and manufacturer's requirements have created a need for lubricants that contain reduced amounts of ash, sulfur and phosphorous. Reduced amounts of sulfur and phosphorous in an oil are known, for example, to have a beneficial effect on emission control catalysts in combustion engine systems.

[011] One objective of the present invention is to provide a low ash, sulfur and phosphorous lubricating composition that exhibits good air release rates. Other objectives of the invention will become apparent from the description which follows.

SUMMARY OF THE INVENTION

[012] It has now been discovered that the rate of air release of lubricating oil compositions can be enhanced by formulating the composition with one or more salicylate detergents.

[013] Thus, one aspect of the invention comprises a method for improving the rate of air release of a lubricating composition comprising a major amount of an oil of lubricating viscosity and a minor amount of a detergent or mixture of detergents, the method comprising using as the detergent or mixture of detergents one or more salicylate detergents.

[014] Another aspect of the invention is a lubricating composition comprising:

(a) a major amount of an oil of lubricating viscosity,

(b) one or more salicylate detergents in an amount sufficient to provide the lubricating composition with a TBN in the range of about 4 to about 8, and

(c) a minor amount of one or more lubricant additives, the composition having less than about 0.8 wt% sulfated ash content and substantially free of a viscoelastic fluid having both a shear stress greater than 11 kPa and a kinematic viscosity greater than about 30 cSt at 100°C.

In another aspect, lubricating oil compositions formulated according to the invention are particularly useful as crankcase lubricants in engines wherein the lubricant provides a lubricating and a hydraulic function.

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

BRIEF DESCRIPTION OF THE DRAWING

[016] The accompanying sole figure is a bar graph illustrating the invention.

DETAILED DESCRIPTION OF THE INVENTION

[017] Throughout the specification, the specific properties referred to have been determined by the following methods:

(1) Air release rate -- ASTM D 3427

(2) TBN or total base number -- ASTM D 2896

(3) Kinematic viscosity at 40°C and 100°C -- ASTM D 445

(4) Viscosity index -- ASTM D 2270

(5) Sulfated ash – ASTM D 874

(6) Sulfur – ASTM D 6443

(7) Phosphorous – ASTM D 4951

(8) Shear stress -- measured as per SAE Paper No. 872043

[018] For convenience, the invention will be described by reference to engine oils such as gas, gasoline and diesel fueled internal combustion engine oils; however, it should be appreciated that the invention is applicable to other oils where the air release rate is an important property. Examples of such oils include gear oil, industrial fluids, automatic transmission fluids and the like.

[019] A key advantage of the present invention is that it provides a method to enhance the air release rate of a lubricating composition by formulating the lubricating composition with one or more salicylate detergents.

[020] Lubricating compositions to which the invention is applicable are especially those comprising one or more oils of lubricating viscosity selected from Group II, III, IV and V base stocks. The base stock groups are defined in the American Petroleum Institute Publication "Engine Oil Licensing and Certification System," Fourteenth Edition, December 1966, Addendum 1, December 1998.

[021] The base stock typically will have a viscosity of about 3 to 12, preferably 4 to 10, and more preferably 4.5 to 8 mm^2/s (cSt) at 100°C.

[022] Group II base stocks generally have a viscosity index (VI) of between about 80 and 120 and contain 0.03 wt% sulfur or less and 90 wt% or more saturates. Group III base stocks generally have a VI greater than about 120, 0.03 wt% or less sulfur and 90 wt% or more saturates. Group IV base stocks are polyalphaolefins (PAO). Group V base stocks are all other base stocks not included in Groups I, II, III or IV, such as esters and alkyl aromatics. A particularly suitable Group III base stock is a gas-to-liquid (GTL) base stock such as a base stock derived from a waxy hydrocarbon produced in a Fischer-Tropsch (F-T) process.

[023] As is known to those skilled in the art, in an F-T synthesis process, a synthesis gas comprising a mixture of H_2 and CO is catalytically converted into hydrocarbons and preferably liquid hydrocarbons. The mole ratio of the hydrogen to the carbon monoxide may broadly range from about 0.5 to 4, but which is more typically within the range of from about 0.7 to 2.75 and preferably from about 0.7 to 2.5. As is well known, F-T synthesis processes include processes in which the catalyst is in the form of a fixed bed, a fluidized bed or as a slurry of catalyst particles in a hydrocarbon slurry liquid.

