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(54) Title: ADDITIVE COMPOSITION FOR WELL TREATMENT FLUIDS AND METHODS FOR THEIR USE

(57) Abstract: There is disclosed an additive composition for a well treatment fluid, as well as a method of increasing the lubricity and reducing the coefficient of friction of a well treatment fluid. The additive composition contains a polymeric ester formed from the reaction product of i) a triglyceride of a hydroxy fatty acid; ii) at least one dicarboxylic acid or an ester or anhydride thereof; iii) and a polyalkylene glycol.

ADDITIVE COMPOSITIONS FOR WELL TREATMENT FLUIDS AND METHODS FOR THEIR USE

[0001] The invention relates to an additive composition for a well treatment fluid, as well as a method of increasing the lubricity and reducing the coefficient of friction of a well treatment fluid. The additive composition may contain a metal dithiophosphate compound or a sulfurized olefin which further enhance the lubricating effect.

BACKGROUND OF THE INVENTION

[0002] A variety of well treatment fluids, including cleanup fluids, completion fluids, drilling fluids, injection fluids, fracturing fluids, and stimulation fluids, including acid fluids, can be used during the process of hydrocarbon recovery from subterranean formations. Such fluids can be aqueous or water-based, or based on organic fluids such as methanol or hydrocarbons, depending upon the desired application.

[0003] Drilling fluids, also referred to as drilling muds, are frequently circulated in a well during drilling operations in order to cool and lubricate the drilling apparatus, lift cuttings out of the wellbore and counterbalance the subterranean formation pressure encountered during drilling. One of the functions of a drilling fluid is to reduce the considerable torque associated with the rotating drill stem caused by the friction between the outside of the drill pipe and the wall of the well and/or casing strings. Drilling through offsets, deep wells and highly deviated or horizontal wells results in increased frictional forces, increasing the demand on the lubricating properties of the drilling fluids.

[0004] Once the total depth of the well is reached, it is a normal practice to replace the drilling mud with a completion fluid. A completion fluid is typically a solids-free (or acid soluble), non-damaging formulation, which is intended to minimize reductions in permeability of the producing zone. The density of the completion fluid is generally selected and controlled to ensure that the hydrostatic head or pressure of the fluid in the wellbore will match the hydrostatic pressure of the column of drilling fluid being displaced.

[0005] Brine solutions have been used by the oil and gas industry for well drilling and well completions. For example, brines can include sodium chloride, potassium chloride, calcium chloride, sodium bromide, calcium bromide, zinc bromide, potassium formate, cesium formate, sodium formate, sodium silicate and potassium silicatebrines.

[0006] While high density brines have been found to be functional in providing the lubricity and viscosity of a well treatment fluid under extreme shear, pressure and temperature variances, they are often ineffective because they are unable to exhibit the constant lubricity which is required during high shear conditions.

[0007] During the operation of deep wells, as well as in extended reach and/or high angle wells, it is necessary for the brine-containing well treatment fluid to exhibit increased lubricity. The need for increased lubricity is most marked in those instances during wellbore cleanup, wireline operations, coil tubing operations and during the running of production tubulars.

[0008] Various additives are known for use as lubricating agents in well treatment fluids. Many of the additives are not, however, compatible with clear brines or well treatment fluids which have brine as a major component. In addition, many additives used as lubricating agents in well treatment fluids today have presented environmental concerns and tend to be costly.

SUMMARY OF THE INVENTION

[0009] The invention described herein provides an additive composition for a well treatment fluid which includes the reaction product of i) at least one triglyceride of a hydroxy fatty acid; ii) at least one dicarboxylic acid or an ester or anhydride thereof; and iii) at least one polyalkylene glycol.

