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(54) Title: LUBRICANT COMPOSITIONS AND METHODS OF MAKING AND USING SAME

(57) Abstract: Lubricant compositions having at least one base oil composition and a friction-reducing composition comprising at least a first diol compound are described. Methods for making such compounds and methods of drilling using such lubricant compositions are also described.



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**TITLE: LUBRICANT COMPOSITIONS AND METHODS OF MAKING AND USING SAME**

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5 **PRIORITY**

[0001] This invention claims priority to and the benefit of USSN 62/186,494 filed June 30, 2015, and EP 15180109.9 filed August 7, 2015, which are incorporated by reference herein.

[0002] This invention also relates to USSN 62/186,503, filed June 30, 2015, entitled  
10 “Glycerol Carbamate Based Lubricant Compositions And Methods Of Making And Using Same”, (Atty. Docket 2015EM141); USSN 62/186,509, filed June 30, 2015, entitled “Lubricant Compositions and Methods of Making and Using Same”, (Atty. Docket 2015EM143); USSN 62/186,516, filed June 30, 2015, entitled “Lubricant Compositions Containing Phosphates and/or Phosphites and Methods of Making and Using Same”, (Atty.  
15 Docket 2015EM144); and USSN 62/186,526, filed June 30, 2015, entitled “Lubricant Compositions Comprising Diol Functional Groups and Methods of Making and Using Same”, (Atty. Docket 2015EM145).

**FIELD OF THE INVENTION**

[0003] The present disclosure relates to lubricant compositions and drilling fluid  
20 compositions useful in drilling of wellbores.

**BACKGROUND OF THE INVENTION**

[0004] The process of drilling a hole in the ground for the extraction of a natural resource requires a fluid for removing the cuttings from the wellbore, lubricating and cooling the drill bit, controlling formation pressures and maintaining hole stability.

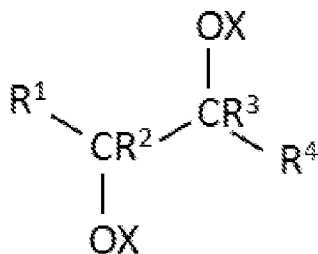
25 [0005] Many formations present difficulties for drilling. For example, the horizontal displacement that occurs in extended reach drilling (ERD) is often limited by torque and drag losses due to friction. Surface interactions, such as rotation of the drill string, is believed to contribute to such frictional losses. In extended reach drilling, frictional losses can be reduced by using a hydrocarbon-based drilling fluid. Additives can be added to the  
30 hydrocarbon-based fluid to further reduce the frictional losses.

[0006] Nevertheless, extended reach drilling could be more useful if longer wellbores could be effectively drilled. Thus, there is need in the art for new lubricant compositions, e.g., for use in drilling operations, particularly extended reach drilling.

**SUMMARY OF THE INVENTION**

[0007] The subject matter of this application relates, in part, to the discovery that certain compositions, when added to a base oil composition that includes water, can significantly reduce the coefficient of friction experienced during drilling. It is believed that such  
 5 reductions in the coefficient of friction can lead to improved drilling, particularly to drill longer wellbores.

[0008] Thus, in one aspect, the subject matter of this application relates to lubricant compositions suitable for use in drilling operations, comprising: a)  $\geq$  about 90 wt% of at least one base oil composition, the base oil composition comprising about 1.0 to about 15.0 wt%  
 10 water, and b) about 1.0 to about 10.0 wt% of a friction-reducing composition comprising: at least one compound represented by Formula I:



Formula I

wherein X is selected from H, Group 1-2 metals,  $\text{NR}_4^+$  and  $\text{PR}_4^+$  groups where each R group is independently selected from H and hydrocarbyl groups, particularly X may be H;  
 15 and each of  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^4$  are individually selected from H, branched or unbranched, substituted or unsubstituted  $\text{C}_1$  to  $\text{C}_{50}$  hydrocarbyl groups.

[0009] In another aspect, the subject matter of this application relates to methods of making a lubricant composition suitable for use in drilling operations. The methods comprise  
 20 a) providing at least one base oil composition, the base oil composition comprising about 1.0 to about 15.0 wt% water, and b) combining  $\geq$  about 90 wt% of the base oil composition with about 1.0 to about 10.0 wt% of a friction-reducing composition comprising a compound following at least one compound represented by Formula I.

[0010] In still another aspect, the subject matter of this application relates to methods of drilling a wellbore. The methods comprise a) providing a friction-reducing composition  
 25 prepared by mixing i)  $\geq$  90 wt% of at least one base oil composition, the base oil composition comprising about 1.0 to about 15.0 wt% water, and from about 1.0 to about 10.0 wt% of a friction-reducing composition comprising: a compound represented by Formula I; and b) introducing the lubricant composition into the wellbore.

**DETAILED DESCRIPTION OF THE INVENTION**

[0011] As used herein, the terms "well" and "wellbore" are used interchangeably and can include, without limitation, an oil, gas or water production well, an injection well, or a geothermal well. As used herein, a "well" includes at least one wellbore. A wellbore can include vertical, inclined, and horizontal portions, and it can be straight, curved, or branched. As used herein, the term "wellbore" includes any cased, and any uncased, open-hole portion of the wellbore. A near-wellbore region is the subterranean material and rock of the subterranean formation surrounding the wellbore. As used herein, a "well" also includes the near-wellbore region. The near-wellbore region is generally considered to be the region within about 10 feet of the wellbore. As used herein, "into a well" means and includes into any portion of the well, including into the wellbore or into the near-wellbore region via the wellbore.

[0012] A portion of a wellbore may be an open hole or cased hole. In an open-hole wellbore portion, a tubing or drill string may be placed into the wellbore. The tubing or drill string allows fluids to be circulated in the wellbore. In a cased-hole wellbore portion, a casing is placed and cemented into the wellbore, which can also contain a tubing or drill string. The space between two cylindrical shapes is called an annulus. Examples of an annulus include, but are not limited to: the space between the wellbore and the outside of a tubing or drill string in an open-hole wellbore; the space between the wellbore and the outside of a casing in a cased-hole wellbore; and the space between the inside of a casing and the outside of a tubing or drill string in a cased-hole wellbore.

[0013] For the purpose of this invention, friction means the mechanical resistance and rubbing of the drill string with the cased hole and the open hole as the drill string or tubing is moved, withdrawn, advanced or rotated. Furthermore it also comprises the mechanical resistance of coiled tubing inside the cased and the open hole; introducing casing; introducing screens; introducing tools for cleaning, fracturing, and perforating; rotating drill string; advancing the wellbore; withdrawing a drill string; and/or withdrawing coiled tubing.

[0014] For the purposes of this invention and the claims thereto, the new numbering scheme for the Periodic Table Groups is used as described in Chemical and Engineering News, (1985), Vol. 63(5), pg. 27.

[0015] The person of ordinary skill in the art will recognize that the alcohol groups on the diols described herein are subject to deprotonation. Thus, the term "glycerol" as used herein includes salts of the diol formed by the reaction thereof with a suitable counterion. Some

suitable counterions include, but are not limited to, Group 1-2 metals, organic cations, e.g.,  $\text{NR}_4^+$  and  $\text{PR}_4^+$  groups, where each R group is independently selected from H and hydrocarbyl groups.

[0016] In any embodiment described herein, Group 1-2 metals includes Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra, preferably Li, Na, K, Cs, Mg and Ca.

[0017] The terms "hydrocarbyl radical," "hydrocarbyl," "hydrocarbyl group," "alkyl radical," and "alkyl" are used interchangeably throughout this document. Likewise the terms "group", "radical", and "substituent" are also used interchangeably in this document. For purposes of this disclosure, "hydrocarbyl radical" is defined to be  $\text{C}_1\text{-C}_{50}$  radicals, that may be linear, branched, or cyclic, and when cyclic, aromatic or non-aromatic. Examples of such radicals include, but are not limited to, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl, iso-amyl, hexyl, octyl cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, and the like including their substituted analogues. Substituted hydrocarbyl radicals are radicals in which at least one hydrogen atom of the hydrocarbyl radical has been substituted with at least one functional group such as  $\text{NR}^*_2$ ,  $\text{OR}^*$ ,  $\text{SeR}^*$ ,  $\text{TeR}^*$ ,  $\text{PR}^*_2$ ,  $\text{AsR}^*_2$ ,  $\text{SbR}^*_2$ ,  $\text{SR}^*$ ,  $\text{BR}^*_2$ ,  $\text{SiR}^*_3$ ,  $\text{GeR}^*_3$ ,  $\text{SnR}^*_3$ ,  $\text{PbR}^*_3$ , and the like, or where at least one heteroatom has been inserted within a hydrocarbyl ring.

[0018] The term "alkenyl" means a straight-chain, branched-chain, or cyclic hydrocarbon radical having one or more double bonds. These alkenyl radicals may be optionally substituted. Examples of suitable alkenyl radicals include, but are not limited to, ethenyl, propenyl, allyl, 1,4-butadienyl cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclohexenyl, cyclooctenyl and the like including their substituted analogues.

[0019] The term "alkoxy" or "alkoxide" means an alkyl ether or aryl ether radical wherein the term alkyl is as defined above. Examples of suitable alkyl ether radicals include, but are not limited to, methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, iso-butoxy, sec-butoxy, tert-butoxy, phenoxy, and the like.

[0020] The term "aryl" or "aryl group" means a six carbon aromatic ring and the substituted variants thereof, including but not limited to, phenyl, 2-methyl-phenyl, xylyl, 4-bromo-xylyl. Likewise heteroaryl means an aryl group where a ring carbon atom (or two or three ring carbon atoms) has been replaced with a heteroatom, preferably N, O, or S. As used herein, the term "aromatic" also refers to pseudoaromatic heterocycles which are heterocyclic substituents that have similar properties and structures (nearly planar) to aromatic heterocyclic ligands, but are not by definition aromatic; likewise the term aromatic also refers to substituted aromatics.

[0021] Where isomers of a named alkyl, alkenyl, alkoxide, or aryl group exist (e.g., n-butyl, iso-butyl, sec-butyl, and tert-butyl) reference to one member of the group (e.g., n-butyl) shall expressly disclose the remaining isomers (e.g., iso-butyl, sec-butyl, and tert-butyl) in the family. Likewise, reference to an alkyl, alkenyl, alkoxide, or aryl group without specifying a particular isomer (e.g., butyl) expressly discloses all isomers (e.g., n-butyl, iso-butyl, sec-butyl, and tert-butyl).