[024] The stoichiometric mole ratio for an F-T synthesis reaction is 2.0, but there are many reasons for using other than a stoichiometric ratio as those skilled in the art know. In cobalt slurry hydrocarbon synthesis process the feed mole ratio of the H_2 to CO is typically about 2.1/1. The synthesis gas comprising a mixture of H_2 and CO is bubbled up into the bottom of the slurry and reacts in the presence of the particulate F-T synthesis catalyst in the slurry liquid at conditions effective to form hydrocarbons, a portion of which are liquid at the reaction conditions and which comprise the hydrocarbon slurry liquid. The synthesized hydrocarbon liquid is separated from the catalyst particles as filtrate by means such as filtration, although other separation means such as centrifugation can be used.

[025] Some of the synthesized hydrocarbons pass out the top of the hydrocarbon synthesis reactor as vapor, along with unreacted synthesis gas and other gaseous reaction products. Some of these overhead hydrocarbon vapors are typically condensed to liquid and combined with the hydrocarbon liquid filtrate. Thus, the initial boiling point of the filtrate may vary depending on whether or not some of the condensed hydrocarbon vapors have been combined with it. Slurry hydrocarbon synthesis process conditions vary somewhat depending on the catalyst and desired products.

[026] Typical conditions effective to form hydrocarbons comprising mostly C_{5+} paraffins, (e.g., C_{5+}-C_{200}) and preferably C_{10+} paraffins, in a slurry hydrocarbon synthesis process employing a catalyst comprising a supported cobalt component include, for example, temperatures, pressures and hourly gas space velocities in the range of from about 320-850°F, 80-600 psi and 100-40,000 V/hr/V, expressed as standard volumes of the gaseous CO and H_2 mixture (0°C, 1 atm) per hour per volume of catalyst, respectively. The term "C_{5+}" is used herein to refer to hydrocarbons with a carbon number of greater than 4, but does not imply that material with carbon number 5 has to be present. Similarly other ranges quoted for carbon number do not imply that hydrocarbons having the limit values of the carbon number range have to be present, or that every carbon number in the quoted range is present. It is preferred that the hydrocarbon synthesis reaction be conducted under conditions in which limited or no water gas shift reaction occurs and more preferably with no water gas shift reaction occurring during the hydrocarbon synthesis. It is also preferred to conduct the reaction under conditions to achieve an alpha of at least 0.85, preferably at least 0.9 and more preferably at least 0.92, so as to synthesize more of the more desirable higher molecular weight hydrocarbons. This has been achieved in a slurry process using a catalyst containing a catalytic cobalt component. Those skilled in the art know that by alpha is meant the Schultz-Flory kinetic alpha. While suitable F-T reaction types of catalyst comprise, for example, one or more Group VIII catalytic metals such as Fe, Ni, Co, Ru and Re, it is preferred that the catalyst comprise a cobalt catalytic component. In one embodiment the catalyst comprises catalytically effective amounts of Co and one or more of Re, Ru, Fe, Ni, Th, Zr, Hf, U, Mg and La on a suitable inorganic support material, preferably one which comprises one or more refractory metal oxides. Preferred supports for Co containing catalysts comprise titania. Particularly useful catalysts and their preparation are known and illustrative, but nonlimiting examples may be found,

for example, in U.S. Pat. Nos. 4,568,663; 4,663,305; 4,542,122; 4,621,072 and 5,545,674.

[027] The waxy hydrocarbon produced in the F-T synthesis process, i.e., the F-T wax, preferably has an initial boiling point in the range of from 650°F to 750°F and preferably boils up to an end point of at least 1050°F. When a boiling range is quoted herein it defines the lower and/or upper distillation temperature used to separate the fraction. Unless specifically stated (for example, by specifying that the fraction boils continuously or constitutes the entire range) the specification of a boiling range does not require any material at the specified limit has to be present, rather it excludes material boiling outside that range.

