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(54) **LUBRICATION OIL COMPOSITIONS**

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(57) **ABSTRACT**

This invention relates to lubrication oil compositions comprising (i) a base fluid stock comprising (a) a PO3G fluid (a polytrimethylene ether glycol that is a fluid at ambient temperature) and (b) a PO3G ester fluid (an ester of a polytrimethylene ether glycol that is a fluid at ambient temperature), and (ii) one or more fuel oil additives.

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LUBRICATION OIL COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is related to commonly owned U.S. application Ser. No. 11/593,954, filed Nov. 7, 2006, entitled "POLYTRIMETHYLENE ETHER GLYCOL ESTERS"; commonly owned U.S. Provisional Application Ser. No. 60/957,728 filed concurrently herewith, entitled "LUBRICATION OIL COMPOSITIONS"; commonly owned U.S. Provisional Application Ser. No. 60/957,716, filed concurrently herewith, entitled "LUBRICATION OIL COMPOSITIONS"; and commonly owned U.S. Provisional Application Ser. No. 60/957,722, filed concurrently herewith, entitled "LUBRICATION OIL COMPOSITIONS".

FIELD OF THE INVENTION

[0002] This invention relates compositions comprising (i) a polytrimethylene ether glycol and (ii) an acid ester (monoester and/or diester) of polytrimethylene ether glycol, and the use of such compositions as lubrication oils.

BACKGROUND

[0003] Certain mono- and diesters of polytrimethylene ether glycol ("PO3G esters") have properties that make them useful in a variety of fields, including as lubricants, as disclosed in commonly owned U.S. application Ser. No. 11/593,954, filed Nov. 7, 2006, entitled "POLYTRIMETHYLENE ETHER GLYCOL ESTERS".

[0004] The present invention is directed to specific lubricant compositions based on combinations of such PO3G esters with polytrimethylene ether glycol (PO3G).

SUMMARY OF THE INVENTION

[0005] In one embodiment, the present invention relates to the use of mixtures of one or more PO3Gs and one or more PO3G esters, along with one or more additives, as a lubrication oils. The present invention thus provides a lubrication oil composition comprising (i) a base fluid stock comprising a mixture of (a) a PO3G fluid (a polytrimethylene ether glycol that is a fluid at ambient temperature) and (b) a PO3G ester fluid (an ester of a polytrimethylene ether glycol that is a fluid at ambient temperature), and (ii) one or more lube oil additives.

[0006] When the PO3G and PO3G ester are based on biologically produced 1,3-propanediol, lubricant compositions with a very high renewable content can be provided.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0007] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In case of conflict, the present specification, including definitions, will control.

[0008] Except where expressly noted, trademarks are shown in upper case.

[0009] Unless stated otherwise, all percentages, parts, ratios, etc., are by weight.

[0010] When an amount, concentration, or other value or parameter is given as either a range, preferred range or a list of upper preferable values and lower preferable values, this is to

be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range.

[0011] When the term "about" is used in describing a value or an end-point of a range, the disclosure should be understood to include the specific value or end-point referred to.

[0012] As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

[0013] Use of "a" or "an" are employed to describe elements and components of the invention. This is done merely for convenience and to give a general sense of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

[0014] The materials, methods, and examples herein are illustrative only and, except as specifically stated, are not intended to be limiting. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described herein.

Base Fluid Stock

[0015] As indicated above, the base fluid stock for use in the lubrication oil compositions of the present invention comprises a mixture of a PO3G and a PO3G ester that is a fluid at ambient temperature (25° C.). The base fluid stock may also comprise other natural and/or synthetic fluid co-lubricants.

[0016] Examples of natural fluid co-lubricants include vegetable oil-based lubricants, which are generally derived from plants and are generally composed of triglycerides. Normally, these are liquid at room temperature. Although many different parts of plants may yield oil, in actual practice oil is generally extracted primarily from the seeds of oilseed plants. These oils include both edible and inedible oils, and include, for example, high oleic sunflower oil, rapeseed oil, soybean oil, castor oil and the like, as well as modified oils such as disclosed in U.S. Pat. No. 6,583,302 (fatty acid esters) and I. Malchev, "Plant-Oil-Based Lubricants" (available from the Department of Plant Agriculture, Ontario Agriculture College, University of Guelph, 50 Stone Road W., Guelph, Ontario, Canada N1G 2W1).

[0017] Synthetic fluid co-lubricants (other than the PO3G and PO3G esters) include lubricating oils such as hydrocarbon oils such as polybutylenes, polypropylenes, propylene-isobutylene copolymers; polyoxyalkylene glycol polymers (other than PO3G) and their derivatives such as ethylene oxide and propylene oxide copolymers; and esters of dicar-

boxylic acids with a variety of alcohols such as dibutyl adipate, di(2-ethylhexyl)sebacate, di-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, and the 2-ethylhexyl diester of linoleic acid dimer.

[0018] Preferably, the base stock comprises a predominant amount of PO3G/PO3G ester mixture (greater than 50 wt % based on the weight of the base stock). In some embodiments, the base stock can comprise the PO3G/PO3G ester mixture in an amount of about 66 wt % or greater, or about 75 wt % or greater, or about 90 wt % or greater, or about 95 wt % or greater, based on the total weight of the base fluid stock. In some preferred embodiments, the base fluid stock comprises only (or substantially only) the PO3G/PO3G ester mixture.

[0019] In one embodiment, the weight ratio of PO3G/PO3G ester in the base fluid stock is greater than 1:1 (the PO3G being the predominant component), or about 1.5:1 or greater, or about 2:1 or greater, or about 5:1 or greater, or about 20:1 or greater. Also, the weight ratio is preferably about 25:1 or less, or about 20:1 or less, or about 10:1 or less.

[0020] In another embodiment, the weight ratio of PO3G ester/PO3G in the base fluid stock is greater than 1:1 (the PO3G ester being the predominant component), or about 1.5:1 or greater, or about 2:1 or greater, or about 5:1 or greater, or about 20:1 or greater. Also, the weight ratio is preferably about 25:1 or less, or about 20:1 or less, or about 10:1 or less.

[0021] In yet another embodiment, the weight ratio of PO3G/PO3G ester in the base fluid stock is about 1:1 (approximately equivalent weight amounts of the two components).

[0022] The lubrication oil composition preferably comprises the base oil stock in an amount of about 50 wt % or greater, based on the total weight of the lubrication oil composition. In various embodiments, the lubrication oil can comprise the base stock in an amount of about 75 wt % or greater, or about 90 wt % or greater, or about 95 wt % or greater, based on the total weight of the lubrication oil composition.

Mono- and Diesters of Polytrimethylene Ether Glycol

[0023] In some embodiments, the PO3G esters comprise one or more compounds of the formula (I):



wherein Q represents the residue of a polytrimethylene ether glycol after abstraction of the hydroxyl groups, R_2 is H or R_3CO , and each of R_1 and R_3 is individually a substituted or unsubstituted aromatic, saturated aliphatic, unsaturated aliphatic or cyclo-aliphatic organic group, containing 4 to 40 carbon atoms, preferably at least 6 carbon atoms, more preferably at least 8 carbon atoms. In some embodiments each of R_1 and R_3 has 20 carbon atoms or fewer, and in some embodiments 10 carbon atoms or fewer. In some preferred embodiments, each of R_1 and R_3 has 8 carbon atoms.