[0010] The invention further provides the additive composition described herein in which the hydroxy fatty acid comprises one or more of 2-hydroxylinolenic acid, 2-hydroxyoleic acid, 2-hydroxytetraconsanic acid, 2-hydroxy-15-tetracosenic acid, 2-hydroxy palmitic acid, 3-hydroxyolylipins, 10-hydroxy-2-decenoic acid, 10-hydroxy-2-decanoic acid, 9,10-hydroxy-2-decenoic acid, 3,10-dihydroxydecanoic acid, 8-hydroxotanoic acid, w-hydroxy octadecenoic acid, 15-hydroxylinoleate, 12-hydroxy-9-octadecenoic acid, 12-hydroxy stearic acid, 14-hydroxy-11-eicosenoic acid, 11-

hydroxy hexadecanoic acid, 15-hydroxy-hexadecanoic acid, or 17-hydroxy-octadecanoic acid.

[0011] The invention further provides an additive composition described herein in which the at least one dicarboxylic acid comprises one or more of an aliphatic acid, an aromatic acid, a dimer acid, a trimer acid or a fatty dimer acid.

[0012] The invention further provides an additive composition described herein in which the dicarboxylic acid comprises oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, maleic acid, fumaric acid, glutaconic acid, traumatic acid, muconic acid, phthalic acid, isophthalic acid, terephthalic acid or diphenic acid.

[0013] The invention further provides an additive composition described herein in which the polyalklyene glycol comprises one or more of polyethylene glycol or polypropylene glycol.

[0014] The invention further provides an additive composition described herein in which the polyalkylene glycol comprises polyethylene glycol having a Mn of from 100 to 10,000.

[0015] The invention further provides an additive composition described herein in which the polyalkylene glycol comprises polypropylene glycol having a Mn of less than 2000.

[0016] The invention further provides an additive composition described herein in which the additive composition comprises a triglyceride of a hydroxy fatty acid reacted with adipic acid and polyethylene glycol.

[0017] The invention further provides an additive composition described herein in which the ratio of equivalent acid groups of hydroxyl fatty acid and dicarboxylic acid to hydroxyl groups of the polyalkylene glycol is from 0.3 to 2.5.

[0018] The invention further provides an additive composition described herein further including a sulfurized olefin.

[0019] The invention provides an additive composition described herein further including a metal thiophosphate compound.

[0020] The invention further provides an additive composition described herein in which the metal thiophosphate compound comprises zinc dialkyldithiophosphate.

[0021] The invention further provides a well treatment fluid containing the additive composition described herein.

[0022] The invention further provides a well treatment fluid which is a completion fluid and contains the additive composition described herein.

[0023] The invention further provides a well treatment fluid which is a drilling fluid and contains the additive composition described herein.

[0024] The invention further provides a well treatment fluid including a) a brine; and b) an additive composition including the reaction product of i) at least one triglyceride of a hydroxy fatty acid; ii) at least one dicarboxylic acid or an ester or anhydride thereof; and iii) at least one polyalkylene glycol.

[0025] The invention further provides a well treatment fluid in which the brine comprises a sodium chloride, a potassium chloride, a calcium chloride, a sodium bromide, a calcium bromide, a sodium bromide, a zinc bromide, a potassium formate, a cesium formate, a sodium formate, a sodium silicate or a potassium silicate.

[0026] The invention further provides a well treatment fluid in which the additive composition is added to the well treatment fluid in an amount from 0.1 wt% to 5 wt%.

[0027] The invention further provides a method of lubricating a well treatment fluid, including adding to the well treatment fluid the reaction product of i) at least one triglyceride of a hydroxy fatty acid; ii) at least one dicarboxylic acid; and iii) at least one polyalkylene glycol.

[0028] The invention further provides a method of increasing the lubricity of a well treatment fluid containing a brine including adding to the brine an additive composition comprising the reaction product of i) at least one triglyceride of a hydroxy fatty acid; ii) at least one dicarboxylic acid or an ester or anhydride thereof; and iii) at least one polyalkylene glycol.

[0029] The invention further provides a method of increasing the lubricity of a well treatment fluid in which the coefficient of friction of the well treatment fluid is decreased in an amount of at least 5%.