[028] The waxy feed preferably comprises the entire 650-750°F+ fraction formed by the hydrocarbon synthesis process, having an initial cut point between 650°F and 750°F determined by the practitioner and an end point, preferably above 1050°F, determined by the catalyst and process variables employed by the practitioner for the synthesis. Such fractions are referred to herein as "650-750°F+ fractions". By contrast, "650-750°F⁻ fractions" refers to a fraction with an unspecified initial cut point and an end point somewhere between 650°F and 750°F. Waxy feeds may be processed as the entire fraction or as subsets of the entire fraction prepared by distillation or other separation techniques. The waxy feed also typically comprises more than 90%, generally more than 95% and preferably more than 98 wt% paraffinic hydrocarbons, most of which are normal paraffins. It has negligible amounts of sulfur and nitrogen compounds (e.g., less than 1 wppm of each), with less than 2,000 wppm, preferably less than 1,000 wppm and more preferably less than 500 wppm of oxygen, in the form of oxygenates. Waxy feeds having these properties and useful in the process of the invention have been made using a slurry F-T process with a catalyst having a catalytic cobalt component, as previously indicated.

[029] The process of making the lubricating base oil from the F-T wax may be characterized as a hydrodewaxing process. This process may be operated in the presence of hydrogen, and hydrogen partial pressures range from about 600 to 6000 kPa. The ratio of hydrogen to the hydrocarbon feedstock (hydrogen circulation rate) typically range from about 10 to 3500 n.l.l.$^{-1}$ (56 to 19,660 SCF/bbl) and the space velocity of the feedstock typically ranges from about 0.1 to 20 LHSV, preferably 0.1 to 10 LHSV.

[030] Hydrodewaxing catalysts useful in the conversion of the n-paraffin waxy feedstocks disclosed herein to form the isoparaffinic hydrocarbon base oil are zeolite catalysts, such as ZSM-5, ZSM-11, ZSM-23, ZSM-35, ZSM-12, ZSM-38, ZSM-48, offretite, ferrierite, zeolite beta, zeolite theta, and zeolite alpha, as disclosed in USP 4,906,350. These catalysts are used in combination with Group VIII metals, in particular palladium or platinum. The Group VIII metals may be incorporated into the zeolite catalysts by conventional techniques, such as ion exchange.

[031] In one embodiment, conversion of the waxy feedstock may be conducted over a combination of Pt/zeolite beta and Pt/ZSM-23 catalysts in the presence of hydrogen. In another embodiment, the process of producing the lubricant oil base stocks comprises hydroisomerization and dewaxing over a single catalyst, such as Pt/ZSM-35. In yet another embodiment, the waxy feed can be fed over Group VIII metal loaded ZSM-48, preferably Group VIII noble metal loaded ZSM-48, more preferably Pt/ZSM-48 in either one stage or two stages. In any case, useful hydrocarbon base oil products may be obtained. Catalyst ZSM-48 is described in USP 5,075,269. The use of the Group VIII metal loaded ZSM-48 family of catalysts, preferably platinum on ZSM-48, in the hydroisomerization of the waxy feedstock eliminates the need for any subsequent, separate dewaxing step, and is preferred.

[032] A dewaxing step, when needed, may be accomplished using either well known solvent or catalytic dewaxing processes and either the entire hydro-isomerate or the 650-750°F+ fraction may be dewaxed, depending on the intended use of the 650-750°F- material present, if it has not been separated from the higher boiling material prior to the dewaxing. In solvent dewaxing, the hydroisomerate may be contacted with chilled solvents such as acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), mixtures of MEK/MIBK, or mixtures of MEK/toluene and the like, and further chilled to precipitate out the higher pour point material as a waxy solid which is then separated from the solvent-containing lube oil fraction which is the raffinate. The raffinate is typically further chilled in scraped surface chillers to remove more wax solids. Low molecular weight hydrocarbons, such as propane, are also used for dewaxing, in which the hydroisomerate is mixed with liquid propane, a least a portion of which is flashed off to chill down the hydroisomerate to precipitate out the wax. The wax is separated from the raffinate by filtration, membrane separation or centrifugation. The solvent is then stripped out of the raffinate, which is then fractionated to produce the preferred base stocks useful in the present invention. Also well known is catalytic dewaxing, in which the hydroisomerate is reacted with hydrogen in the presence of a suitable dewaxing catalyst at conditions effective to lower the pour point of the hydroisomerate. Catalytic dewaxing also converts a portion of the hydroisomerate to lower boiling materials, in the boiling range, for example, 650-750°F-, which are separated from the heavier 650-750°F+ base stock fraction and the base stock fraction fractionated into two or more base stocks. Separation of the lower boiling material may be accomplished either prior to or during fractionation of the 650-750°F+ material into the desired base stocks.