[0024] PO3G esters are preferably prepared by polycondensation of hydroxyl groups-containing monomers (monomers containing 2 or more hydroxyl groups) predominantly comprising 1,3-propanediol to form a PO3G (as disclosed in further detail below), followed by esterification with a mono-

carboxylic acid (or equivalent), as disclosed in U.S. application Ser. No. 11/593,954, filed Nov. 7, 2006, entitled "POLY-TRIMETHYLENE ETHER GLYCOL ESTERS".

[0025] The PO3G ester thus prepared is a composition preferably comprising from about 50 to 100 wt %, more preferably from about 75 to 100 wt %, diester and from 0 to about 50 wt %, more preferably from 0 to about 25 wt %, monoester, based on the total weight of the esters. Preferably the mono- and diesters are esters of 2-ethylhexanoic acid.

[0026] The PO3G used for preparing the ester need not be the same as the PO3G co-component of the base fluid stock.

Polytrimethylene Ether Glycol (PO3G)

[0027] PO3G for the purposes of the present invention is an oligomeric or polymeric ether glycol in which at least 50% of the repeating units are trimethylene ether units. More preferably from about 75% to 100%, still more preferably from about 90% to 100%, and even more preferably from about 99% to 100%, of the repeating units are trimethylene ether units.

[0028] PO3G is preferably prepared by polycondensation of monomers comprising 1,3-propanediol, preferably in the presence of an acid catalyst, thus resulting in polymers or copolymers containing $-(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})-$ linkage (e.g., trimethylene ether repeating units). As indicated above, at least 50% of the repeating units are trimethylene ether units.

[0029] When a sulfur-based acid catalyst is utilized (such as sulfuric acid) to prepare the PO3G, the resulting product preferably contains less than about 20 ppm, more preferably less than about 10 ppm, of sulfur.

[0030] In addition to the trimethylene ether units, lesser amounts of other units, such as other polyalkylene ether repeating units, may be present. In the context of this disclosure, the term "polytrimethylene ether glycol" encompasses PO3G made from essentially pure 1,3-propanediol, as well as those oligomers and polymers (including those described below) containing up to about 50% by weight of comonomers.

[0031] The 1,3-propanediol employed for preparing the PO3G may be obtained by any of the various well known chemical routes or by biochemical transformation routes. Preferred routes are described in, for example, U.S. Pat. No. 5,015,789, U.S. Pat. No. 5,276,201, U.S. Pat. No. 5,284,979, U.S. Pat. No. 5,334,778, U.S. Pat. No. 5,364,984, U.S. Pat. No. 5,364,987, U.S. Pat. No. 5,633,362, U.S. Pat. No. 5,686,276, U.S. Pat. No. 5,821,092, U.S. Pat. No. 5,962,745, U.S. Pat. No. 6,140,543, U.S. Pat. No. 6,232,511, U.S. Pat. No. 6,235,948, U.S. Pat. No. 6,277,289, U.S. Pat. No. 6,297,408, U.S. Pat. No. 6,331,264, U.S. Pat. No. 6,342,646, U.S. Pat. No. 7,038,092, U.S. Pat. No. 7,084,311, U.S. Pat. No. 7,098,368, U.S. Pat. No. 7,009,082 and US20050069997A1.

[0032] Preferably, the 1,3-propanediol is obtained biochemically from a renewable source ("biologically-derived" 1,3-propanediol).

[0033] A particularly preferred source of 1,3-propanediol is via a fermentation process using a renewable biological source. As an illustrative example of a starting material from a renewable source, biochemical routes to 1,3-propanediol (PDO) have been described that utilize feedstocks produced from biological and renewable resources such as corn feed stock. For example, bacterial strains able to convert glycerol into 1,3-propanediol are found in the species *Klebsiella*, *Citrobacter*, *Clostridium*, and *Lactobacillus*. The technique is disclosed in several publications, including U.S. Pat. No.

5,633,362, U.S. Pat. No. 5,686,276 and U.S. Pat. No. 5,821,092. U.S. Pat. No. 5,821,092 discloses, inter alia, a process for the biological production of 1,3-propanediol from glycerol using recombinant organisms. The process incorporates *E. coli* bacteria, transformed with a heterologous pdu diol dehydratase gene, having specificity for 1,2-propanediol. The transformed *E. coli* is grown in the presence of glycerol as a carbon source and 1,3-propanediol is isolated from the growth media. Since both bacteria and yeasts can convert glucose (e.g., corn sugar) or other carbohydrates to glycerol, the processes disclosed in these publications provide a rapid, inexpensive and environmentally responsible source of 1,3-propanediol monomer.

[0034] The biologically-derived 1,3-propanediol, such as produced by the processes described and referenced above, contains carbon from the atmospheric carbon dioxide incorporated by plants, which compose the feedstock for the production of the 1,3-propanediol. In this way, the biologically-derived 1,3-propanediol preferred for use in the context of the present invention contains only renewable carbon, and not fossil fuel-based or petroleum-based carbon. The PO3G and esters thereon utilizing the biologically-derived 1,3-propanediol, therefore, have less impact on the environment as the 1,3-propanediol used in the compositions does not deplete diminishing fossil fuels and, upon degradation, releases carbon back to the atmosphere for use by plants once again. Thus, the compositions of the present invention can be characterized as more natural and having less environmental impact than similar compositions comprising petroleum based glycols.

[0035] The biologically-derived 1,3-propanediol, PO3G and PO3G esters, may be distinguished from similar compounds produced from a petrochemical source or from fossil fuel carbon by dual carbon-isotopic finger printing. This method usefully distinguishes chemically-identical materials, and apportions carbon in the copolymer by source (and possibly year) of growth of the biospheric (plant) component. The isotopes, ^{14}C and ^{13}C , bring complementary information to this problem. The radiocarbon dating isotope (^{14}C), with its nuclear half life of 5730 years, clearly allows one to apportion specimen carbon between fossil ("dead") and biospheric ("alive") feedstocks (Currie, L. A. "Source Apportionment of Atmospheric Particles," *Characterization of Environmental Particles*, J. Buffle and H. P. van Leeuwen, Eds., 1 of Vol. I of the IUPAC Environmental Analytical Chemistry Series (Lewis Publishers, Inc) (1992) 3-74). The basic assumption in radiocarbon dating is that the constancy of ^{14}C concentration in the atmosphere leads to the constancy of ^{14}C in living organisms. When dealing with an isolated sample, the age of a sample can be deduced approximately by the relationship:

$$t = (-5730/0.693) \ln(A/A_0)$$

wherein t =age, 5730 years is the half-life of radiocarbon, and A and A_0 are the specific ^{14}C activity of the sample and of the modern standard, respectively (Hsieh, Y., *Soil Sci. Soc. Am J.*, 56, 460, (1992)). However, because of atmospheric nuclear testing since 1950 and the burning of fossil fuel since 1850, ^{14}C has acquired a second, geo-chemical time characteristic. Its concentration in atmospheric CO_2 , and hence in the living biosphere, approximately doubled at the peak of nuclear testing, in the mid-1960s. It has since been gradually returning to the steady-state cosmogenic (atmospheric) baseline isotope rate ($^{14}\text{C}/^{12}\text{C}$) of ca. 1.2×10^{-12} , with an approximate relaxation "half-life" of 7-10 years. (This latter half-life must not

be taken literally; rather, one must use the detailed atmospheric nuclear input/decay function to trace the variation of atmospheric and biospheric ^{14}C since the onset of the nuclear age.) It is this latter biospheric ^{14}C time characteristic that holds out the promise of annual dating of recent biospheric carbon. ^{14}C can be measured by accelerator mass spectrometry (AMS), with results given in units of "fraction of modern carbon" (f_M). f_M is defined by National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs) 4990B and 4990C, known as oxalic acids standards HOxI and HOxII, respectively. The fundamental definition relates to 0.95 times the $^{14}\text{C}/^{12}\text{C}$ isotope ratio HOxI (referenced to AD 1950). This is roughly equivalent to decay-corrected pre-Industrial Revolution wood. For the current living biosphere (plant material), $f_M \approx 1.1$.