[0030] The invention further provides method of making an additive composition for increasing the lubricity and decreasing the coefficient of friction of a well treatment fluid including the step of mixing i) at least one triglyceride of a hydroxy fatty acid; ii) at least one dicarboxylic acid or an ester or anhydride thereof; and iii) at least one polyalkylene glycol to form the additive composition.

DETAILED DESCRIPTION OF THE INVENTION

[0031] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0032] The additive composition described herein is a polymeric ester prepared from the reaction of at least one triglyceride of a hydroxy fatty acid, a dicarboxylic acid or an ester or anhydride thereof, and a polyalkylene glycol. The additive composition described herein is effective in one or more of increasing the lubricity and/or decreasing the coefficient of friction of a well treatment composition. The additive composition, in some embodiments, can further include either a sulfurized olefin or a metal dithiophosphate, which act in combination with the polymeric ester to produce a synergistic effect and provide increased lubricity and/or a reduced coefficient of friction to a well treatment fluid.

The Hydroxy Fatty Acid Component

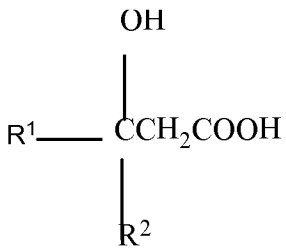
[0033] The additive composition of the invention described herein is made using i) a triglyceride of a hydroxy fatty acid. Suitable hydroxy fatty acids may have a saturated or unsaturated alkyl group. The saturated alkyl group in the hydroxycarboxylic acids has, in one embodiment, from 3 to 40 carbon atoms, and in one embodiment, from 12 to 20 carbon atoms. The number of the hydroxyl group in these may be generally 1 or more, or in one embodiment 2, or in one embodiment 3, or in another embodiment from between 1 to 3; and the number of the carboxyl group in these may be in one embodiment 1 or more, and in another embodiment from 1 to 10.

[0034] The hydroxy fatty acid component, in one embodiment, includes saturated fatty acids having one hydroxyl group and one carboxyl group.

[0035] Specific examples of those having a linear alkyl group in the alkyl moiety may include 2-hydroxyvaleric acid, 2-hydroxycaproic acid, 6-hydroxycaproic acid, 2-hydroxyenanthic acid, 7-hydroxyenanthic acid, 2-hydroxycaprylic acid, 3-hydroxycaprylic acid, 8-hydroxycaprylic acid, 2-hydroxypelargonic acid, 3-hydroxypelargonic acid, 9-hydroxypelargonic acid, 2-hydroxycapric acid, 3-hydroxycapric acid, 10-hydroxycapric acid, 2-hydroxyundecanoic acid, 3-hydroxyunde canoic acid, 11-hydroxyundecanoic acid, 2-hydroxylauric acid, 3-hydroxylauric acid, 12-hydroxylauric acid, 2-hydroxytridecanoic acid, 3-hydroxytridecanoic acid, 13-hydroxytridecanoic acid, 2-hydroxymyristic acid, 3-hydroxymyristic acid, 14-hydroxymyristic acid, 2-hydroxypentadecanoic acid, 3-hydroxypentadecanoic acid, 15-hydroxypentadecanoic acid, 2-hydroxypalmitic acid, 3-hydroxypalmitic acid, 16-hydroxypalmitic acid, 2-hydroxymargaric acid, 3-hydroxymargaric acid, 17-hydroxymargaric acid, 2-hydroxystearic acid, 3-hydroxystearic acid, 4-hydroxystearic acid, 5-hydroxystearic acid, 6-hydroxystearic acid, 7-hydroxystearic acid, 8-hydroxystearic acid, 9-hydroxystearic acid, 10-hydroxy stearic acid, 11-hydroxystearic acid, 12-hydroxystearic acid, 13-hydroxystearic acid, 14-hydroxystearic acid, 15-hydroxystearic acid, 16-hydroxystearic acid, 17-hydroxystearic acid, 18-hydroxystearic acid, 2-hydroxynonadecanoic acid, 3-hydroxynonadecanoic acid, 19-hydroxynonadecanoic acid, 2-hydroxyarachic acid, 3-hydroxyarachic acid, 20-hydroxyarachic acid, 3-hydroxyheneicosanoic acid, 21-hydroxyheneicosanoic acid, 2-hydroxybehenic acid, 3-hydroxybehenic acid, 3-hydroxytricosanoic acid, 2-hydroxylignoceric acid, 3-hydroxylignoceric acid, 2-hydroxyhexacosanoic acid, 2-hydroxytriacontanoic acid, and 2-hydroxytetratriacontanoic acid.