[033] Any dewaxing catalyst which will reduce the pour point of the hydroisomerate and preferably those which provide a large yield of lube oil base stock from the hydroisomerate may be used. These include shape selective molecular sieves which, when combined with at least one catalytic metal component, have been demonstrated as useful for dewaxing petroleum oil fractions and include, for example, ferrierite, mordenite, ZSM-5, ZSM-11, ZSM-23, ZSM-35, ZSM-22 also known as theta one or TON, and the silicoaluminophosphates known as SAPO's. A dewaxing catalyst which has been found to be unexpectedly particularly effective comprises a noble metal, preferably Pt, composited with H-mordenite. The dewaxing may be accomplished with the catalyst in a fixed, fluid or slurry bed. Typical dewaxing conditions include a temperature in the range of from about 400-600°F, a pressure of 500-900 psig, H_2 treat rate of 1500-3500 SCF/B for flow-through reactors and LHSV of 0.1-10, preferably 0.2-2.0. The dewaxing is typically conducted to convert no more than 40 wt% and preferably no more than 30 wt% of the hydroisomerate having an initial boiling point in the range of 650-750°F to material boiling below its initial boiling point.

[034] The GTL base stock suitable for use in the invention will have a kinematic viscosity in the range of about 2 to 50 mm^2/s at 100°C and preferably in the range of about 3.5 to 30 mm^2/s at 100°C and a VI greater than about 130, preferably greater than 135 and more preferably 140 or greater.

[035] The GTL base stock of the invention is further characterized as having a pour point of -5°C or lower, preferably about -10°C or lower and under some conditions advantageously having pour points of about -25°C to about -40°C. A preferred GTL base stock is one comprising paraffinic hydrocarbon components in which the extent of branching, as measured by the percentage of methyl hydrogens (BI), and the proximity of branching, as measured by the percentage

of recurring methylene carbons which are four or more carbons removed from an end group or branch ($CH_2 \geq 4$), are such that: (a) BI-0.5($CH_2 \geq 4$) >15; and (b) BI+0.85($CH_2 \geq 4$) <45 as measured over said liquid hydrocarbon composition as a whole.

[036] The preferred GTL base stock can be further characterized, if necessary, as having less than 0.1 wt% aromatic hydrocarbons, less than 20 wppm nitrogen containing compounds, less than 20 wppm sulfur containing compounds, a pour point of less than -18°C, preferably less than -30°C, a preferred BI $\geq$ 25.4 and ($CH_2 \geq 4$) $\leq$ 22.5. They have a nominal boiling point of 370°C+, on average they average fewer than 10 hexyl or longer branches per 100 carbon atoms and on average have more than 16 methyl branches per 100 carbon atoms. They also can be characterized by a combination of dynamic viscosity, as measured by CCS at -40°C, and kinematic viscosity, as measured at 100°C represented by the formula: DV (at -40°C) < 2900 (KV @ 100°C) - 7000.

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

[038] In the above the Branching Index (BI), Branching Proximity ($CH_2 \geq 4$), and Free Carbon Index (FCI) are determined as follows:

Branching Index

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

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

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

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

Branching Proximity ($CH_2 \geq 4$)

[042] A 90.5 MHz^{3}CMR single pulse and 135 Distortionless Enhancement by Polarization Transfer (DEPT) NMR spectra are obtained on a Brucker 360 MHzAMX spectrometer using 10% solutions in $CDCL_3$. TMS is the internal chemical shift reference. $CDCL_3$ solvent gives a triplet located at 77.23 ppm in the ^{13}C spectrum. All single pulse spectra are obtained under quantitative

conditions using 45 degree pulses (6.3 μs), a pulse delay time of 60 s, which is at least five times the longest carbon spin-lattice relaxation time (T_1), to ensure complete relaxation of the sample, 200 scans to ensure good signal-to-noise ratios, and WALTZ-16 proton decoupling.

[043] The C atom types CH_3, CH_2, and CH are identified from the 135 DEPT ^{13}C NMR experiment. A major CH_2 resonance in all ^{13}C NMR spectra at ~29.8 ppm is due to equivalent recurring methylene carbons which are four or more removed from an end group or branch (CH2 > 4). The types of branches are determined based primarily on the ^{13}C chemical shifts for the methyl carbon at the end of the branch or the methylene carbon one removed from the methyl on the branch.