[0022] As used herein, the term "heterogeneous blend" means a composition having two or more morphological phases in the same state. For example a blend of immiscible components, e.g., oil and water, where one component forms discrete packets dispersed in a matrix of another component is said to be heterogeneous. By continuous phase is meant the matrix phase in a heterogeneous blend. By discontinuous phase is meant the dispersed phase in a heterogeneous blend.

[0023] Kinematic viscosity (also referred to as viscosity) is determined by ASTM D445, and is typically measured at 40°C (Kv40) or 100°C (Kv100). If temperature is not indicated, the viscosity is Kv100.

#### **Lubricant Composition**

[0024] Lubricant compositions that are the subject of this disclosure typically comprise a base oil composition and a friction-reducing agent. The base oil composition is typically present in the lubricant composition in an amount of  $\geq$  about 50.0 wt%,  $\geq$  about 55.0 wt%,  $\geq$  about 60.0 wt%,  $\geq$  about 65.0 wt%,  $\geq$  about 70.0 wt%,  $\geq$  about 75.0 wt%,  $\geq$  about 80.0 wt%,  $\geq$  about 85.0 wt%,  $\geq$  about 90.0 wt%,  $\geq$  about 95.0 wt%, or  $\geq$  about 97.0 wt%, of the lubricant composition. Additionally or alternatively, the lubricant composition comprises  $\leq$  about 99.0 wt%, e.g.,  $\leq$  about 97.0 wt%,  $\leq$  about 95.0 wt%,  $\leq$  about 90.0 wt%,  $\leq$  about 80.0 wt%,  $\leq$  about 75.0 wt%,  $\leq$  about 70.0 wt%,  $\leq$  about 65.0 wt%,  $\leq$  about 60.0 wt%,  $\leq$  or about 55.0 wt% base oil composition. Ranges of the amount of base oil composition in the lubricant composition include ranges formed from any combination of the above-enumerated values, e.g., about 50.0 to about 99.0 wt%, about 55.0 to about 97.0 wt%, about 60.0 to about 95.0 wt%, about 65.0 to about 90.0 wt%, about 70.0 to about 85.0 wt%, about 75.0 to about 80.0 wt%, about 70.0 to about 95.0 wt%, about 85.0 to about 95.0 wt%, etc.

[0025] In a preferred embodiment of the invention, the base oil composition comprises a base oil that is present in the lubricant composition in ranges from about 50.0 to about 99.0 wt%, about 55.0 to about 97.0 wt%, about 60.0 to about 95.0 wt%, about 65.0 to about 90.0 wt%, about 70.0 to about 85.0 wt%, about 75.0 to about 80.0 wt%, about 70.0 to about 95.0

wt%, about 85.0 to about 95.0 wt%, and the friction-reducing composition is typically present in the lubricant composition in the amount of about 0.5 to about 10.0 wt%, about 1.0 to about 9.0 wt%, about 1.5 to about 8.0 wt%, about 2.0 to about 7.0 wt%, about 2.5 to about 6.0 wt%, about 3.0 to about 5.0 wt%, about 3.5 to about 4.5 wt%, about 1.0 to about 5.0 wt%, about 2.0 to about 4.0 wt%.

**[0026]** The friction-reducing composition is typically present in the lubricant composition in an amount of  $\geq$  about 0.5 wt%, e.g.,  $\geq$  about 1.0 wt%,  $\geq$  about 1.5 wt%,  $\geq$  about 2.0 wt%,  $\geq$  about 2.5 wt%,  $\geq$  about 3.0 wt%,  $\geq$  about 3.5 wt%,  $\geq$  about 4.0 wt%,  $\geq$  about 4.5 wt%,  $\geq$  about 5.0 wt%,  $\geq$  about 6.0 wt%,  $\geq$  about 7.0 wt%,  $\geq$  about 8.0 wt%, or  $\geq$  about 9.0 wt%. Additionally or alternatively, the lubricant composition comprises  $\leq$  about 10.0 wt% e.g.,  $\leq$  about 9.0 wt%,  $\leq$  about 8.0 wt%,  $\leq$  about 7.0 wt%,  $\leq$  about 6.0 wt%,  $\leq$  about 5.0 wt%,  $\leq$  about 4.5 wt%,  $\leq$  about 4.0 wt%,  $\leq$  about 3.5 wt%,  $\leq$  about 3.0 wt%,  $\leq$  about 2.5 wt%,  $\leq$  about 2.0 wt%,  $\leq$  about 1.5 wt%, or  $\leq$  about 1.0 wt% friction-reducing agent. Ranges of the amount of friction-reducing composition in the lubricant composition include ranges formed from any combination of the above-enumerated values, e.g., about 0.5 to about 10.0 wt%, about 1.0 to about 9.0 wt%, about 1.5 to about 8.0 wt%, about 2.0 to about 7.0 wt%, about 2.5 to about 6.0 wt%, about 3.0 to about 5.0 wt%, about 3.5 to about 4.5 wt%, about 1.0 to about 5.0 wt%, about 2.0 to about 4.0 wt%, about 0.1 wt% to about 5.0 wt%, etc.

**[0027]** All weight percentages are based on the total weight of the base oil and the friction-reducing compositions.

**[0028]** Lubricant compositions generally have a coefficient of friction less than that of the base oil composition. Some lubricant compositions have a coefficient of friction of  $\leq$  about 0.12, e.g.,  $\leq$  about 0.10,  $\leq$  about 0.08,  $\leq$  about 0.06,  $\leq$  about 0.04, or  $\leq$  about 0.02. Additionally or alternatively, the coefficient of friction may be  $\geq$  about 0.01, e.g.,  $\geq$  about 0.03,  $\geq$  about 0.05,  $\geq$  about 0.07,  $\geq$  about 0.09, or  $\geq$  about 0.11. Ranges of the coefficient of friction of the lubricant composition include ranges formed from any combination of the above-enumerated values, e.g., about 0.01 to about 0.12, about 0.3 to about 0.10, about 0.05 to about 0.08, about 0.06 to about 0.07, about 0.08 to about 0.12, about 0.08 to about 0.10, etc.

**[0029]** Additionally or alternatively, the lubricant composition may be characterized by a change in the coefficient of friction relative to the coefficient of friction of the base oil composition without the friction-reducing agent. In other words, the lubricant composition having the friction reducing agent may have a coefficient of friction that is at least about 20.0% less than, e.g., is at least about 25.0% lower than, is at least about 30.0% lower than, is

at least about 35.0% lower than, is at least about 40.0% lower than, is at least about 45.0% lower than, is at least about 50.0% lower than, is at least about 55.0% lower than, is at least about 60.0% lower than, the coefficient of friction of the base oil composition in the absence of the additive composition. Ranges of the reduction in the coefficient of friction of the lubricant composition relative to the base oil composition without the friction-reducing composition include ranges formed from any combination of the above-enumerated values, e.g., about 20.0 to about 60.0% lower, about 25.0 to about 55.0% lower, about 30.0 to about 50.0% lower, about 35.0 to about 45.0% lower, about 40.0% lower, about 30.0 to about 60.0% lower, about 35.0 to about 60.0% lower, about 40.0 to about 60.0% lower, about 45.0 to about 60.0% lower, about 40.0 to about 55.0% lower, etc. For clarity, an exemplary lubricant composition may comprise 4.0 g of friction reducing agent and 96.0 g of a base oil composition comprising 86.0 g of base oil and 10.0 g of other additives. The reduction in the coefficient of friction would be determined by comparing the coefficient of friction of this exemplary composition would be compared to the coefficient of friction of a composition comprising 86.0 g base oil and 10.0 g of the other additives.

#### **Base Oil Composition**

[0030] Generally, the base oil composition may include a base oil and one or more base oil additives. Numerous base oils are known in the art. Particular base oils that are useful in the present disclosure include natural oils and synthetic oils, as well as unconventional oils (or mixtures thereof), which can be used unrefined, refined, or re-refined (the latter is also known as reclaimed or reprocessed oil). Unrefined oils are those obtained directly from a natural or synthetic source and used without added purification. These include shale oil obtained directly from retorting operations, petroleum oil obtained directly from primary distillation, and ester oil obtained directly from an esterification process. Refined oils are similar to the oils discussed for unrefined oils except refined oils are subjected to one or more purification steps to improve at least one base oil property. One skilled in the art is familiar with many purification processes. These processes include solvent extraction, secondary distillation, acid extraction, base extraction, filtration, and percolation. Re-refined oils are obtained by processes analogous to refined oils but using an oil that has been previously used as a feed stock.

[0031] Groups I, II, III, IV, and V are broad lube base oil stock categories developed and defined by the American Petroleum Institute (API Publication 1509; [www.API.org](http://www.API.org)) to create guidelines for base oils. Group I base stocks have a viscosity index of 80 to 120 and contain > 0.03% sulfur and/or less than 90% saturates. Group II base stocks have a viscosity index of

80 to 120, and contain  $\leq 0.03\%$  sulfur and  $\geq 90\%$  saturates. Group III stocks have a viscosity index  $> 120$  and contain  $\leq 0.03\%$  sulfur and  $> 90\%$  saturates. Group IV includes polyalphaolefins (PAO) and Gas-to-Liquid (GTL) materials. Group V base stock includes base stocks not included in Groups I-IV. The table below summarizes properties of each of these five groups.

Exemplary Base Oil Properties

	Saturates (wt%)	Sulfur (wt%)	Viscosity Index (cSt)
Group I	$< 90$ and/or	$> 0.03$ and/or	80 to 120
Group II	$\geq 90$ and	$\leq 0.03$ and	80 to 120
Group III	$\geq 90$ and	$\leq 0.03$ and	$\geq 120$
Group IV	Includes PAO's and GTL's		
Group V	All other base oil stocks not included in Groups I-IV		

[0032] Useful GTL's include those described as high purity hydrocarbon feedstocks at paragraphs [0245]-[0303] of US 2008/0045638. PAO's useful herein include those described in paragraphs [0243]-[0266] of US 2008/0045638. Useful Group III Base Oils include those described at paragraphs [0304]-[0306] of US 2008/0045638.

[0033] Natural oils include animal oils, vegetable oils (castor oil and lard oil, for example), and mineral oils. Animal and vegetable oils possessing favorable thermal oxidative stability can be used. Of the natural oils, mineral oils are preferred. Mineral oils vary widely as to their crude source, for example, as to whether they are paraffinic, naphthenic, or mixed paraffinic-naphthenic. Oils derived from coal or shale are also useful. Natural oils vary also as to the method used for their production and purification, for example, their distillation range and whether they are straight run or cracked, hydrorefined, or solvent extracted.