[0036] The stable carbon isotope ratio ($^{13}\text{C}/^{12}\text{C}$) provides a complementary route to source discrimination and apportionment. The $^{13}\text{C}/^{12}\text{C}$ ratio in a given biosourced material is a consequence of the $^{13}\text{C}/^{12}\text{C}$ ratio in atmospheric carbon dioxide at the time the carbon dioxide is fixed and also reflects the precise metabolic pathway. Regional variations also occur. Petroleum, C_3 plants (the broadleaf), C_4 plants (the grasses), and marine carbonates all show significant differences in $^{13}\text{C}/^{12}\text{C}$ and the corresponding $\delta^{13}\text{C}$ values. Furthermore, lipid matter of C_3 and C_4 plants analyze differently than materials derived from the carbohydrate components of the same plants as a consequence of the metabolic pathway. Within the precision of measurement, ^{13}C shows large variations due to isotopic fractionation effects, the most significant of which for the instant invention is the photosynthetic mechanism. The major cause of differences in the carbon isotope ratio in plants is closely associated with differences in the pathway of photosynthetic carbon metabolism in the plants, particularly the reaction occurring during the primary carboxylation, i.e., the initial fixation of atmospheric CO_2 . Two large classes of vegetation are those that incorporate the " C_3 " (or Calvin-Benson) photosynthetic cycle and those that incorporate the " C_4 " (or Hatch-Slack) photosynthetic cycle. C_3 plants, such as hardwoods and conifers, are dominant in the temperate climate zones. In C_3 plants, the primary CO_2 fixation or carboxylation reaction involves the enzyme ribulose-1,5-diphosphate carboxylase and the first stable product is a 3-carbon compound. C_4 plants, on the other hand, include such plants as tropical grasses, corn and sugar cane. In C_4 plants, an additional carboxylation reaction involving another enzyme, phosphoenol-pyruvate carboxylase, is the primary carboxylation reaction. The first stable carbon compound is a 4-carbon acid, which is subsequently decarboxylated. The CO_2 thus released is refixed by the C_3 cycle.

[0037] Both C_4 and C_3 plants exhibit a range of $^{13}\text{C}/^{12}\text{C}$ isotopic ratios, but typical values are ca. -10 to -14 per mil (C_4) and -21 to -26 per mil (C_3) (Weber et al., *J. Agric. Food Chem.*, 45, 2942 (1997)). Coal and petroleum fall generally in this latter range. The ^{13}C measurement scale was originally defined by a zero set by pee dee belemnite (PDB) limestone, where values are given in parts per thousand deviations from this material. The " $\delta^{13}\text{C}$ " values are in parts per thousand (per mil), abbreviated ‰, and are calculated as follows:

$$\delta^{13}\text{C} \equiv \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{standard}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} \times 1000\text{‰}$$

Since the PDB reference material (RM) has been exhausted, a series of alternative RMs have been developed in cooperation with the IAEA, USGS, NIST, and other selected international isotope laboratories. Notations for the per mil deviations from PDB is $\delta^{13}\text{C}$. Measurements are made on CO_2 by high precision stable ratio mass spectrometry (IRMS) on molecular ions of masses 44, 45 and 46.

[0038] Biologically-derived 1,3-propanediol, and compositions comprising biologically-derived 1,3-propanediol, therefore, may be completely distinguished from their petrochemical derived counterparts on the basis of ^{14}C (f_M) and dual carbon-isotopic finger-printing, indicating new compositions of matter. The ability to distinguish these products is beneficial in tracking these materials in commerce. For example, products comprising both “new” and “old” carbon isotope profiles may be distinguished from products made only of “old” materials. Hence, the instant materials may be followed in commerce on the basis of their unique profile and for the purposes of defining competition, for determining shelf life, and especially for assessing environmental impact.

[0039] Preferably the 1,3-propanediol used as the reactant or as a component of the reactant will have a purity of greater than about 99%, and more preferably greater than about 99.9%, by weight as determined by gas chromatographic analysis. Particularly preferred are the purified 1,3-propanediols as disclosed in U.S. Pat. No. 7,038,092, U.S. Pat. No. 7,098,368, U.S. Pat. No. 7,084,311 and US20050069997A1, as well as PO3G made therefrom as disclosed in US20050020805A1.

[0040] The purified 1,3-propanediol preferably has the following characteristics:

[0041] (1) an ultraviolet absorption at 220 nm of less than about 0.200, and at 250 nm of less than about 0.075, and at 275 nm of less than about 0.075; and/or

[0042] (2) a composition having $L^*a^*b^*$ “b*” color value of less than about 0.15 (ASTM D6290), and an absorbance at 270 nm of less than about 0.075; and/or

[0043] (3) a peroxide composition of less than about 10 ppm; and/or

[0044] (4) a concentration of total organic impurities (organic compounds other than 1,3-propanediol) of less than about 400 ppm, more preferably less than about 300 ppm, and still more preferably less than about 150 ppm, as measured by gas chromatography.

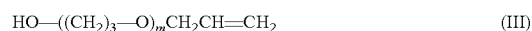
[0045] The starting material for making PO3G will depend on the desired PO3G, availability of starting materials, catalysts, equipment, etc., and comprises “1,3-propanediol reactant.” By “1,3-propanediol reactant” is meant 1,3-propanediol, and oligomers and prepolymers of 1,3-propanediol preferably having a degree of polymerization of 2 to 9, and mixtures thereof. In some instances, it may be desirable to use up to 10% or more of low molecular weight oligomers where they are available. Thus, preferably the starting material comprises 1,3-propanediol and the dimer and trimer thereof. A particularly preferred starting material is comprised of about 90% by weight or more 1,3-propanediol, and more preferably 99% by weight or more 1,3-propanediol, based on the weight of the 1,3-propanediol reactant.

[0046] PO3G can be made via a number of processes known in the art, such as disclosed in U.S. Pat. No. 6,977,291 and U.S. Pat. No. 6,720,459. The preferred processes are as set forth in U.S. Pat. No. 7,074,969, U.S. Pat. No. 7,157,607, U.S. Pat. No. 7,161,045 and U.S. Pat. No. 7,164,046.

[0047] As indicated above, PO3G may contain lesser amounts of other polyalkylene ether repeating units in addition to the trimethylene ether units. The monomers for use in preparing polytrimethylene ether glycol can, therefore, contain up to 50% by weight (preferably about 20 wt % or less, more preferably about 10 wt % or less, and still more preferably about 2 wt % or less), of comonomer polyols in addition to the 1,3-propanediol reactant. Comonomer polyols that are suitable for use in the process include aliphatic diols, for example, ethylene glycol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,12-dodecanediol, 3,3,4,4,5,5-hexafluoro-1,5-pentanediol, 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol, and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluoro-1,12-dodecanediol; cycloaliphatic diols, for example, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol and isosorbide; and polyhydroxy compounds, for example, glycerol, trimethylolpropane, and pentaerythritol. A preferred group of comonomer diols is selected from the group consisting of ethylene glycol, 2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol, $\text{C}_6\text{--C}_{10}$ diols (such as 1,6-hexanediol, 1,8-octanediol and 1,10-decanediol) and isosorbide, and mixtures thereof. A particularly preferred diol other than 1,3-propanediol is ethylene glycol, and $\text{C}_6\text{--C}_{10}$ diols can be particularly useful as well.