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

a. calculate the average carbon number of the molecules in the sample which is accomplished with sufficient accuracy for lubricating oil materials by simply dividing the molecular weight of the sample oil by 14 (the formula weight of CH_2);

b. divide the total carbon-13 integral area (chart divisions or area counts) by the average carbon number from step a. to obtain the integral area per carbon in the sample;

c. measure the area between 29.9 ppm and 29.6 ppm in the sample; and

d. divide by the integral area per carbon from step b. to obtain FCI.

[045] Branching measurements can be performed using any Fourier Transform NMR spectrometer. Preferably, the measurements are performed using a spectrometer having a magnet of 7.0T or greater. In all cases, after verification by Mass Spectrometry, UV or an NMR survey that aromatic carbons were absent, the spectral width was limited to the saturated carbon region, about 0-80 ppm vs. TMS (tetramethylsilane). Solutions of 15-25 percent by weight in chloroform-d1 were excited by 45 degrees pulses followed by a 0.8 sec acquisition time. In order to minimize non-uniform intensity data, the proton decoupler was gated off during a 10 sec delay prior to the excitation pulse and on during acquisition. Total experiment times ranged from 11-80 minutes. The DEPT and APT sequences were carried out according to literature descriptions with minor deviations described in the Varian or Bruker operating manuals.

[046] DEPT is Distortionless Enhancement by Polarization Transfer. DEPT does not show quaternaries. The DEPT 45 sequence gives a signal for all carbons bonded to protons. DEPT 90 shows CH carbons only. DEPT 135 shows CH and CH_3 up and CH_2 180 degrees out of phase (down). APT is Attached Proton Test. It allows all carbons to be seen, but if CH and CH_3 are up, then quaternaries and CH_2 are down. The sequences are useful in that every branch methyl should have a corresponding CH. And the methyls are clearly identified by chemical shift and phase. The branching properties of each sample are determined by C-13 NMR using the assumption in the calculations that the entire sample is isoparaffinic. Corrections are not made for n-paraffins or cyclo-paraffins, which may be present in the oil samples in varying amounts. The cycloparaffins content is measured using Field Ionization Mass Spectroscopy (FIMS).

[047] Suitable polyalphaolefins (PAOs) for use in compositions of the invention comprise relatively low molecular weight hydrogenated polymers or oligomers of alphaolefins such as C_2 to C_{32} alphaolefins with C_8 to C_{16} alphaolefins being preferred.

[048] The PAO base stocks are conveniently made by the polymerization of alphaolefins in the presence of a polymerization catalyst such as the Friedel-Crafts catalysts. Examples of PAO synthesis can be found in US 3,742,082; US 3,769,363; US 4,413,156; US 4,434,408; US 4,910,355; and US 4,956,122 to mention a few.

[049] A lubricating composition of the invention comprises a major amount of an oil of lubricating viscosity and especially one or more oils selected from Group II, Group III (including GTL), Group IV and Group V base stocks. By major amount is meant greater than 50 wt%, conveniently between 75 wt% to 90 wt% and preferably between 65 wt% to 80 wt%, based on the total weight of the lubricating composition. When a mixture of oils is used, preferably the mixture will comprise Group III and Group IV base stocks.

[050] According to the present invention, the air release rate of a lubricating composition comprising a major amount of an oil of lubricating viscosity and a minor amount of a detergent can be improved by using as the detergent one or more salicylate detergents. Suitable salicylate detergents include sulfur-free salicylate detergents, such as alkali and alkaline earth metal salts of alkyl salicylic acid and ashless salicylate detergents such as amides and esters of alkyl salicylic acid. Typically, the alkylsalicylic acid will have one or more alkyl groups of at least 8 carbon atoms in the alkyl groups with 10 to 20 carbon atoms often being preferred. In the case of ashless salicylate detergents, the alkyl groups of the amide will have from about 2 to about 50 carbon atoms and preferably 8 to 20 carbon atoms. The esters of alkyl salicylic acid will be formed

from alcohols having about 4 to about 20 carbon atoms and preferably 6 to 12 carbon atoms. These detergents may be neutral or overbased or mixtures thereof. Borated salicylate detergents may also be used.