[0034] Group II and/or Group III hydroprocessed or hydrocracked basestocks, including synthetic oils, are also well known basestock oils.

[0035] Synthetic oils include hydrocarbon oil. Hydrocarbon oils include oils such as polymerized and interpolymerized olefins (polybutylenes, polypropylenes, propylene isobutylene copolymers, ethylene-olefin copolymers, and ethylene-alphaolefin copolymers, for example). Polyalphaolefin (PAO) oil base stocks are commonly used synthetic hydrocarbon oil. By way of example, PAOs derived from  $C_8$  to  $C_{14}$  olefins, e.g.,  $C_8$ ,  $C_{10}$ ,  $C_{12}$ ,  $C_{14}$  olefins or mixtures thereof, may be utilized. Some such PAO's are described in US 4,956,122; US 4,827,064; and US 4,827,073, each of which is incorporated herein by reference in its entirety.

[0036] The number average molecular weights of the PAOs, which are known materials and generally available on a major commercial scale from suppliers such as ExxonMobil Chemical Company, Chevron Phillips Chemical Company, BP, and others, typically vary from 250 to 3,000 g/mol, although PAO's are typically made in Kinematic viscosities up to 5 3,500 cSt (100°C). The PAOs are typically comprised of relatively low molecular weight hydrogenated polymers or oligomers of alphaolefins which include, but are not limited to, C<sub>2</sub> to C<sub>32</sub> alphaolefins with the C<sub>8</sub> to C<sub>16</sub> alphaolefins, such as 1-octene, 1-decene, 1-dodecene and the like, being preferred. The preferred polyalphaolefins are poly-1-octene, poly-1-decene and poly-1-dodecene and mixtures thereof and mixed olefin-derived polyolefins. 10 However, the dimers of higher olefins in the range of C<sub>14</sub> to C<sub>18</sub> may be used to provide low viscosity basestocks of acceptably low volatility. Depending on the viscosity grade and the starting oligomer, the PAOs may be predominantly trimers and/or tetramers of the starting olefins, with minor amounts of the higher oligomers, having a Kinematic viscosity range of 1.5 to 3,500 cSt (Kv100), such as from 1.5 to 12 cSt.

15 [0037] The PAO fluids may be conveniently made by the polymerization of an alphaolefin in the presence of a polymerization catalyst such as the Friedel-Crafts catalysts including, for example, aluminum trichloride, boron trifluoride or complexes of boron trifluoride with water, alcohols such as ethanol, propanol or butanol, carboxylic acids or esters, such as ethyl acetate or ethyl propionate. For example the methods disclosed by 20 US 4,149,178 or 3,382,291 may be conveniently used herein. Other descriptions of PAO synthesis are found in the following: US 3,742,082; US 3,769,363; US 3,876,720; US 4,239,930; US 4,367,352; US 4,413,156; US 4,434,408; US 4,910,355; US 4,956,122; and US 5,068,487. The dimers of the C<sub>14</sub> to C<sub>18</sub> olefins are described in US 4,218,330. The PAO's may be produced using a metallocene catalyst compound as described in 25 US 8,535,514 and US 8,247,358.

[0038] The hydrocarbyl aromatics can be used as base oil or base oil component and can be any hydrocarbyl molecule that contains at least 5% of its weight derived from an aromatic moiety such as a benzenoid moiety or naphthenoid moiety, or their derivatives. These hydrocarbyl aromatics include alkyl benzenes, alkyl naphthalenes, alkyl diphenyl oxides, 30 alkyl naphthols, alkyl diphenyl sulfides, alkylated bis-phenol A, alkylated thiodiphenol, and the like. The aromatic can be mono-alkylated, dialkylated, polyalkylated, and the like. The aromatic can be mono- or poly-functionalized. The hydrocarbyl groups can also be comprised of mixtures of alkyl groups, alkenyl groups, alkynyl, cycloalkyl groups, cycloalkenyl groups and other related hydrocarbyl groups. The hydrocarbyl groups can range

from C<sub>6</sub> to C<sub>60</sub> with a range of C<sub>8</sub> to C<sub>20</sub> often being preferred. A mixture of hydrocarbyl groups is often preferred, and up to three such substituents may be present. The hydrocarbyl group can optionally contain sulfur, oxygen, and/or nitrogen containing substituents. The aromatic group can also be derived from natural (petroleum) sources, provided at least 5% of the molecule is comprised of an above-type aromatic moiety. Viscosities at 100°C of approximately 3 cSt to 50 cSt are preferred, with viscosities of approximately 3.4 cSt to 20 cSt often being more preferred for the hydrocarbyl aromatic component. In one embodiment, an alkyl naphthalene where the alkyl group is primarily comprised of 1-hexadecene is used. Other alkylates of aromatics can be advantageously used. Naphthalene or methyl naphthalene, for example, can be alkylated with olefins such as octene, decene, dodecene, tetradecene or higher, mixtures of similar olefins, and the like. Useful concentrations of hydrocarbyl aromatic in a base oil composition can be 2% to 25%, preferably 4% to 20%, and more preferably 4% to 15%, depending on the application.

**[0039]** Other useful fluids for use as base oils include non-conventional or unconventional base stocks that have been processed, preferably catalytically, or synthesized to provide high performance characteristics.

**[0040]** Non-conventional or unconventional base stocks/base oils include one or more of a mixture of base stock(s) derived from one or more Gas-to-Liquids (GTL) materials, as well as isomerate/isodewaxate base stock(s) derived from natural wax or waxy feeds, mineral and or non-mineral oil waxy feed stocks such as slack waxes, natural waxes, and waxy stocks such as gas oils, waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, or other mineral, mineral oil, or even non-petroleum oil derived waxy materials such as waxy materials received from coal liquefaction or shale oil, and mixtures of such base stocks.

**[0041]** GTL materials are materials that are derived via one or more synthesis, combination, transformation, rearrangement, and/or degradation/deconstructive processes from gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks such as hydrogen, carbon dioxide, carbon monoxide, water, methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane, butylenes, and butynes. GTL base stocks and/or base oils are GTL materials of base oil viscosity that are generally derived from hydrocarbons; for example, waxy synthesized hydrocarbons, that are themselves derived from simpler gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks. GTL base stock(s) and/or base oil(s) include oils boiling in the lube oil boiling range (1) separated/fractionated from synthesized

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

**[0042]** GTL base stock(s) and/or base oil(s) derived from GTL materials, especially, hydrodewaxed or hydroisomerized/followed by cat and/or solvent dewaxed wax or waxy feed, preferably F-T material derived base stock(s) and/or base oil(s), are characterized typically as having Kinematic viscosities at 100°C of from 2 cSt to 50 cSt (ASTM D445). They are further characterized typically as having pour points of -5°C to -40°C or lower (ASTM D97). They are also characterized typically as having viscosity indices of 80 to 140 or greater (ASTM D2270).

**[0043]** In addition, the GTL base stock(s) and/or base oil(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stock(s) and/or base oil(s) typically have very low sulfur and nitrogen content, generally containing less than 10 ppm, and more typically less than 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock(s) and/or base oil(s) obtained from F-T material, especially F-T wax, is essentially nil. In addition, the absence of phosphorous and aromatics make this material especially suitable for the formulation of low SAP products.

**[0044]** The term GTL base stock and/or base oil and/or wax isomerate base stock and/or base oil is to be understood as embracing individual fractions of such materials of wide viscosity range as recovered in the production process, mixtures of two or more of such fractions, as well as mixtures of one or two or more low viscosity fractions with one, two or more higher viscosity fractions to produce a blend wherein the blend exhibits a target Kinematic viscosity.

**[0045]** The GTL material, from which the GTL base stock(s) and/or base oil(s) is/are derived is preferably an F-T material (i.e., hydrocarbons, waxy hydrocarbons, wax). In

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

**[0046]** Base oils for use in the formulated base oil compositions useful in the present disclosure are any of the variety of oils corresponding to API Group I, Group II, Group III, Group IV, and Group V oils, and mixtures thereof, preferably API Group II, Group III, Group  
15 IV, and Group V oils, and mixtures thereof, more preferably the Group III to Group V base oils due to their exceptional volatility, stability, viscometric and cleanliness features. Minor quantities of Group I stock, such as the amount used to dilute additives for blending into formulated lube oil products, can be tolerated but should be kept to a minimum, i.e., amounts only associated with their use as diluents/carrier oil for additives used on an "as-received"  
20 basis. Even in regard to the Group II stocks, it is preferred that the Group II stock be in the higher quality range associated with that stock, i.e., a Group II stock having a viscosity index in the range of 100 to 120.

**[0047]** Some base oils may have an ester content  $\leq$  about 50 wt%, e.g.,  $\leq$  about 40 wt%,  $\leq$  about 30 wt%,  $\leq$  about 5.0 wt%, or  $\leq$  about 1.0 wt%. Additionally or alternatively, some base  
25 oils may have an ester content  $\geq$  about 40 wt%, e.g.,  $\geq$  about 50 wt%,  $\geq$  about 70 wt%, or  $\geq$  about 90 wt%.

**[0048]** Some base oils may have an aromatic contents  $\leq$  about 15.0 wt%, e.g.,  $\leq$  about 10.0 wt%,  $\leq$  about 5.0 wt%,  $\leq$  about 1.0 wt%,  $\leq$  about 0.50 wt%,  $\leq$  about 0.10 wt%,  $\leq$  about 0.05 wt%,  $\leq$  about 0.01 wt%, or  $\leq$  about 0.005 wt%. Additionally or alternatively, the  
30 aromatics content may be  $\geq$  about 0.005 wt%, e.g.,  $\geq$  about 0.01 wt%,  $\geq$  about 0.05 wt%,  $\geq$  about 0.10 wt%,  $\geq$  about 0.5 wt%,  $\geq$  about 0.1 wt%,  $\geq$  about 1.0 wt%,  $\geq$  about 5.0 wt%, or  $\geq$  about 10.0 wt%. Ranges of the aromatics content expressly disclosed herein include all combinations of the above-enumerated values, e.g., about 0.005 to about 15.0 wt%, about 0.01 to about 10.0 wt%, about 0.05 to about 5.0 wt%, about 0.10 to about 1.0 wt%, etc.