[0048] One preferred PO3G containing comonomers is poly(trimethylene-ethylene ether)glycol such as described in US20040030095A1. Preferred poly(trimethylene-ethylene ether)glycols are prepared by acid catalyzed polycondensation of from 50 to about 99 mole % (preferably from about 60 to about 98 mole %, and more preferably from about 70 to about 98 mole %) 1,3-propanediol and up to 50 to about 1 mole % (preferably from about 40 to about 2 mole %, and more preferably from about 30 to about 2 mole %) ethylene glycol.

[0049] Preferably, the PO3G after purification has essentially no acid catalyst end groups, but may contain very low levels of unsaturated end groups, predominately allyl end groups, in the range of from about 0.003 to about 0.03 meq/g. Such a PO3G can be considered to comprise or consist essentially of the compounds having the following formulae (II) and (III):



wherein m is in a range such that the M_n (number average molecular weight) is within the range of from about 200 to about 10000, with compounds of formula (III) being present in an amount such that the allyl end groups (preferably all unsaturation ends or end groups) are present in the range of from about 0.003 to about 0.03 meq/g.

[0050] The preferred PO3G for use in the invention has an M_n (number average molecular weight) of at least about 250, more preferably at least about 1000, and still more preferably at least about 2000. The M_n is preferably less than about 10000, more preferably less than about 5000, and still more preferably less than about 3500. Blends of PO3Gs can also be used. For example, the PO3G can comprise a blend of a higher and a lower molecular weight PO3G, preferably wherein the higher molecular weight PO3G has a number average molecular weight of from about 1000 to about 5000, and the lower molecular weight PO3G has a number average molecu-

lar weight of from about 200 to about 950. The Mn of the blended PO3G will preferably still be in the ranges mentioned above.

[0051] PO3G preferred for use herein is typically polydisperse having a polydispersity (i.e. Mw/Mn) of preferably from about 1.0 to about 2.2, more preferably from about 1.2 to about 2.2, and still more preferably from about 1.5 to about 2.1. The polydispersity can be adjusted by using blends of PO3G.

[0052] PO3G for use in the present invention preferably has a color value of less than about 100 APHA, and more preferably less than about 50 APHA, and a viscosity which is preferably greater than the viscosity of the PO3G ester. A preferred viscosity is about 100 cS or greater at 40° C.

Acid and Equivalents

[0053] The esterification of the PO3G is carried out by reaction with an acid and/or equivalent, preferably a monocarboxylic acid and/or equivalent.

[0054] By "monocarboxylic acid equivalent" is meant compounds that perform substantially like monocarboxylic acids in reaction with polymeric glycols and diols, as would be generally recognized by a person of ordinary skill in the relevant art. Monocarboxylic acid equivalents for the purpose of the present invention include, for example, esters of monocarboxylic acids, and ester-forming derivatives such as acid halides (e.g., acid chlorides) and anhydrides.

[0055] Preferably, a monocarboxylic acid is used having the formula R—COOH, wherein R is a substituted or unsubstituted aromatic, aliphatic or cycloaliphatic organic moiety containing from 6 to 40 carbon atoms.

[0056] Mixtures of different monocarboxylic acids and/or equivalents are also suitable.

[0057] As indicated above, the monocarboxylic acid (or equivalent) can be aromatic, aliphatic or cycloaliphatic. In this regard, "aromatic" monocarboxylic acids are monocarboxylic acids in which a carboxyl group is attached to a carbon atom in a benzene ring system such as those mentioned below. "Aliphatic" monocarboxylic acids are monocarboxylic acids in which a carboxyl group is attached to a fully saturated carbon atom or to a carbon atom which is part of an olefinic double bond. If the carbon atom is in a ring, the equivalent is "cycloaliphatic."

[0058] The monocarboxylic acid (or equivalent) can contain any substituent groups or combinations thereof (such as functional groups like amide, amine, carbonyl, halide, hydroxyl, etc.), so long as the substituent groups do not interfere with the esterification reaction or adversely affect the properties of the resulting ester product.

[0059] The monocarboxylic acids and equivalents can be from any source, but preferably are derived from natural sources or are bio-derived.

[0060] The following acids and their derivatives are specifically preferred: lauric, myristic, palmitic, stearic, arachidic, benzoic, caprylic, erucic, palmitoleic, pentadecanoic, heptadecanoic, nonadecanoic, linoleic, arachidonic, oleic, valeric, caproic, capric and 2-ethylhexanoic acids, and mixtures thereof. Particularly preferred acids or derivatives thereof are 2-ethylhexanoic acid, benzoic acid, stearic acid, lauric acid and oleic acid.

Esterification Process

[0061] For preparation of the esters, the PO3G can be contacted, preferably in the presence of an inert gas, with the

monocarboxylic acid(s) at temperatures ranging from about 100° C. to about 275° C., preferably from about 125° C. to about 250° C. The process can be carried out at atmospheric pressure or under vacuum. During the contacting water is formed and can be removed in the inert gas stream or under vacuum to drive the reaction to completion.

[0062] To facilitate the reaction of PO3G with carboxylic acid an esterification catalyst is generally used, preferably a mineral acid catalyst. Examples of mineral acid catalysts include but are not restricted to sulfuric acid, hydrochloric acid, phosphoric acid, hydriodic acid, and heterogeneous catalysts such as zeolites, heteropolyacid, amberlyst, and ion exchange resin. Preferred esterification acid catalysts are selected from the group consisting of sulfuric acid, phosphoric acid, hydrochloric acid and hydroiodic acid. A particularly preferred mineral acid catalyst is sulfuric acid.

[0063] The amount of catalyst used can be from about 0.01 wt % to about 10 wt % of the reaction mixture, preferably from 0.1 wt % to about 5 wt %, and more preferably from about 0.2 wt % to about 2 wt %, of the reaction mixture.

[0064] Any ratio of carboxylic acid, or derivatives thereof, to glycol hydroxyl groups can be used. The preferred ratio of acid to hydroxyl groups is from about 3:1 to about 1:2, where the ratio can be adjusted to shift the ratio of monoester to diester in the product. Generally to favor production of diesters slightly more than a 1:1 ratio is used. To favor production of monoesters, a 0.5:1 ratio or less of acid to hydroxyl is used.

[0065] A preferred method for esterification comprises polycondensing 1,3-propanediol reactant to polytrimethylene ether glycol using a mineral acid catalyst, then adding carboxylic acid and carrying out the esterification without isolating and purifying the PO3G. In this method, the etherification or polycondensation of 1,3-propanediol reactant to form polytrimethylene ether glycol is carried out using an acid catalyst as disclosed in U.S. Pat. No. 6,977,291 and U.S. Pat. No. 6,720,459. The etherification reaction may also be carried out using a polycondensation catalyst that contains both an acid and a base as described in JP2004-182974A. The polycondensation or etherification reaction is continued until desired molecular weight is reached, and then the calculated amount of monocarboxylic acid is added to the reaction mixture. The reaction is continued while the water byproduct is removed. At this stage both esterification and etherification reactions occur simultaneously. Thus, in this preferred esterification method the acid catalyst used for polycondensation of diol is also used for esterification. If necessary additional esterification catalyst can be added at the esterification stage.