[051] In the invention, it is preferred that the salicylate detergent constitutes the sole detergent in the composition. Preferably, the detergent is an alkaline earth metal salicylate and mixtures of calcium and magnesium salicylate or mixtures of calcium and magnesium salicylates, especially a calcium and magnesium salicylate.

[052] In one embodiment of the invention, three salicylate detergents are used, each with a different total base number (TBN). One detergent will have a TBN greater than 200; a second will have a TBN of about 100 to 200; and a third, a TBN of less than about 100. For example, in an especially preferred embodiment, the detergent comprises three calcium salicylate detergents, one with a 270 TBN, another with a 170 TBN and yet another with a 70 TBN. On an active ingredient basis, the composition according to this preferred embodiment would comprise each of the detergents in an amount of about 0.1 wt% to about 2 wt%, based on the total weight of the lubricating composition.

[053] In the compositions of the invention, the salicylate detergent(s) will typically be used in an amount sufficient to provide the composition with a TBN in the range of about 4 to 8 and preferably about 5 to 7. Conveniently, on an active ingredient basis, the composition will comprise about 1 wt% to about 6 wt% and preferably 1 wt% to 3 wt% salicylate detergent(s) based on the total weight of the composition.

[054] The instant invention can be used with additional lubricant components in effective amounts typically used in lubricant compositions such as alkyl-aromatic lubricant oils, and performance additives such as, for example but not

limited to, oxidation inhibitors, corrosion and rust inhibitors, metal deactivators, antiwear agents, extreme pressure additives, pour point depressants, wax modifiers, viscosity modifiers, lubricating agents, defoamants, demulsifiers and others.

[055] Examples of suitable antioxidants include aminic antioxidants and phenolic antioxidants. Typical aminic antioxidants include alkylated aromatic amines, especially those in which the alkyl group contains no more than 14 carbon atoms. Typical phenolic antioxidants include derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or p- position to each other and which contain alkyl substituents. Mixtures of phenolic and aminic antioxidants also may be used. Such additives may be used in an amount of about 0.02 to 5 wt%, and preferably about 0.1 wt% to about 2 wt% based on the total weight of the composition.

[056] Rust inhibitors selected from the group consisting of nonionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, and aminic alkyl sulfonic acids may be used. Corrosion inhibitors that may be used include benzotriazoles, tolyltriazoles and their derivatives.

[057] Suitable dispersants include succinimide dispersants, ester dispersants, ester-amide dispersants, and the like. Preferably, the dispersant is a succinimide dispersant, especially a polybutenyl succinimide. The molecular weight of the polybutenyl group may range from about 800 to about 4000 or more and preferably from about 1300 to about 2500. The dispersant may be head capped or borated or both.

[058] A commonly used class of antiwear additives is zinc dialkyldithiophosphates in which the alkyl groups typically have from 3 to about 18 carbon atoms with 3 to 10 carbon atoms being preferred. Suitable antifoam additives

include silicone oils or polysiloxane oils usually used in amounts of from 0.0001 to 0.01 wt% active ingredient. Pour point depressants are well known lubricant additives. Typical examples are dialkylfumarates, polyalkylmethacrylates, and the like. The number and types of friction modifiers are voluminous. In general, they include metal salts of fatty acids, glycerol esters and alkoxylated fatty amines to mention a few.

[059] Another additive often used in crankcase lubricants is a VI improver such as linear or radial styrene-isoprene VI improvers, olefin copolymers, polymethacrylates, and the like. In general, on an active ingredient basis, the various lubricant additives will comprise from about 0.5 wt% to about 25 wt% and preferably from about 2 wt% to about 10 wt% based on the total weight of the composition except where otherwise specified herein. The composition of the invention is substantially free of added viscoelastic fluids that have both a shear stress greater than 11 kPa and a kinematic viscosity greater than 30 cSt at 100°C. Any amount of such material that does not affect the air release rate of the composition may be present; however, it is preferred that the composition be totally free of such material.

Examples

[060] A series of multigrade, internal combustion, engine oils were prepared according to the formulations show in Table 1, in which PAO 6 is a polyalpha-olefin basestock with a KV at 100°C of 5.8 cSt. Different detergents were used in quantities providing engine oils with a TBN of 7. Each of the blends contained the same polybutenylsuccinimide dispersant zinc dialkyldithio-phosphate antiwear additive, ashless antioxidant, silicone defoamant, friction modifier and VI improving compounds in the same amounts (i.e., 15.47 wt% of the total composition). Additionally, a reference blend without detergent, but containing all other additives in the same amounts was prepared. All of the

blends were tested for air release rate according to ASTM D 3427. The results are shown graphically in the accompanying figure. As can be seen, salicylate detergents provide a significant performance benefit by quickly releasing entrained air.