[0049] Some exemplary base oils have been characterized by their Kinematic viscosity at 40°C (Kv40). For example, particular base oils may have a viscosity  $\geq$  about 1.0 cSt, e.g.,  $\geq$  about 1.3 cSt,  $\geq$  about 1.5 cSt,  $\geq$  about 1.7 cSt,  $\geq$  about 1.9 cSt,  $\geq$  about 2.1 cSt,  $\geq$  about 2.3 cSt,  $\geq$  about 2.5 cSt,  $\geq$  about 2.7 cSt,  $\geq$  about 2.9 cSt,  $\geq$  about 3.1 cSt,  $\geq$  about 3.3 cSt, 5  $\geq$  about 3.5 cSt,  $\geq$  about 3.7 cSt,  $\geq$  about 4.0 cSt,  $\geq$  about 4.5 cSt, or  $\geq$  about 4.8 cSt, at 40°C. Additionally or alternatively, the viscosity at 40°C. may be  $\leq$  about 5.0 cSt, e.g.,  $\leq$  about 4.8 cSt,  $\leq$  about 4.5 cSt,  $\leq$  about 4.0 cSt,  $\leq$  about 3.7 cSt,  $\leq$  about 3.5 cSt,  $\leq$  about 3.3 cSt,  $\leq$  about 3.1 cSt,  $\leq$  about 2.9 cSt,  $\leq$  about 2.7 cSt,  $\leq$  about 2.5 cSt,  $\leq$  about 2.3 cSt,  $\leq$  about 2.1 cSt,  $\leq$  about 1.9 cSt,  $\leq$  about 1.7 cSt,  $\leq$  about 1.5 cSt,  $\leq$  about 1.3 cSt, or  $\leq$  about 1.1 cSt, 10 at 40°C. Some such base oils are available from ExxonMobil Chemical Company under the tradename Escaid™, e.g., Escaid™ 110 comprises a desulfurized hydrogenated hydrocarbon containing less than 0.50 wt% aromatics and having a viscosity of about 1.7 cSt at 40°C, Escaid™ 115 having a viscosity of about 2.1 cSt at 40°C, Escaid™ 120 having a flash point above 100°C, and Escaid™ 120 ULA having an aromatics content  $<$  0.01 wt%.

#### 15 **Base Oil Additives**

[0050] Often, the base oil composition includes additional additives. Preferably, one or more of the additional additives form a heterogeneous blend with the base oil. In such aspects, the base oil composition is preferably a heterogeneous blend having base oil as the continuous phase and one or more additional additives as the dispersed or internal phase. 20 Alternatively or additionally, one or more of the additional additives can solubilize in the base oil.

[0051] For example, the base oil composition can include additional additives including, but not limited to, an internal phase, which is typically water or a brine (i.e., the base oil composition is an inverted emulsion), a pH buffer, a viscosifier, an emulsifier, a wetting 25 agent, a weighting agent, a fluid loss additive, and a friction reducer.

[0052] For example, the base oil composition may include a pH buffer selected from the group consisting of magnesium oxide, potassium hydroxide, calcium oxide, and calcium hydroxide. Commercially available examples of a pH buffer include lime. The pH buffer can be in a concentration in the range of about 0.5 to about 10.0 pounds per barrel (ppb) of 30 the base oil composition. Useful base oil compositions can have a pH ranging from a low of about 7, 8, 9, 10, 11, or 12 to a high of about 14, such as from 10 to 14.

[0053] The base oil composition may optionally include a viscosifier. The viscosifier may be selected from the group consisting of inorganic viscosifier, fatty acids, including but not limited to dimer and trimer poly carboxylic fatty acids, diamines, polyamides,

organophilic clays and combinations thereof. Commercially available examples of a suitable viscosifier include, but are not limited to, VG-PLUS™, available from M-I Swaco, a Schlumberger Company; RHEMOD L™, TAU-MOD™, RM-63™, and combinations thereof, marketed by Halliburton Energy Services, Inc. According to an embodiment, the  
5 viscosifier is in a concentration of at least 0.5 ppb of the base oil composition. The viscosifier can also be in a concentration in the range of about 0.5 to about 20 ppb, alternatively of about 0.5 to about 10 ppb, of the base oil composition.

**[0054]** The base oil composition may further include a lubricant in addition to the friction-reducing composition described herein. In particular embodiments, the additional  
10 base oil composition comprises a particulated material, e.g., graphite such as Steelseal™, available from Halliburton.

**[0055]** The base oil composition can further include an emulsifier. The emulsifier can be selected from the group consisting of tall oil-based fatty acid derivatives such as amides, amines, amidoamines, and imidazolines made by reactions of fatty acids and various  
15 ethanolamine compounds, vegetable oil-based derivatives, and combinations thereof. Commercially available examples of a suitable emulsifier include, but are not limited to, EZ MUL™ NT, INVERMUL™ NT, LE SUPERMUL™, and combinations thereof, marketed by Halliburton Energy Services, Inc, MEGAMUL™, VersaMul™, VersaCoat™, marketed by MISwaco, a Schlumberger Company. According to an embodiment, the  
20 emulsifier is in at least a sufficient concentration such that the base oil composition maintains a stable emulsion or invert emulsion. According to yet another embodiment, the emulsifier is in a concentration of at least 1 ppb of the base oil composition. The emulsifier can also be in a concentration in the range of about 1 to about 20 ppb of the base oil composition.

**[0056]** The base oil composition can further include a weighting agent. The weighting  
25 agent can be selected from the group consisting of barite, hematite, manganese tetroxide, calcium carbonate, and combinations thereof. Commercially available examples of a suitable weighting agent include, but are not limited to, BAROID™, BARACARB™, BARODENSE™, and combinations thereof, marketed by Halliburton Energy Services, Inc and MICROMAX™, marketed by Elkem. According to an embodiment, the weighting agent  
30 is in a concentration of at least 10 ppb of the base oil composition. The weighting agent can also be in a concentration in the range of about 10 to about 1000 ppb, such as 10-800 ppb, of the base oil composition.

**[0057]** The base oil composition can further include a fluid loss additive. The fluid loss additive can be selected from the group consisting of oleophilic polymers, including

crosslinked oleophilic polymers, particulates. Commercially available examples of a suitable fluid loss additive include, but are not limited to VERSATROL™, available from M-I Swaco; N-DRIL™ HT PLUS, ADAPTA™, marketed by Halliburton Energy Services, Inc. The fluid loss additive can also be in a concentration in the range of about 0.5 to about 5 10 ppb of the base oil composition.

**[0058]** The base oil composition can further include an ester additive. The ester additive can be in a concentration in the range of about 1% to 20%.

**[0059]** The base oil composition may also optionally include one or more metal salts,  $MX_y$ , where M is a Group 1 or Group 2 metal, X is a halogen, and y is 1 to 2. Exemplary 10 such salts include, NaCl, KCl,  $CaCl_2$ ,  $MgCl_2$ , etc. The total amount of such salts in the base oil composition is typically about 10 – 35 wt% in the water phase. Organic additives that lower the water activity may also be used.

**[0060]** Water may also be present in the base oil composition at any convenient concentration, typically at a relatively low concentration, e.g.,  $\leq$  about 15.0 wt%,  $\leq$  about 15 12.5 wt%,  $\leq$  about 10.0 wt%,  $\leq$  about 7.5 wt%,  $\leq$  about 5.0 wt%,  $\leq$  about 2.5 wt%, or  $\leq$  about 1.0 wt%, the wt% being based on the total weight of the base oil and the water. Additionally or alternatively, the concentration of water may be  $\geq$  about 0.5 wt%, e.g.,  $\geq$  about 1.0 wt%,  $\geq$  about 2.5 wt%,  $\geq$  about 5.0 wt%,  $\geq$  about 7.5 wt%,  $\geq$  about 10.0 wt%,  $\geq$  about 12.5 wt%, or  $\geq$  about 15.0 wt%. In particular embodiments, the amount of water may be about 1 to about 20 21 gallons per barrel of base oil composition, such as about 1 to about 10 gallons per barrel of base oil composition. Range of the water content that are expressly disclosed comprise ranges formed from any of the above-enumerated values, e.g., about 0.5 to about 20.0 wt%, about 0.5 to about 15.0 wt%, about 0.5 to about 12.5 wt%, about 0.5 to about 10.0 wt%, about 0.5 to about 7.5 wt%, about 0.5 to about 5.0 wt%, about 0.5 to about 2.5 wt%, about 25 0.5 to about 1.0 wt%, about 1.0 to about 10.0 wt%, about 1.0 to about 7.5 wt%, about 1.0 to about 5.0 wt%, about 1.0 to about 2.5 wt%, about 2.5 to about 10.0 wt%, about 2.5 to about 7.5 wt%, about 2.5 to about 5.0 wt%, about 5.0 to about 10.0 wt%, about 5.0 to about 7.5 wt%, etc.

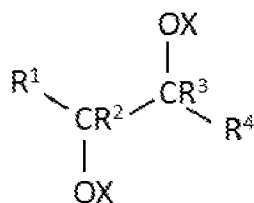
**[0061]** The base oil composition can further include wetting agents. The wetting agents 30 can be selected from the group consisting of tall oil-based fatty acid derivatives such as amides, amines, amidoamines, and imidazolines made by reactions of fatty acids and various ethanolamine compounds, vegetable oil-based derivatives, and combinations thereof. Commercially available examples of suitable wetting agents include, but are not limited to, DrillTreat™, OMC™, marketed by Halliburton Energy Services, Inc., VersaWet™, marketed

by MISwaco, a Schlumberger Company. According to an embodiment, the wetting agent is in at least a sufficient concentration such that the base oil composition maintains a stable emulsion or invert emulsion. According to yet another embodiment, the wetting agent is in a concentration of at least 0.25 ppb of base oil composition. The wetting agent can also be in a concentration in the range of about 0.05 to about 20 ppb, such as about 0.25 to about 20 ppb of the base oil composition.

[0062] In another embodiment, the wetting agent is absent from the base oil composition.