[0066] In this procedure, the viscosity (molecular weight) of the resulting product is controlled by the point at which the carboxylic acid is added.

[0067] In an alternative procedure, the esterification reaction can be carried out on purified PO3G by addition of an esterification catalyst and carboxylic acid followed by heating and removal of water. In this procedure, viscosity of the resulting product is predominantly a function of the molecular weight of the PO3G utilized.

[0068] Regardless of which esterification procedure is followed, after the esterification step any by products are removed, and then the catalyst residues remaining from polycondensation and/or esterification are removed in order to obtain an ester product that is stable, particularly at high temperatures. This may be accomplished by hydrolysis of the crude ester product by treatment with water at about 80° C. to

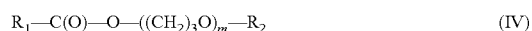
about 100° C. for a time sufficient to hydrolyze any residual acid esters derived from the catalyst without impacting significantly the carboxylic acid esters. The time required can vary from about 1 to about 8 hours. If the hydrolysis is carried out under pressure, higher temperatures and correspondingly shorter times are possible. At this point the product may contain diesters, monoesters, or a combination of diesters and monoesters, and small amounts of acid catalyst, unreacted carboxylic acid and diol depending on the reaction conditions. The hydrolyzed polymer is further purified to remove water, acid catalyst and unreacted carboxylic acid by the known conventional techniques such as water washings, base neutralization, filtration and/or distillation. Unreacted diol and acid catalyst can, for example, be removed by washing with deionized water. Unreacted carboxylic acid also can be removed, for example, by washing with deionized water or aqueous base solutions, or by vacuum stripping.

[0069] Hydrolysis is generally followed by one or more water washing steps to remove acid catalyst, and drying, preferably under vacuum, to obtain the ester product. The water washing also serves to remove unreacted diol. Any unreacted monocarboxylic acid present may also be removed in the water washing, but may also be removed by washing with aqueous base or by vacuum stripping.

[0070] If desired, the product can be fractionated further to isolate low molecular weight esters by a fractional distillation under reduced pressure.

[0071] Proton NMR and wavelength X-ray fluorescence spectroscopic methods can be used to identify and quantify any residual catalyst (such as sulfur) present in the polymer. The proton NMR can, for example, identify the sulfate ester groups present in the polymer chain, and wavelength x-ray fluorescence method can determine the total sulfur (inorganic and organic sulfur) present in the polymer. The esters of the invention made from the process described above are substantially sulfur free and thus useful for high temperature applications.

[0072] Preferably, the PO3G esters after purification have essentially no acid catalyst end groups, but may contain very low levels of unsaturated end groups, predominately allyl end groups, in the range of from about 0.003 to about 0.03 meq/g. Such PO3G ester can be considered to comprise (consist essentially of) the compounds having the following formulae (IV) and (V):



wherein R_2 is H or $R_3C(O)$; each of R_1 and R_3 is individually a substituted or unsubstituted aromatic, saturated aliphatic, unsaturated aliphatic, or cycloaliphatic organic group containing from 6 to 40 carbon atoms; m is in a range such that the Mn is within the range of from about 200 to about 10000; and with compounds of formula (III) being present in an amount such that the allyl end groups (preferably all unsaturation ends or end groups) are present in the range of from about 0.003 to about 0.03 meq/g.

[0073] Preferably, the PO3G ester has a viscosity which is less than the viscosity of PO3G. Preferred viscosities of PO3G esters range from about 20 cS to about 150 cS at 40° C., and more preferably are about 100 cS or less.

[0074] Other preferred properties of the PO3G esters can be determined based upon the preferences stated above for PO3G in and of itself. For example, preferred molecular

weights and polydispersities are based on the preferred molecular weights and polydispersities of the PO3G component of the ester.

Additives

[0075] Synthetic lube oil compositions in accordance with the present invention comprise a mixture of the base stock and one or more additives, where each additive is employed for the purpose of improving the performance and properties of the base stock in its intended application, e.g., as a hydraulic fluid, a gear oil, a brake fluid, a compressor lubricant, a textile and calender lubricant, a metalworking fluid, a refrigeration lubricant, a two-cycle engine lubricant and/or crankcase lubricant.

[0076] The additives can generally be added in amounts based on the type of additive and desired level of additive effect, which can generally be determined by those skilled in the relevant art.

[0077] Preferably the additives are miscible in either or both of the PO3G and PO3G esters.

[0078] Preferably, the lube oil additive(s) comprise at least one of ashless dispersant, metal detergent, viscosity modifier, anti-wear agent, antioxidant, friction modifier, pour point depressant, anti-foaming agent, corrosion inhibitor, demulsifier, rust inhibitor and mixtures thereof.

[0079] When the lube oil composition is used as a refrigeration lubricant, the lube oil additive(s) preferably comprise at least one of extreme pressure and antiwear additive, oxidation and thermal stability improver, corrosion inhibitor, viscosity index improver, pour point depressant, floc point depressant, detergent, anti-foaming agent, viscosity adjuster and mixtures thereof.

[0080] It is intended to be within the scope of the present invention to use any one or more of the specified additives alone or in combination with one or more of the remaining specified additives. It is also within the scope of the present invention to use more than one of any specified additive, e.g., one or more friction modifiers, either alone or in combination of one or more of the other specified additives, e.g., in combination with one or more corrosion inhibitors.

[0081] The individual additives may be incorporated into a base stock in any convenient way. Thus, each of the components can be added directly to the base stock by dispersing or dissolving it in the base stock at the desired level of concentration. Such blending may occur at ambient temperature or at an elevated temperature.

[0082] Alternatively, all or some of the additives can be blended into a concentrate or additive package that is subsequently blended into base stock to make finished lubricant. The concentrate will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration in the formulation when the concentrate is combined with a predetermined amount of base lubricant.

[0083] Non-limiting, illustrative examples of various additives follow.

[0084] The ashless dispersant comprises polymeric hydrocarbon backbone having functional groups that are capable of associating with particles to be dispersed. Typically, the dispersants comprise amine, alcohol, amide and/or ester polar moieties attached to the polymer backbone often via a bridging group. The ashless dispersant may be, for example, selected from salts, esters, amino-esters, amides, imides and oxazolines of long chain hydrocarbon substituted mono- and dicarboxylic acids and/or their anhydrides, thiocarboxylate

derivatives of long chain hydrocarbons, long chain aliphatic hydrocarbons having a polyamine attached directly thereto, and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine.

[0085] The viscosity modifier (VM) functions to impart high and low temperature operability to a lubricating oil. The VM used may have that sole function, or may be multifunctional.

[0086] Multifunctional viscosity modifiers that also function as dispersants are also known. Illustrative viscosity modifiers 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.

[0087] Metal-containing or ash-forming detergents function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with long hydrophobic tail, with the polar head comprising a metal salt of an acid organic compound. The salts may contain a substantially stoichiometric amount of the metal in which they are usually described as normal or neutral salts, and would typically have a total base number (TBN), as may be measured by ASTM D-2896 of from 0 to about 80. It is possible to include large amounts of a metal base by reacting an excess of a metal compound such as an oxide or hydroxide with an acid gas such as carbon dioxide. The resulting overbased detergent comprises neutralized detergent as the outer layer of a metal base (e.g., carbonate) micelle. Such overbased detergents may have a TBN of about 150 or greater, and typically from about 250 to about 450 or more.