Table 1

Common Additives	15.47	15.47	15.47	15.47	15.47
PAO 6 Basestock	84.53	81.03	81.71	82.17	82.81
P5090 Salicylate detergent	0	3.5	0	0	0
Calcium Phenate	0	0	2.82	0	0
Ca sulfonate	0	0	0	2.36	0
Mg sulfonate	0	0	0	0	1.72

[061] All US patents, applications and non-patent references cited in this application are hereby incorporated in their entirety by reference.

CLAIMS:

1. A method for improving the air release rate of a lubricating composition comprising a major amount of a lubricating base oil and one or more detergents, the method comprising using as the one or more detergents an alkyl salicylate detergent.

2. The method of Claim 1 wherein the one or more alkyl salicylate detergents are used in an amount sufficient to provide the composition with a TBN in the range of about 4 to about 8.

3. The method of Claim 2 wherein the alkyl salicylate detergent is an alkaline earth metal alkyl salicylate.

4. The method of Claim 3 wherein the alkaline earth metal is calcium.

5 . The method of Claim 3 wherein the alkaline earth metal is magnesium.

6. The method of Claim 2 wherein the alkyl salicylate detergent is an ashless nitrogen-containing detergent.

7. A lubricating composition comprising:

(a) a major amount of an oil of lubricating viscosity,

(b) one or more salicylate detergents in an amount sufficient to provide the composition with a TBN in the range of about 4 to about 8, and

(c) a minor amount of one or more lubricant additives,

the composition having less than about 0.8 wt% sulfated ash and being substantially free of a viscoelastic fluid, said fluid having both a shear stress greater than 11 kPa and a kinematic viscosity greater than 30 cSt at 100°C.

8. The composition of Claim 7 wherein the salicylate detergent is an alkali or alkaline earth metal salt of an alkyl salicylic acid having one or more alkyl groups of at least 8 carbon atoms.

9. The composition of Claim 8 wherein the salicylate detergent is a calcium salicylate.

10. The composition of Claim 9 wherein the composition has a TBN of from 5 to 7.

11. The composition of Claim 10 wherein the calcium salicylate detergent comprises a mixture of calcium salicylates, one having a TBN greater than 200, a second having a TBN of about 100 to 200 and a third having a TBN of less than 100.

12. The composition of Claim 7 wherein the salicylate detergent is an ashless salicylate detergent.

13. The composition of Claims 8 and 12 wherein the composition has a sulfur content less than about 0.25 wt% based on the total weight of the composition.

14. A lubricating composition comprising:

(a) greater than 50 wt% of a base oil of lubricating viscosity comprising one or more oils selected from Group II, Group III (including GTL), Group IV and Group V base stocks; and

(b) one or more detergents selected from sulfur-free alkyl salicylate detergents in an amount to provide the oil of lubricating viscosity with a TBN of from about 4 to about 8;

(c) one or more lubricant performance enhancing additives,

the composition having less than 0.8 wt% sulfated ash and being free of a viscoelastic fluid having both a shear stress greater than 11 kPa and a kinematic viscosity greater than 30 cSt at 100°C.

15. The composition of Claim 14 wherein the detergent is a calcium alkyl salicylate detergent.

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

17. The use of one or more alkyl salicylate detergents to improve the air release rate of a lubricating composition.

18. The use according to claim 17, wherein the lubricating composition comprises at least 50 wt% of an oil of lubricating viscosity, based on the total weight of the lubricating composition.

19. The use according to any of claims 17 or 18, wherein the lubricating composition comprises 1 wt% to 6 wt% alkyl salicylate detergent, based on the total weight of the lubricating composition.

20. The use according to any of claims 17 to 19, wherein the alkyl salicylate detergent is an alkaline earth metal salicylate detergent, preferably a calcium or magnesium salicylate detergent.

21. The use according to any of claims 17 to 20, wherein the alkyl salicylate detergent is an ashless nitrogen-containing detergent.