### **Friction-Reducing Composition**

[0063] Lubricant compositions according to the subject matter of the disclosure also include at least one friction-reducing composition comprising a compound represented by Formula I:

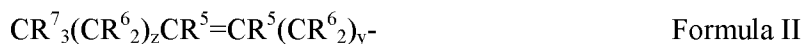


Formula I

wherein X may be selected from H, Group 1-2 metals,  $\text{NR}_4^+$  and  $\text{PR}_4^+$  groups where each R group is independently selected from H and hydrocarbyl groups, particularly X may be H; and

wherein each of  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^4$  are individually selected from H, branched or unbranched, substituted or unsubstituted,  $\text{C}_1$  to  $\text{C}_{50}$  hydrocarbyl groups, e.g.,  $\text{C}_5$  to  $\text{C}_{40}$  hydrocarbyl groups,  $\text{C}_{10}$  to  $\text{C}_{30}$  hydrocarbyl groups,  $\text{C}_{15}$  to  $\text{C}_{25}$  hydrocarbyl groups, or  $\text{C}_{15}$  to  $\text{C}_{20}$  hydrocarbyl groups. In some embodiments,  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^4$  are individually selected from the group consisting of branched or unbranched alkyl groups, alkenyl groups and combinations thereof. Exemplary alkyl groups include methyl, and ethyl, as well as branched and unbranched isomers of propyl; butyl; pentyl; hexyl; heptyl; octyl; nonyl; decyl; undecyl; dodecyl; tridecyl; tetradecyl; pentadecyl; hexadecyl; heptadecyl; octadecyl; nonadecyl; icosyl; heneicosanediol; docosyl; tricosyl; and tetracosyl. In particular embodiments, octadecyl is preferred, particularly where  $\text{R}^1$  is octadecyl.

[0064] Exemplary alkenyl groups are represented by Formula II:



[0065] In Formula II, each of  $\text{R}^5$ ,  $\text{R}^6$ , and  $\text{R}^7$  in Formula II is individually selected from H and  $\text{C}_1$  to  $\text{C}_{20}$  hydrocarbyl groups, such as exemplary alkyl groups which include methyl, and ethyl, as well as branched and unbranched isomers of propyl; butyl; pentyl; hexyl; heptyl;

octyl; nonyl; decyl; undecyl; dodecyl; tridecyl; tetradecyl; pentadecyl; hexadecyl; heptadecyl; octadecyl; nonadecyl; icosyl; heneicosanediol; docosyl; tricosyl; and tetracosyl, preferably  $R^5$  is H or methyl, particularly H. The variable y may be  $\geq 1$ , e.g.,  $\geq 2$ ,  $\geq 5$ ,  $\geq 7$ ,  $\geq 8$ ,  $\geq 10$ ,  $\geq 12$ ,  $\geq 14$ ,  $\geq 16$ ,  $\geq 18$ ,  $\geq 20$ ,  $\geq 22$ ,  $\geq 24$ ,  $\geq 26$ ,  $\geq 28$ ,  $\geq 30$ ,  $\geq 32$ ,  $\geq 34$ ,  $\geq 36$ ,  $\geq 38$ ,  $\geq 40$ ,  $\geq 42$ , or  $\geq 44$ .  
 5 Additionally or alternatively, y may be  $\leq 47$ , e.g.,  $\leq 44$ ,  $\leq 42$ ,  $\leq 40$ ,  $\leq 38$ ,  $\leq 36$ ,  $\leq 34$ ,  $\leq 32$ ,  $\leq 30$ ,  $\leq 28$ ,  $\leq 26$ ,  $\leq 24$ ,  $\leq 22$ ,  $\leq 20$ ,  $\leq 18$ ,  $\leq 16$ ,  $\leq 14$ ,  $\leq 12$ ,  $\leq 10$ ,  $\leq 8$ ,  $\leq 7$ , or  $\leq 5$ . In Formula II, z may be  $\geq 0$ , e.g.,  $\geq 1$ ,  $\geq 5$ ,  $\geq 7$ ,  $\geq 8$ ,  $\geq 10$ ,  $\geq 12$ ,  $\geq 14$ ,  $\geq 16$ ,  $\geq 18$ ,  $\geq 20$ ,  $\geq 22$ ,  $\geq 24$ ,  $\geq 26$ ,  $\geq 28$ ,  $\geq 30$ ,  $\geq 32$ ,  $\geq 34$ ,  $\geq 36$ ,  $\geq 38$ ,  $\geq 40$ ,  $\geq 42$ , or  $\geq 44$ . Additionally or alternatively, z may be  $\leq 47$ , e.g.,  $\leq 44$ ,  $\leq 42$ ,  $\leq 40$ ,  $\leq 38$ ,  $\leq 36$ ,  $\leq 34$ ,  $\leq 32$ ,  $\leq 30$ ,  $\leq 28$ ,  $\leq 26$ ,  $\leq 24$ ,  $\leq 22$ ,  $\leq 20$ ,  $\leq 18$ ,  $\leq 16$ ,  $\leq 14$ ,  $\leq 12$ ,  $\leq 10$ ,  $\leq 8$ ,  $\leq 7$ , or  $\leq 5$ . Ranges of y and z values that are expressly disclosed herein include ranges formed by any combination of the above-recited individual values. In particular embodiments, y ranges from about 5 to about 10, e.g., 8, and z ranges from about 5 to about 10, e.g., 7, i.e.,  $\text{CH}_3(\text{CH}_2)_7\text{C}=\text{C}(\text{CH}_2)_8$ -, also referred to as an oleyl group. The alkenyl group may optionally include two, three, four etc., double bonded and/or triple  
 15 bonded carbon atoms in the hydrocarbyl chain. The double bond may have cis- or trans-configuration. In particular embodiments, the cis-configuration may be particularly useful. Where the hydrocarbyl chain of the carboxylic acid has more than one carbon-carbon double bond, the bonds may have any combination of cis- and/or trans-configurations. The double bonds may be arranged in a conjugated manner, e.g., conjugated (9Z, 11E)-linoleic acid, or separated by at least one methylene group, e.g., linoleic acid, linolenic acid etc.) Other exemplary alkenyl groups include capryl, lauryl, myristyl, palmityl, isopalmityl, stearyl, isostearyl, oleyl, etc. The alkenyl group may optionally include functional groups such as, but not limited to, epoxy, hydroxyl, amine, mercaptan, halogen, etc.

**[0066]** In particular embodiments, 1,2-diols are suitable. Thus,  $R^1$  may be any of the  $C_{1-25}$   $C_{50}$  hydrocarbyl groups described above, while  $R^2$ ,  $R^3$ , and  $R^4$  are each H. In other embodiments, compounds according to Formula I may be any diol consistent with Formula I, e.g., a 2,3-diol, a 3,4-diol, a 4,5-diol, a 5,6-diol, a 6,7-diol, etc.

**[0067]** Thus, in particular embodiments,  $R^1$  is selected from unbranched  $C_{10}$  to  $C_{20}$  alkyl, particularly  $C_{15}$  to  $C_{20}$  alkyl group, and  $R^2$ ,  $R^3$ ,  $R^4$  are each H, e.g.,  $R^1$  is selected from decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl, heneicosanediol, docosyl, tricosyl, and tetracosyl, particularly pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl, more particularly octadecyl. In other embodiments,  $R^1$  is selected from and  $C_{10}$  to  $C_{20}$  alkenyl, particularly  $C_{15}$  to  $C_{20}$  alkenyl groups, and  $R^2$ ,  $R^3$ ,  $R^4$  are each H, e.g.,  $R^1$  is selected from capryl, lauryl, myristyl, palmityl,

isopalmyl, stearyl, isostearyl, oleyl groups, particularly oleyl.

[0068] Particular compounds according to Formula I include, but are not limited to, 1,2-decanediol; 1,2-undecanediol; 1,2-dodecanediol; 1,2-tridecanediol; 1,2-tetradecanediol; 1,2-pentadecanediol; 1,2-hexadecanediol; 1,2-heptadecanediol; 1,2-octadecanediol; 1,2-  
5 nonadecanediol; 1,2-eicosanediol; 1,2-heneicosanediol; 1,2-docosanediol; 1,2-tricosanediol; and 1,2-tetracosanediol, particularly 1,2-octadecanediol.

[0069] Diols useful in the lubricant compositions described herein are either commercially available or are readily prepared from the corresponding  $\alpha$ -olefin by methods well known in the art. For example, the olefin is first reacted with peracid, such as  
10 peroxyacetic acid or hydrogen peroxide plus formic acid to form an alkane-1,2-epoxide, which is readily hydrolyzed under acid or base catalysis to the alkane-1,2-diol. In another process, the olefin is first halogenated to a 1,2-dihalo-alkane and subsequently hydrolyzed to an alkane-1,2-diol by reaction first with sodium acetate and then with sodium hydroxide.

[0070]  $\alpha$ -Olefins are available from the thermal cracking of waxes. This process  
15 produces olefins of all carbon numbers.  $\alpha$ -Olefins having an even number of carbon atoms are prepared by the well-known ethylene "growth" reaction. Olefins obtained by either of these processes are essentially linear in structure with little or no branching. Linear olefins are the preferred olefins for conversion into alkane-1,2-diols.

[0071] The friction-reducing composition may, optionally, include one or more  
20 secondary friction-reducing components. Secondary friction-reducing components may be selected from nitrogen-containing compounds; substituted imidazolines and amides (described in PCT: \_\_\_\_\_, corresponding to USSN: 62/186,509 filed on Jun 30, 2015, entitled "Lubricant Compositions and Methods of Making and Using Same", Attorney Docket No. 2015EM143); glycerol carbamates; e.g., oleyl glycerol carbamate (described in  
25 PCT: \_\_\_\_\_, corresponding to USSN: 62/186,503 filed on June 30, 2015, entitled "Glycerol Carbamate Based Lubricant Compositions and Methods of Making and Using Same", Attorney Docket No. 2015EM141); hydrocarbyl thioglycerols, e.g., octadecyl thioglycerol; and hydrocarbyl-substituted glycerols, e.g., glycerol monostearate (described in  
30 PCT: \_\_\_\_\_, corresponding to USSN: 62/186,526 filed on June 30, 2015, entitled "Lubricant Compositions Comprising Diol Functional Groups and Methods of Making and Using Same", Attorney Docket No. 2015EM145) and phosphate esters and dihydrocarbyl hydrogen phosphites, e.g., tri-oleyloxy phosphate; and polyethyleneglycol-containing hydrocarbyl ether phosphate esters (described in PCT: \_\_\_\_\_, corresponding to USSN: 62/186,516 filed on June 30, 2015, entitled "Lubricant Compositions Containing Phosphates

and/or Phosphites and Methods of Making and Using Same”, Attorney Docket No. 2015EM144), each of which is incorporated by reference in its entirety as a part of this disclosure.