[0088] Illustrative detergents include neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals, e.g., sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present in detergents used in a lubricant, and mixtures of calcium and/or magnesium with sodium. Particularly convenient metal detergents are neutral and overbased calcium sulfonates having TBN of from about 20 to about 450, and neutral and overbased calcium phenates and sulfurized phenates having TBN of from about 50 to about 450.

[0089] Dihydrocarbyl dithiophosphate metal salts are frequently used as anti-wear and antioxidant agents. The metal may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. The zinc salts are most commonly used in lubricating oil in amounts of from about 0.1 to about 10 wt %, preferably from about 0.2 to about 2 wt %, based upon the total weight of the lubricating oil composition. They may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with P_2S_5 and then neutralizing the formed DDPA with a zinc compound. For example, a dithiophosphoric acid may be made by reacting mixtures of pri-

mary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the zinc salt any basic or neutral zinc compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to use of an excess of the basic zinc compound in the neutralization reaction.

[0090] In one embodiment, however, the lube oil compositions are preferably substantially zinc free.

[0091] Oxidation inhibitors or antioxidants reduce the tendency of base stocks to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by viscosity growth. Such oxidation inhibitors include hindered phenols, alkaline earth metal salts of alkylphenolthioesters having preferably C_5 to C_{12} alkyl side chains, calcium nonylphenol sulfide, ashless oil soluble phenates and sulfurized phenates, phosphosulfurized or sulfurized hydrocarbons, phosphorous esters, metal thiocarbamates, oil-soluble copper compounds as described in U.S. Pat. No. 4,867,890, and molybdenum containing compounds.

[0092] Friction modifiers may be included to improve fuel economy. Oil-soluble alkoxyated mono- and di-amines are well known to improve boundary layer lubrication. The amines may be used as such or in the form of an adduct or reaction product with a boron compound such as boric oxide, boron halide, metaborate, boric acid or a mono-, di- or tri-alkyl borate.

[0093] Other friction modifiers are known. Among these are esters formed by reacting carboxylic acids and anhydrides with alkanols. Other conventional friction modifiers generally consist of a polar terminal group (e.g. carboxyl or hydroxyl) covalently bonded to an oleophilic hydrocarbon chain. Esters of carboxylic acids and anhydrides with alkanols are described in U.S. Pat. No. 4,702,850. An example of another conventional friction modifier is organo-metallic molybdenum.

[0094] Illustrative rust inhibitors are selected from the group of nonionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, and anionic alkyl sulfonic acids.

[0095] Copper and lead bearing corrosion inhibitors may also be used. Typically such compounds are the thiadiazole polysulfides containing from 5 to 50 carbon atoms, their derivatives and polymers thereof. Other additives are the thio- and polythio-sulfenamides of thiadiazoles such as those described in UK1560830. Benzotriazole derivatives also fall within this class of additives.

[0096] An illustrative example of demulsifying component is described in EP-A-0330522. It is obtained by reacting an alkylene oxide with an adduct obtained by reacting a bis-epoxide with a polyhydric alcohol.

[0097] Pour point depressants, otherwise known as lube oil improvers, lower the minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Typical of those additives which improve the low temperature fluidity of the fluid are C_8 and C_{18} dialkyl fumarate/vinyl acetate copolymers, polyalkylmethacrylates and the like.

[0098] Foam control can be provided by many compounds including an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

[0099] Some of the above-mentioned additives can provide a multiplicity of effects; thus, for example, a single additive may act as a dispersant-oxidation inhibitor. This approach is well known and does not require further elaboration.

[0100] Illustrative, non-limiting examples of additives specific to use in compression refrigeration systems follow.

[0101] Illustrative extreme pressure and antiwear additives include phosphates, phosphate esters (bicesyl phosphate), phosphites, thiophosphates (zinc diorganodithiophosphates) chlorinated waxes, sulfurized fats and olefins, organic lead compounds, fatty acids, molybdenum complexes, halogen substituted organosilicon compounds, borates, organic esters, halogen substituted phosphorous compounds, sulfurized Diels Alder adducts, organic sulfides, compounds containing chlorine and sulfur, metal salts of organic acids.

[0102] Illustrative oxidation and thermal stability improvers include sterically hindered phenols (BHT), aromatic amines, dithiophosphates, phosphites, sulfides and metal salts of dithio acids.

[0103] Illustrative corrosion inhibitors include organic acids, organic amines, organic phosphates, organic alcohols, metal sulfonates and organic phosphites.

[0104] Viscosity index is the measure of the change in viscosity with temperature, and a high number suggests that the change in viscosity with temperature is minimal. In view of the high viscosity index of the lube oil compositions of the present invention, it is possible to formulate a lube oil composition which is free of viscosity index improver. However, there may be applications where it is desirable to further improve viscosity index. Illustrative viscosity index improvers include polyisobutylene, polymethacrylate and polyalkylstyrenes.

[0105] Illustrative pour point and or floc point depressants include polymethacrylate ethylene-vinyl acetate copolymers, succinamic acid-olefin copolymers, ethylene-alpha olefin copolymers and Friedel-Crafts condensation products of wax with naphthalene or phenols.

[0106] Illustrative detergents include sulfonates, long-chain alkyl substituted aromatic sulfonic acids, phosphonates, thiophosphonates, phenolates, metal salts of alkyl phenols, alkyl sulfides, alkylphenol-aldehyde condensation products, metal salts of substituted salicylates, N-substituted

oligomers or polymers from the reaction products of unsaturated anhydrides and amines and co-polymers which incorporate polyester linkages such as vinyl acetate-maleic anhydride co-polymers.

[0107] Illustrative anti-foaming agents are silicone polymers.

[0108] Illustrative viscosity adjusters include polyisobutylene, polymethacrylates, polyalkylstyrenes, naphthenic oils, alkylbenzene oils, paraffinic oils, polyesters, polyvinylchloride and polyphosphates.

[0109] In the present invention, the additive(s) should be at least partially (greater than about 50% by weight) miscible in the base stock. Generally, this means that the additives used will be oil soluble at least to some extent, and preferably to a substantial extent.

[0110] The lube oil composition should thus preferably be a substantially uniform mixture, with substantially no settling or phase separation of components.

[0111] The lubrication oil composition preferably comprises the additives in an amount of less than 50 wt %, based on the total weight of the lubrication oil composition. In various embodiments, the lubrication oil can comprise the additives in an amount of about 25 wt % or less, or about 10 wt % or less, or about 5 wt % or less, based on the total weight of the lubrication oil composition.

EXAMPLES

[0112] All parts, percentages, etc., are by weight unless otherwise indicated.

[0113] The number-average molecular weights (Mn) of polyether glycol and polyether glycol ester were determined either by analyzing end-groups using NMR spectroscopic methods or by titration of hydroxyl groups.

[0114] ASTM method D445-83 and ASTM method D792-91 were used to determine the kinematic viscosity and density of the polymer, respectively.

[0115] Additional ASTM methods were used as listed in the Tables below.

[0116] The materials of the present invention were tested with and without a lube oil additive package. The package used during the testing comprised the components listed in Table 1.