5 [0072] Useful secondary friction-reducing components include, e.g., Vikinol™ 18, ColaLube™ 3410, ColaLube™3407, and additives under the tradename ColaMid™.

[0073] The secondary friction-reducing component may be present in the friction reducing composition in an amount  $\geq$  about 5.0 wt%, e.g.,  $\geq$  about 10.0 wt%,  $\geq$  about 15.0 wt%,  $\geq$  about 20.0 wt%,  $\geq$  about 25.0 wt%,  $\geq$  about 30.0 wt%,  $\geq$  about 35.0 wt%,  $\geq$  about 40.0 wt%,  $\geq$  about 45.0 wt%,  $\geq$  about 50.0 wt%,  $\geq$  about 55.0 wt%,  $\geq$  about 10 60.0 wt%,  $\geq$  about 65.0 wt%,  $\geq$  about 70.0 wt%,  $\geq$  about 75.0 wt%,  $\geq$  about 80.0 wt%,  $\geq$  about 85.0 wt%, or  $\geq$  about 90 wt%, based on the total weight of the friction-reducing composition. Additionally or alternatively, the secondary friction-reducing component may be present in an amount  $\leq$  about 95 wt%, e.g.,  $\leq$  about 90.0 wt%,  $\leq$  about 85.0 wt%,  $\leq$  about 80.0 wt%,  $\leq$  about 75.0 wt%,  $\leq$  about 70.0 wt%,  $\leq$  about 65.0 wt%,  $\leq$  about 60.0 wt%,  $\leq$  15 about 55.0 wt%,  $\leq$  about 50.0 wt%,  $\leq$  about 45.0 wt%,  $\leq$  about 40.0 wt%,  $\leq$  about 35.0 wt%,  $\leq$  about 30.0 wt%,  $\leq$  about 25.0 wt%,  $\leq$  about 20.0 wt%,  $\leq$  about 15.0 wt%, or  $\leq$  about 10.0 wt%, based on the total weight of the friction-reducing composition. Ranges of the amount of secondary friction-reducing component that are expressly disclosed herein include ranges formed by any combination of the above-recited individual values, e.g., about 5.0 to 20 about 95.0 wt%, about 10.0 to about 90.0 wt%, about 15.0 to about 85.0 wt%, about 20.0 to about 80.0 wt%, about 25.0 to about 75.0 wt%, about 30.0 to about 70.0 wt%, about 35.0 to about 65.0 wt%, about 40.0 to about 60.0 wt%, about 45.0 to about 55.0 wt%, etc.

#### **Methods of Making the Lubricant Composition**

[0074] Lubricant compositions described herein can be made by mixing a friction-reducing composition described above and at least one base oil composition comprising about 25 1.0 to about 15.0 wt% water. The method may additionally include mixing the base oil composition prior to blending with the friction-reducing agent. In some embodiments, the mixture of the base oil composition and the friction reducing agent is heated during mixing, e.g., for 5-48 hours at a temperature of about 30 to about 70°C, e.g., about 24 hours at about 30 60°C. In some methods, the heating includes providing a nitrogen head pressure to the heating vessel of about 30 to about 50 psi. Mixing at speeds of about 2000 to about 5000 rpm. Typically, mixtures are cooled for 10-24 hours at about 25°C before testing or use.

**Methods of Drilling**

[0075] Lubricant compositions described herein are useful in any number of drilling methods. One exemplary method comprises mixing a friction-reducing composition and at least one base oil composition comprising about 1.0 to about 15.0 wt% water; and  
5 introducing the lubricant composition into the well.

[0076] The step of introducing can comprise pumping the lubricant composition into the well. The pumping may be done continuously, i.e., providing a constant flow of lubricant composition, periodically, or intermittently, i.e., alternating between periods of flow and no flow of lubricant composition. Particular methods further include continuously, periodically,  
10 or intermittently providing a second amount of friction-reducing composition to the lubricant composition already provided to the well. In some methods, the continuous provision of the friction reducing composition provides an overall reduction in the amount of friction-reducing agent used during the drilling process. Alternatively, the continuous provision of the friction-reducing agent may allow smoother drilling operation of the drilling process. The  
15 well can be, without limitation, an oil, gas, or water production well, or an injection well. Methods may further include one or more steps of advancing a downhole tool in the well.

[0077] The introduced lubricant composition may be exposed to temperatures in the well ranging from a low of about 70°C, 80°C, 90°C, 100°C, or 125°C to a high of about 170°C, and pressures ranging from ambient pressure to a high of about 100 bar (10,000 kPa), 200 bar  
20 (20,000 kPa), 300 bar (30,000 kPa), 400 bar (40,000 kPa), 500 bar (50,000 kPa), or 600 bar (60,000 kPa). The introduced lubricant composition may be utilized when system components have rotation speed of  $\leq$  about 1000 rpm, e.g.,  $\leq$  about 800 rpm,  $\leq$  about 700 rpm, and  $\geq$  about 0 rpm, such as from 1 to 1000 rpm. The introduced lubricant composition may also be utilized with minimal rotation but instead longitudinal motion at a speed of  $\leq$  10,000  
25 m/hr (meters per hour);  $\leq$  1,000 m/hr;  $\leq$  100; and/or  $\leq$  10m/hr.

[0078] According to an embodiment, the well penetrates a reservoir or is located adjacent to a reservoir. The methods can further include the step of removing at least a portion of the lubricant composition after the step of introducing. The methods can include any number of additional optional steps. For example, some methods include one or more of the following  
30 optional steps: mounting and cementing of well pipes in the first well; mounting of a blowout preventer or lubricator in the top of the well; drilling, at a distance from the well, a second well against a section of the first well to the effect that the second well gets into operational contact with the first well; mounting and cementing of well pipes in the second well; mounting of a blowout preventer or lubricator in the top of the second well; whereafter the

drilling from one of the first or second well continues down into the reservoir and the other well which is not drilled to the reservoir is filled wholly or partially with a fluid and a drilling tool is placed in the other well and the other well is subsequently closed so that the other well can be accessed at a later point in time, and that the tool is left in the other well so that this  
5 tool can establish a connection to the one of the first or second wells into which the drilling continued.

[0079] Still other optional steps include one or more of the following: calculating a desired path for a well of interest relative to a reference well; measuring a position of the well of interest relative to the reference well at a location along a wellbore of the well; calculating  
10 an actual path of the well of interest based at least in part on the measured position of the well of interest relative to the at least one reference well; comparing the actual path of the at least one well of interest to the desired path of the well of interest; and adjusting a drilling system to modify the actual path of the well of interest based at least in part on a deviation between the actual path of the well of interest and the desired path of the well of interest.

15 Experimental

[0080] *Viscosity Index* is determined from the Kinematic viscosity according to ASTM D2270 -10e1.

[0081] *Kinematic Viscosity* is determined according to ASTM D445.

[0082] *Coefficient of Friction (CoF)* is determined using a block-on-ring tribometer available  
20 from CETR, Inc., USA. The block is made of P110 steel and the ring is a nitrided Timken ring having a radius of 17.5 mm (35 m OD) and a width of 6.35 mm. The bocks are machined to a final surface roughness,  $R_a$ , of 0.18  $\mu\text{m}$ . The ring has a surface roughness,  $R_a$ , of about 0.01  $\mu\text{m}$ . The ring is partially submerged into 100 ml of the fluid to be tested such that about 10 ml of the ring is beneath the surface of the fluid. The block applies a 5.6 kg load on the ring. Testing is  
25 performed at 25°C. The ring is turned at 25 rpm, 50 rpm, 100 rpm, 250 rpm, 500 rpm, and 750 rpm for 4 mins at each speed to obtain the Stribeck response of the fluid. It should be noted that initial measurements may be significantly affected by changes in the contacting surfaces, reaction of surface active components, entrainment of fluid in the inlet zone of the instrument etc. Care should be taken to allow steady state operation to be achieved before the coefficient of friction is  
30 recorded. Typically, steady state boundary friction response is obtained by continuing the test for an additional 30 mins at 25 rpm. The steady state boundary friction response is reported as the coefficient of friction is the results reported herein.

[0083] *Operating Torque*: Drilling operations may be constrained due to torque limits at the drilling rig. The constraints may be due to maximum torque that a driver can deliver

and/or the maximum torque that the drilling string can withstand before metal failure will occur; such constraints are therefore different for different drilling rigs due to either the size of the driver and/or the drill string in use. The Operating Torque can be measured by a dedicated device (e.g., a torque sub) and/or by measured power usage by the driver.

5 Typically, drilling operations are conducted with at least a 10% safety margin between the Operating Torque and the torque limit. When the Operating Torque is nearing or exceeding what is considered to be a reasonable value, this will limit the length of the wellbore that is achievable. Operating changes can be performed to reduce the Operating Torque, e.g., reducing the rate of penetration (the forward rate of drilling), removing accumulated cuttings

10 from the wellbore, removing the drill string from the wellbore and replacing/refurbishing worn components, and/or reducing the amount of low gravity solids (ground down cuttings) from the circulating base oil composition. These steps to reduce the operating torque can be expensive and time consuming, and may offer little benefit. Therefore, use of a friction reduction additive is beneficial to reduce the operating torque so as to increase rate of

15 penetration and/or allow for greater length of the wellbore.

#### Example 1

[0084] In Example 1, a base oil composition comprising about 210 g Escaid™ 110, about 8.0 g VG Plus™, and about 7 g of lime are added and mixed for about 5 minutes. About 9.0 g of MegaMul™ is added to the resulting mixture followed by about 5 minutes of further

20 mixing. About 18.5 g calcium chloride is mixed with about 50 ml of water and added to the mixture, followed by about 225 g of barite weighting agent. The combination is mixed for about

10 minutes before addition of about 6.0 grams of Versitrol M™ followed by an additional 5 minutes of mixing. Thereafter, about 45.0 g of Rev Dust™ is added followed by

25 10 minutes of mixing. The base oil composition is hot aged for about 16 hours at a temperature of about 120°C. The coefficient of friction (CoF) of the base oil composition is measured as a baseline and reported in Table I.

#### Example 2

[0085] In Example 2, Example 1 is substantially repeated, except that the composition

30 comprises about 97 wt% of composition of Example 1 and about 3 wt% of a conventional friction reducing agent available under the tradename Ultralube II, available from Integrity Industries, Inc., Kingsville, TX, USA. The mixture is covered and heated to about 60°C while being mixed for about 60 minutes. The sample is cooled at about 25°C for 16 hours. The cooled sample is mixed for about 30 minutes at about 4000 rpm. The coefficient of

friction (CoF) of the sample is measured and reported in Table I.