TABLE 1

Additive	Description	Function	Available From
IRGALUBE ® TPPT	Triphenyl phosphorothionate, typically containing 9% phosphorus and 9.4% sulfur	Anti-wear/extreme pressure	Ciba Specialty Chemicals, Tarrytown, NY
VANLUBE ® 7723	Methylene bis(dibutylthiocarbamate)	Ashless anti-oxidant and extreme pressure antioxidant	RT Vanderbilt Company Inc Norwalk, CT
VANLUBE ® 887E	Tolutriazole	antioxidant	RT Vanderbilt Company Inc Norwalk, CT
PANA	Phenyl anaphthamine	antioxidant	Akrochem, Akron OH
VANLUBE ® RD	Polymerized 1,2-dihydro-2,2,4-trimethylquinoline	antioxidant	R.T. Vanderbilt Co., Inc., Norwalk, CT
IRGANOX ® 1135	Hindered phenol	antioxidant	Ciba Specialty Chemicals, Tarrytown, NY

TABLE 1-continued

Additive	Description	Function	Available From
IRGALUBE® 349	Mixture of amine phosphates	EP/AW & corrosion inhibitor	Ciba Specialty Chemicals, Tarrytown, NY
VANLUBE® 8912E	Calcium sulfonate	Rust inhibitor	RT Vanderbilt Company Inc Norwalk, CT
CUVAN® 826	2,5 dimercapto-1,3,4-thiadiazole derivative	Corrosion inhibitor & metal deactivator	R.T. Vanderbilt Co., Inc., Norwalk, CT

Preparation of PO3G Homopolymer—PO3G1

[0117] A 22-L, 4-necked, round-bottomed flask, equipped with a nitrogen inlet, and a distillation head was charged with 11877 g of 1,3-propanediol. The liquid was sparged with nitrogen at a rate of 10 L/min. and mechanical stirring (using a stirring magnet driven by a magnetic stirrer below the flask) was done for about 15 min. After 15 min., 108 g of sulfuric acid was slowly added drop-wise from a separatory funnel through one of the ports over a period of at least 5 minutes. When this was finished, 15 g of 1,3-propanediol (PDO) was added to the separatory funnel and swirled to remove any residual sulfuric acid. This was added to the flask. The mixture was stirred and sparged as above and heated to 160° C. The water of reaction was removed by distillation and was collected continuously during the polymerization reaction. The reaction was continued for 25 hours, after which it was allowed to cool (while stirring and sparging were maintained) to 45° C.

[0118] The crude material was hydrolyzed as follows. The crude polymer was added to a 22-L, 5-necked, round-bottom flask, (equipped with a condenser and a mechanical mixer) along with an equal volume of distilled water. This mixture was stirred mechanically, sparged with nitrogen at a rate of about 150 mL/min. and heated to 100° C. It was allowed to reflux for 4 hours after which the heat was turned off and the mixture allowed to cool to 45° C. The stirring was discontinued and the sparging reduced to a minimum. Phase separation occurred during cooling. The aqueous phase water was removed and discarded. A volume of distilled water equal to the initial amount was added to the wet polymer remaining in the flask. Mixing, sparging and heating to 100° C. was done again for 1 hour after which the heat was turned off and the material allowed to cool as before. The aqueous phase was removed and discarded.

[0119] The residual sulphuric acid was determined by titration and neutralized with an excess of calcium hydroxide. The polymer was dried under reduced pressure at 90° C. for 3 hours and then filtered through a Whatman filter paper pre-coated with a CEL-PURE C-65 filter aid. The resulting PO3G had a number average molecular weight of 940.

Preparation of Poly(trimethylene-Ethylene Ether)Glycol Copolymer—PO3G2

[0120] The above procedure described was repeated except for variation in the amounts of 1,3-propanediol (8811.2 g), 1,2-ethanediol (3080.8 g) and sulfuric acid (108 g) to obtain

a poly(trimethylene-ethylene ether)glycol copolymer having a number average molecular weight (Mn) of 890.

Preparation of a 2-Ethylhexanoate PO3G Ester

[0121] 1,3-propanediol (2.4 kg, 31.5 moles) was charged into a 5 L flask fitted with a stirrer, a condenser and an inlet for nitrogen. The liquid in the flask was flushed with dry nitrogen for 30 minutes at room temperature and then heated to 170° C. while being stirred at 120 rpm. When the temperature reached 170° C., 12.6 g (0.5 wt %) of concentrated sulfuric acid was added. The reaction was allowed to proceed at 170° C. for 3 hours, and then the temperature was raised to 180° C. and held at 180° C. for 135 minutes. A total of 435 mL of distillate was collected. The reaction mixture was cooled, and then 2.24 kg (14.6 moles) of 2-ethylhexanoic acid (99%) was added. The reaction temperature was then raised to 160° C. under nitrogen flow with continuous agitation at 180 rpm and maintained at that temperature for 6 hours. During this period an additional 305 mL of distillate water was collected. Heating and agitation were stopped and the reaction mixture was allowed to settle. The product was decanted from about 5 g of a lower, immiscible by-product phase. NMR analysis of the by-product phase confirmed that no carboxylic acid esters were present.

[0122] 2.0 kg of the polytrimethylene ether glycol ester product was mixed with 0.5 kg of water, and then the resulting mixture was heated at 95° C. for 6 hours. The aqueous phase was separated from the polymer phase, and then the polymer phase was washed twice with 2.0 kg of water. The resulting product was heated at 120° C. at 200 mTorr to remove volatiles (255 g). The resulting PO3G ester product has the following properties:

Number average molecular weight (Mn)=500

Viscosity at 40° C. and 100° C.=24 and 5.5 cSt, respectively

Viscosity Index (VI)=180

[0123] The resulting PO3G ester was analyzed using proton NMR. No peaks associated with sulfate esters and unreacted 2-ethylhexanoic acid were found. There was no sulfur detected in the polymer when analyzed using WDXRF spectroscopy method.

Example 1

[0124] PO3G1 (25 wt % based on the weight of the base fluid stock) and the PO3G ester (75 wt % based on the weight of the base fluid stock) prepared above were mixed and a lube

composition was prepared as follows (wt % below based on the total composition weight):

Blend of base fluids	97.3%
IRGALUBE ® TPPT	0.40%
VANLUBE ® 7723	0.30%
VANLUBE ® 887E	0.20%
PANA	0.40%
VANLUBE ® RD	0.80%
IRGALUBE ® 349	0.40%
CUVAN ® 826	0.10%

Table 2 lists the lube properties of the blend fluid.

TABLE 2

Property	ASTM Method	Example 2
Viscosity @ 40° C., cSt	D445	38.5
Viscosity Index		182
Pour point, ° C.	D97	0
Flash Point, ° C.	D-92	240
Evaporation	D-972	0.42%
Foaming sequence 1, 2, 3	D-892	None
Copper corrosion	D-130	1b
Four Ball Wear Scar, mm	D-4172	0.69
Load Wear Index	D-2783	24.5
Last nonseizure load, (scar, mm)	D-2783	40 kg (.31)
Last seizure load (scar, mm)		160 kg (2.59)
Weld Load, kg		200
Falex Pin & V block Max load, lbs	D3233	3400

Example 2

[0125] PO3G1 (75 wt % based on the weight of the base fluid stock) and the PO3G ester (25 wt % based on the weight of the base fluid stock) prepared above were mixed and a lube oil composition was prepared by adding the following additives (wt % below based on the total composition weight):

Blend of base fluids	97.6%
TPPT	0.50%
PANA	0.50%
VANLUBE ® RD	1.00%
IRGALUBE ® 349	0.30%
CUVAN ® 826	0.10%

Example 3

[0126] PO3G2 (75 wt % based on the weight of the base fluid stock) and the PO3G ester (25 wt % based on the weight of the base fluid stock) prepared above were mixed and a lube oil composition was prepared by adding the following additives (wt % based on total composition weight).