**Example 3**

[0086] In Example 3, Example 2 is substantially repeated, except that the composition comprises about 97 wt% of composition of Example 1 and about 3 wt% octadecyl-1,2-diol available under the tradename Vikinol™ 18. The coefficient of friction (CoF) of the base oil composition and additive package are reported in Table I.

**Table I**

	<b>Ex. 1</b>	<b>Ex. 2</b>	<b>Ex. 3</b>
<b>CoF</b>	0.17	0.14	0.10
<b>Relative CoF *</b>	1	0.82	0.59
<b>% Reduction</b>	--	18	41
<b>CoF**</b>			

\*Relative CoF is as compared to Example 1.

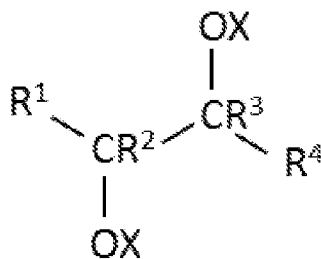
\*\*% Reduction CoF=1-Relative CoF.

10 **Particular Embodiments**

This invention relates to:

[0087] Embodiment 1. A lubricant composition suitable for use in drilling operations, comprising:

- 15 a)  $\geq 90$  wt% of at least one base oil composition, the base oil composition comprising about 1.0 to about 15.0 wt% water, and
- b) from about 1.0 to about 10.0 wt% of a friction-reducing composition comprising: at least one compound represented by Formula I:



Formula I

20 wherein X is selected from H, Group 1-2 metals,  $\text{NR}_4^+$  and  $\text{PR}_4^+$  groups where each R group is independently selected from H and hydrocarbyl groups, particularly X may be H; and

wherein each of  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^4$  are individually selected from H, branched or unbranched, substituted or unsubstituted  $\text{C}_1$  to  $\text{C}_{50}$  hydrocarbyl groups.

- [0088] Embodiment 2. The composition of Embodiment 1, wherein R<sup>1</sup> is selected from branched or unbranched, substituted or unsubstituted C<sub>10</sub> to C<sub>30</sub> alkyl or alkenyl groups.
- [0089] Embodiment 3. The composition of Embodiment 1 or 2, wherein R<sup>2</sup> is H.
- [0090] Embodiment 4. The composition of any of Embodiments 1 to 3, wherein R<sup>3</sup> is H.
- 5 [0091] Embodiment 5. The composition of any of Embodiments 1 to 4, wherein R<sup>4</sup> is H.
- [0092] Embodiment 6. The composition of any of Embodiments 1 to 5, wherein R<sup>1</sup> is selected from unbranched C<sub>15</sub> to C<sub>20</sub> alkyl groups, and wherein R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> are each H.
- [0093] Embodiment 7. The composition of any of Embodiments 1 to 6, wherein the at least one compound represented by Formula I comprises 1, 2-decanediol; 1,2-undecanediol;
- 10 1, 2-dodecanediol; 1, 2-tridecanediol; 1,2-tetradecanediol; 1,2-pentadecanediol; 1,2- hexadecanediol; 1, 2-heptadecanediol; 1,2-octadecanediol; 1, 2-~nonadecanediol; 1,2-eicosanediol; 1,2- heneicosanediol; 1,2-docosanediol; 1, 2-tricosanediol; or 1,2-tetracosanediol.
- [0094] Embodiment 8. The composition of any of Embodiments 1 to 7, wherein the at least one compound following Formula I comprises 1,2-octadecanediol.
- 15 [0095] Embodiment 9. The composition of any of Embodiments 1 to 8, wherein the composition comprises ≤ 0.01 wt% of a phosphorus compound represented by Formula III:
- $$(R^5O)_2PH=O \qquad \text{Formula III}$$
- wherein, R<sup>5</sup> is an alkyl group or an alkenyl group with from 12 to 18 carbon atoms.
- 20 [0096] Embodiment 10. A lubricant composition made by the process comprising:
- a) providing at least one base oil composition, the base oil composition comprising about 1.0 to about 15.0 wt% water, and
  - b) combining ≥ about 90 wt% of the base oil composition with about 1.0 to about 10.0 wt% of the composition at any of Embodiments 1 to 8.
- 25 [0097] Embodiment 11. A method of making a lubricant composition comprising:
- a) providing at least one base oil composition, the base oil composition comprising about 1.0 to about 15.0 wt% water, and
  - b) combining ≥ about 90 wt% of the base oil composition with about 1.0 to about 10.0 wt% of the composition of any of Embodiments 1 to 10.
- 30 [0098] Embodiment 12. A method of drilling a wellbore comprising:
- a) providing a friction-reducing composition prepared by mixing i) ≥ 90 wt% of at least one base oil composition, the base oil composition comprising about 1.0 to about 15.0 wt% water, and from about 1.0 to about 10.0 wt% of the composition of any of Embodiments 1 to 10.

[0099] Embodiment 13. A method of providing a lubricant composition to a drilling operation, comprising:

- a) providing to said drilling operation at least one base oil composition, the base oil composition comprising about 1.0 to about 15.0 wt% water,
- 5 b) operating said drilling operation for a period of time with said base oil composition, and
- c) adding to the drilling operation a friction-reducing composition comprising the composition of any of Embodiments 1 to 10.

[00100] Embodiment 14. The method of Embodiment 13, wherein adding the friction-reducing composition comprises adding the friction-reducing composition at a rate sufficient to provide a concentration of the friction reducing additive in the lubricant composition of about 0.5% to about 10.0 wt% after a time period of about 3 hours to 180 days.

[00101] Embodiment 15. The method of Embodiments 13 or 14, wherein said drilling operation comprises one or more of: introducing a drill string; introducing coiled tubing; 15 introducing casing; introducing screens; introducing tools for cleaning, fracturing, and perforating; rotating drill string; advancing the wellbore; withdrawing a drill string; and/or withdrawing coiled tubing.

[00102] Embodiment 16. The method of any of Embodiments 13 to 15, wherein adding the friction reducing composition comprises adding the friction-reducing composition 20 intermittently to maintain a desired Operating Torque.

[00103] Embodiment 17. The method of any of Embodiments 13 to 16, wherein said drilling operation has an Operating Torque  $< 95\%$ , e.g.,  $\leq$  about 90.0%,  $\leq$  about 85.0%,  $\leq$  about 80.0%,  $\leq$  about 75.0%,  $\leq$  about 70.0%,  $\leq$  about 65.0%,  $\leq$  about 60.0%, of the Operating Torque of the same drilling operation performed with the base oil composition, but 25 lacking the friction-reducing composition.

[00104] Embodiment 18. A method of preparing a wellbore comprising providing a lubricant composition according to any of Embodiments 1 to 10 to the wellbore.

[00105] Embodiment 19. A method of producing hydrocarbons comprising providing a lubricant composition according to any of Embodiments 1 to 10 to the wellbore.

30 [00106] As demonstrated above, embodiments of the invention provide new lubricating compositions that may be useful in a variety of lubricating operations, e.g., wellbore extension, well completion, etc. The new lubricants may have one or more of the following advantages. For example, the compositions may have a lower coefficient of friction than currently known compositions, thereby facilitating wellbore lengths not before achievable. In

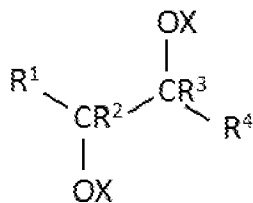
some instances, the compositions may have better durability or persistence in the drilling environment. Other characteristics and additional advantages are apparent to those skilled in the art.

[00107] It is believed that some diols surprisingly interact with iron and/or iron-containing particles in the drilling environment. It had been thought that the reduction in coefficient of friction is to the amount of iron that the friction-reducing composition can adsorb (i.e., the  $\mu\text{mols}$  of iron that could be adsorbed by a gram of friction-reducing composition). Surprisingly, it has been found that greater reduction in the coefficient of friction may be achieved by selecting the friction-reducing composition based, not on the adsorption capacity, but rather upon the free energy of adsorption,  $\Delta G^{\circ}_{\text{abs}}$ . When properly selected so that the friction reducing composition has a free-energy of adsorption for iron  $\leq$  about -18.0 kJ/mol, e.g.,  $\leq$  about -20.0 kJ/mol,  $\leq$  about -22.0 kJ/mol,  $\leq$  about -24.0 kJ/mol,  $\leq$  about -26.0 kJ/mol,  $\leq$  about -28.0 kJ/mol,  $\leq$  about -30.0 kJ/mol,  $\leq$  about -35.0 kJ/mol show improved reduction in the coefficient of friction. Particular compositions have a free energy of adsorption of about -18.0 to about -35.0 kJ/mol, about -20.0 to about -30.0 kJ/mol, about -22.0 to about -28.0 kJ/mol, about -24.0 to about -26.0 kJ/mol. In this way, less friction-reducing composition may need to be used than otherwise believed.

[00108] All documents described herein are incorporated by reference herein for purposes of all jurisdictions where such practice is allowed, including any priority documents and/or testing procedures to the extent they are not inconsistent with this text. As is apparent from the foregoing general description and the specific embodiments, while forms of the invention have been illustrated and described, various modifications can be made without departing from the spirit and scope of the invention. Accordingly, it is not intended that the invention be limited thereby. For example, the compositions described herein may be free of any component, or composition not expressly recited or disclosed herein. Any method may lack any step not recited or disclosed herein. Likewise, the term “comprising” is considered synonymous with the term “including.” And whenever a method, composition, element or group of elements is preceded with the transitional phrase “comprising,” it is understood that we also contemplate the same composition or group of elements with transitional phrases “consisting essentially of,” “consisting of,” “selected from the group of consisting of,” or “is” preceding the recitation of the composition, element, or elements and vice versa.

**CLAIMS***What Is Claimed Is:*

1. A lubricant composition suitable for use in drilling operations, comprising:
  - a)  $\geq$  about 90 wt% of at least one base oil composition, the base oil composition comprising about 1.0 to about 15.0 wt% water, and
  - b) from about 1.0 to about 10.0 wt% of a friction-reducing composition comprising: at least one compound represented by Formula I:



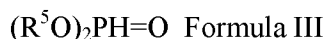
Formula I

wherein X is selected from H, Group 1-2 metals,  $\text{NR}_4^+$  and  $\text{PR}_4^+$  groups where each R group is independently selected from H and hydrocarbyl groups; each of  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^4$  are individually selected from H, branched or unbranched, substituted or unsubstituted  $\text{C}_1$  to  $\text{C}_{50}$  hydrocarbyl groups; and

preferably wherein the base oil composition comprises a base oil, wherein the base oil is present in the lubricant composition in the range from about 50.0 to about 99.0 wt% and the friction-reducing composition is present in the lubricant composition in the amount of about 0.1 to about 5.0 wt%.