Blend of base fluid	97.60%
IRGALUBE ® TPPT	0.50%
PANA	0.50%
VANLUBE ® RD	1.00%

-continued

IRGALUBE ® 349	0.30%
CUVAN ® 826	0.10%

[0127] Table 3 lists the lube properties of the blend fluid.

Example 4

[0128] PO3G2 (25 wt % based on the weight of the base fluid stock) and the PO3G ester (75 wt % based on the weight of the base fluid stock) prepared above were mixed and a lube oil composition was prepared by adding the following additives (wt % based on total composition weight).

Blend of base fluid	97.60%
IRGALUBE ® TPPT	0.50%
PANA	0.50%
VANLUBE ® RD	1.00%
IRGALUBE ® 349	0.30%
CUVAN ® 826	0.10%

[0129] Table 3 lists the lube properties of the blend fluid.

TABLE 3

Property	Test Method	Example 3	Example 4
Four ball wear, mm	ASTM D-4172	0.40	0.63
Load wear Index	ASTM	33.6	27.2
Last nonseizure load (scar)	D-2783	63 kg (0.36 mm)	50 kg (0.33 mm)
Last seizure load (scar)		160 kg (2.69 mm)	160 kg (2.68 mm)
Weld load		200 kg	200 kg
Falex Pin & V block test	ASTM	4500	4500
Max Load, lbs	D-3233		

Example 5

[0130] A lube oil composition was prepared by adding the following additive package to a poly(trimethylene-ethylene ether)glycol (Mn=1100, PO3G3) to form an initial composition.

PO3G3	97.85%
Defoamer DC 200 cSt	0.0025%
VANLUBE ® 7723	0.3%
VANLUBE ® 887E	0.4%
IRGANOX ® 1135	0.2%
IRGALUBE ® TPPT	0.5%
IRGALUBE ® 349	0.4%
VANLUBE ® RD	0.25%
CUVAN ® 826	0.1%

[0131] This lube oil composition (90 wt % based on total weight) was blended with the 2-Ethylhexanoate PO3G Ester (10 wt % based on total weight) prepared as described above.

[0132] Table 4 lists the lube properties of the finished product which is suitable, for example, as a rotating machinery lubricant (gears, bearings) and as a hydraulic fluid.

TABLE 4

Property	ASTM Method	
Viscosity @ 40 C, cSt		236
Viscosity Index		206
Pour point, ° C.	D97	-45
Flash Point, ° C.	D-92	288
Four Ball Wear Scar, mm	D-4172	0.37
Coefficient of friction	D-4172	0.033
Load Wear Index	D-2783	61.5
Last nonseizure load, (scar, mm)	D-2783	160 kg (.52)
Weld Load, kg		200
Falex Pin & V block Max load, lbs	D3233	3000
Oxidation Test Data	D4636	
Viscosity change, %	24 hrs @ 190 C.	1.49
Acid number change (mg/KOH/g)		0.07
% Evaporation loss,		0.65
Sediment weight, mg		4.4
Copper corrosion	D-4646	Dull-ib

What is claimed is:

1. A lubrication oil composition comprising: (i) a base fluid stock comprising a mixture of (a) a polytrimethylene ether glycol that is a fluid at ambient temperature, and (b) an acid ester of a polytrimethylene ether glycol that is a fluid at ambient temperature, and (ii) one or more lube oil additives.

2. The lubrication oil composition of claim 1, wherein the base fluid stock is about 50 wt % or greater, based on the total weight of the lubrication oil composition.

3. The lubrication oil composition of claim 2, wherein the base fluid stock is about 75 wt % or greater, based on the total weight of the lubrication oil composition.

4. The lubrication oil composition of claim 3, wherein the base fluid stock is about 95 wt % or greater, based on the total weight of the lubrication oil composition.

5. The lubrication oil composition of claim 1, wherein the base fluid stock consists essentially of the mixture of the polytrimethylene ether glycol and the acid ester of the polytrimethylene ether glycol.

6. The lubrication oil composition of claim 1, wherein the weight ratio of the polytrimethylene ether glycol/acid ester of the polytrimethylene ether glycol in the base fluid stock is 1:1 or greater.

7. The lubrication oil composition of claim 1, wherein the weight ratio of the acid ester of the polytrimethylene ether glycol/polytrimethylene ether glycol in the base fluid stock is 1:1 or greater.

8. The lubrication oil composition of claim 1, wherein the acid ester of the polytrimethylene ether glycol comprises from about 50 to 100 wt % diester, and from 0 to about 50 wt % monoester, based on the weight of the acid ester.

9. The lubrication oil composition of claim 1, further comprising a lube oil additive comprising at least one selected from the group consisting of ashless dispersants, metal detergents, viscosity modifiers, anti-wear agents, antioxidants,

friction modifiers, pour point depressants, anti-foaming agents, corrosion inhibitors, demulsifiers and rust inhibitors.

10. The lubrication oil composition of claim 1, wherein said lube oil additive is at least 50% miscible in the base fluid stock.

11. The lubrication oil composition claim 1, wherein said lube oil composition is a substantially uniform mixture, with substantially no settling or phase separation, of the components.

12. The lubrication oil composition of claim 1, wherein the acid ester of the polytrimethylene ether glycol is an acid ester of a monocarboxylic acid and/or equivalent.

13. The lubrication oil composition of claim 12, wherein the monocarboxylic acid has the formula $R-COOH$, wherein R is a substituted or unsubstituted aromatic, aliphatic or cycloaliphatic organic moiety containing from 6 to 40 carbon atoms.

14. The lubrication oil composition of claim 1 wherein the acid ester of the polytrimethylene glycol one or more compounds of the formula (I):



wherein Q represents the residue of a polytrimethylene ether glycol after abstraction of the hydroxyl groups, R_2 is H or R_3CO , and each of R_1 and R_3 is individually a substituted or unsubstituted aromatic, saturated aliphatic, unsaturated aliphatic or cycloaliphatic organic group, containing from 6 to 40 carbon atoms.

15. The lubrication oil composition of claim 1, wherein the acid ester has a number average molecular weight based on a polytrimethylene ether glycol having a number average molecular weight of at least about 250 to less than about 10000.

16. The lubrication oil of claim 1, wherein the polytrimethylene ether glycol has a number average molecular weight of at least about 250 to less than about 10000.

17. The lubrication oil of claim 1, wherein from 99% to 100% of repeating units in the polytrimethylene ether glycol are trimethylene ether units.

18. The lubrication oil of claim 1, wherein the polytrimethylene glycol comprises trimethylene ether units and a lesser amount of other polyoxyalkylene ether repeat units.

19. The lubrication oil composition of claim 1, wherein the acid ester is prepared from biologically produced 1,3-propane diol.

20. The lubrication oil composition of claim 1, wherein the polytrimethylene ether glycol is prepared from biologically produced 1,3-propane diol.

21. The lubrication oil composition of claim 1, wherein the acid ester of the polytrimethylene ether glycol has a viscosity that is less than the viscosity of the polytrimethylene ether glycol.

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