2. The lubricant composition of claim 1, one or more of  $\text{R}^2$ ,  $\text{R}^3$ , or  $\text{R}^4$  is H.
3. The lubricant composition of claim 1, wherein  $\text{R}^1$  is selected from unbranched  $\text{C}_{15}$  to  $\text{C}_{20}$  alkyl groups, and wherein  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^4$  are each H.
4. The lubricant composition of claim 1, wherein the at least one compound represented by Formula I comprises 1,2-decanediol; 1,2-undecanediol; 1,2-dodecanediol; 1,2-tridecanediol; 1,2-tetradecanediol; 1,2-pentadecanediol; 1,2-hexadecanediol; 1,2-heptadecanediol; 1,2-octadecanediol; 1,2-nonadecanediol; 1,2-eicosanediol; 1,2-heneicosanediol; 1,2-docosanediol; 1,2-tricosanediol; or 1,2-tetracosanediol.
5. The lubricant composition of claim 1, wherein the at least one compound represented by Formula I comprises 1,2-octadecanediol.

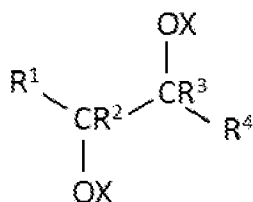
6. The lubricant composition of claim 1, wherein the composition comprises  $\leq 0.01$  wt% of a phosphorus compound represented by Formula III:



wherein  $R^5$  is an alkyl group or an alkenyl group with from 12 to 18 carbon atoms.

7. A method of making a lubricant composition suitable for use in drilling operations comprising:

- a) providing at least one base oil composition, the base oil composition comprising about 1.0 to about 15.0 wt% water, and
- b) combining  $\geq$  about 90 wt% of the base oil composition with about 1.0 to about 10.0 wt% of a friction-reducing composition comprising at least one compound represented by Formula I:



Formula I

wherein X is selected from H, Group 1-2 metals,  $NR_4^+$  and  $PR_4^+$  groups where each R group is independently selected from H and hydrocarbyl groups; and

wherein each of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are individually selected from H, branched or unbranched, substituted or unsubstituted  $C_1$  to  $C_{50}$  hydrocarbyl groups.

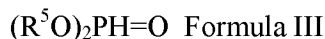
8. The method of claim 7, wherein one or more of  $R^2$ ,  $R^3$ , or  $R^4$  is H.

9. The method of claim 7, wherein  $R^1$  is selected from unbranched  $C_{15}$  to  $C_{20}$  alkyl groups, and wherein  $R^2$ ,  $R^3$ , and  $R^4$  are each H.

10. The method of claim 7, wherein the at least one compound represented by Formula I comprises 1,2-decanediol; 1,2-undecanediol; 1,2-dodecanediol; 1,2-tridecanediol; 1,2-tetradecanediol; 1,2-pentadecanediol; 1,2-hexadecanediol; 1,2-heptadecanediol; 1,2-octadecanediol; 1,2-nonadecanediol; 1,2-eicosanediol; 1,2-heneicosanediol; 1,2-docosanediol; 1,2-tricosanediol; or 1,2-tetracosanediol.

11. The method of claim 7, wherein the at least one compound represented by Formula I comprises 1,2-octadecanediol.

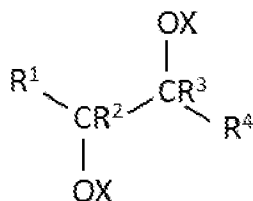
12. The method of claim 7, wherein the composition comprises  $\leq 0.01$  wt% of a phosphorus compound represented by Formula III:



wherein  $R^5$  is an alkyl group or an alkenyl group with from 12 to 18 carbon atoms.

13. A method of drilling a wellbore comprising:

a) providing a friction-reducing composition prepared by mixing i)  $\geq 90$  wt% of at least one base oil composition, the base oil composition comprising about 1.0 to about 15.0 wt% water, and from about 1.0 to about 10.0 wt% of a friction-reducing composition comprising: a compound represented by Formula I:



Formula I

wherein X is selected from H, Group 1-2 metals,  $NR_4^+$  and  $PR_4^+$  groups where each R group is independently selected from H and hydrocarbyl groups; and

wherein each of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are individually selected from H, branched or unbranched, substituted or unsubstituted  $C_1$  to  $C_{50}$  hydrocarbyl groups; and

b) introducing the lubricant composition into the wellbore.

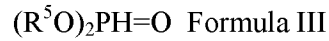
14. The method of claim 13, wherein one or more of  $R^2$ ,  $R^3$ , or  $R^4$  is H.

15. The method of claim 13, wherein  $R^1$  is selected from unbranched  $C_{15}$  to  $C_{20}$  alkyl groups, and wherein  $R^2$ ,  $R^3$ , and  $R^4$  are each H.

16. The method of claim 13, wherein the at least one compound represented by Formula I comprises 1,2-decanediol; 1,2-undecanediol; 1,2-dodecanediol; 1,2-tridecanediol; 1,2-tetradecanediol; 1,2-pentadecanediol; 1,2-hexadecanediol; 1,2-heptadecanediol; 1,2-octadecanediol; 1,2-nonadecanediol; 1,2-eicosanediol; 1,2-heneicosanediol; 1,2-docosanediol; 1,2-tricosanediol; or 1,2-tetracosanediol.

17. The method of claim 13, wherein the at least one compound represented by Formula I comprises 1,2-octadecanediol.

18. The method of claim 13, wherein the composition comprises  $\leq 0.01$  wt% of a phosphorus compound represented by Formula III:



wherein  $R^5$  is an alkyl group or an alkenyl group with from 12 to 18 carbon atoms.

19. A method of providing a lubricant composition to a drilling operation, comprising:

- a) providing to said drilling operation at least one base oil composition, the base oil composition comprising about 1.0 to about 15.0 wt% water,
- b) operating said drilling operation for a period of time with said base oil composition, and
- c) adding to the drilling operation a friction-reducing composition comprising the composition in claim 1.

20. The method of claim 19, wherein adding the friction-reducing composition comprises adding the friction-reducing composition at a rate sufficient to provide a concentration of the friction reducing additive in the lubricant composition of about 0.5% to about 10.0 wt% after a time period of about 3 hours to 180 days.

21. The method of claim 19, wherein said drilling operation comprises one or more of: introducing a drill string; introducing coiled tubing; introducing casing; introducing screens; introducing tools for cleaning, fracturing, and perforating; rotating drill string; advancing the wellbore; withdrawing a drill string; and/or withdrawing coiled tubing.

22. The method of claim 19, wherein adding the friction reducing composition comprises adding the friction-reducing composition intermittently to maintain a desired Operating Torque.

23. The method of claim 19, wherein said drilling operation has an Operating Torque  $< 95\%$  of the Operating Torque of the same drilling operation performed with the base oil composition, but lacking the friction-reducing composition.

24. A method of preparing a wellbore comprising providing the lubricant composition of claim 1 to the wellbore.

25. A method of producing hydrocarbons comprising providing the lubricant composition according to claim 1 to a wellbore.

## INTERNATIONAL SEARCH REPORT

International application No.  
**PCT/US2016/035538****A. CLASSIFICATION OF SUBJECT MATTER****C10M 129/02(2006.01)I, C10M 169/04(2006.01)I, C09K 8/32(2006.01)I, C09K 8/34(2006.01)I, C10N 30/06(2006.01)N**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C10M 129/02; C10M 141/10; C09K 7/02; C10M 137/10; C10M 159/24; C10M 141/08; C10M 129/08; C10M 173/00; C10M 169/04; C09K 8/32; C09K 8/34; C10N 30/06

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) &amp; Keywords: lubricant, drilling, drilling fluid, 1,2-diol, vicinal diol, hydrocarbyl diol, polyol, wellbore, oil field, subterranean, phosphonate

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4781848 A (BIRESAW, GIRMA et al.) 01 November 1988 See abstract; column 1, line 18 - column 3, line 44; and claims 1-15.	1-12, 19-23
A		13-18, 24, 25
A	US 2015-0087567 A1 (USHIODA, NOBUO) 26 March 2015 See abstract; paragraphs [0007]-[0036]; and claims 1-4.	1-25
A	WO 2010-115864 A1 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 14 October 2010 See abstract; and claims 1-10.	1-25
A	US 2012-0202726 A1 (BARTON, WILLIAM R. S. et al.) 09 August 2012 See abstract; paragraphs [0028]-[0033]; and claim 1.	1-25
A	US 2005-0037930 A1 (HORTON, DAVID P.) 17 February 2005 See abstract; and paragraphs [0006]-[0026].	1-25

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

\* Special categories of cited documents:

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

13 September 2016 (13.09.2016)

Date of mailing of the international search report

**19 September 2016 (19.09.2016)**

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

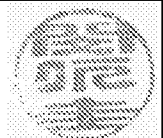
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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/US2016/035538**

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4781848 A	01/11/1988	EP 0362430 A1	11/04/1990
US 2015-0087567 A1	26/03/2015	CN 104449977 A EP 2851413 A1 JP 2015-061906 A	25/03/2015 25/03/2015 02/04/2015
WO 2010-115864 A1	14/10/2010	JP 2010-248284 A JP 5441480 B2	04/11/2010 12/03/2014
US 2012-0202726 A1	09/08/2012	CN 102575184 A CN 102575184 B CN 104479807 A EP 2467457 A1 EP 2467457 B1 EP 2891700 A1 EP 2891701 A1 US 2013-0157914 A1 US 2013-0296208 A1 US 2013-0303417 A1 US 8404625 B2 US 8530395 B1 US 8557755 B2 US 8722599 B2 US 8728996 B2 WO 2011-022317 A1	11/07/2012 26/11/2014 01/04/2015 27/06/2012 22/07/2015 08/07/2015 08/07/2015 20/06/2013 07/11/2013 14/11/2013 26/03/2013 10/09/2013 15/10/2013 13/05/2014 20/05/2014 24/02/2011
US 2005-0037930 A1	17/02/2005	US 2005-0037927 A1 US 7081438 B2	17/02/2005 25/07/2006