[0036] In some embodiments, the hydroxy fatty acid may have a branched alkyl group in the alkyl moiety. Specific examples may include 2-methyl-2-hydroxyenanthic acid, 2-methyl-3-hydroxypelargonic acid, 3-methyl-3-hydroxypelargonic acid, 2-methyl-3-hydroxycapric acid, 2-methyl-3-hydroxyundecanoic acid, 3-methyl-3-hydroxyundecanoic acid, 2-methyl-2-hydroxylauric acid, 2-methyl-3-hydroxylauric acid, 2-methyl-2-hydroxytridecanoic acid, 2-methyl-3-hydroxytridecanoic acid, 3-methyl-3-hydroxytridecanoic acid, 2-

methyl-2-hydroxymyristic acid, 2-methyl-3-hydroxymyristic acid, 2-methyl-2-hydroxypentadecanoic acid, 2-methyl-3-hydroxypentadecanoic acid, 3-methyl-3-hydroxypentadecanoic acid, 2-methyl-2-hydroxypalmitic acid, 2-methyl-2-hydroxymargaric acid, 2-methyl-3-hydroxymargaric acid, 3-methyl-3-hydroxymargaric acid, 2-methyl-2-hydroxystearic acid, 2-methyl-2-hydroxynonadecanoic acid, 2-methyl-3-hydroxynonadecanoic acid, and 3-methyl-3-hydroxynonadecanoic acid. Also useful herein are 3,3-dialkyl-3-hydroxypropionic acids of a general formula



wherein R^1 represents an alkyl group having from 1 to 25 carbon atom; R^2 represents an alkyl group having from 5 to 25 carbon atoms; and R^1 and R^2 may be the same or different. As specific examples of the compounds, mentioned are those having alkyl groups shown in Table 1 below.

Table 1

R^1	R^2	R^1	R^2
C_2H_5	n-$C_{11}H_{23}$	n-C_6H_{13}	n-$C_{11}H_{23}$
n-C_7H_{15}	n-C_7H_{15}	n-C_5H_{11}	n-$C_{12}H_{25}$
n-C_6H_{13}	n-C_8H_{17}	n-C_4H_9	n-$C_{13}H_{27}$
n-C_5H_{11}	n-C_9H_{19}	n-C_3H_7	n-$C_{14}H_{29}$
n-C_4H_9	n-$C_{10}H_{21}$	C_2H_5	n-$C_{15}H_{31}$
n-C_3H_7	n-$C_{11}H_{23}$	CH_3	n-$C_{16}H_{33}$
C_2H_5	n-$C_{12}H_{25}$	n-C_9H_{19}	n-C_9H_{19}
n-C_7H_{15}	n-C_6H_{17}	n-C_8H_{17}	n-$C_{10}H_{21}$
n-C_6H_{13}	n-C_9H_{19}	n-C_7H_{15}	n-$C_{11}H_{23}$
n-C_5H_{11}	n-$C_{10}H_{21}$	n-C_6H_{13}	n-$C_{12}H_{25}$
n-C_4H_9	n-$C_{11}H_{23}$	n-C_5H_{11}	n-$C_{13}H_{27}$
n-C_3H_7	n-$C_{12}H_{25}$	n-C_4H_9	n-$C_{14}H_{29}$
C_2H_5	n-$C_{13}H_{27}$	n-C_3H_7	n-$C_{15}H_{31}$
n-C_8H_{17}	n-C_6H_{17}	C_2H_5	n-$C_{16}H_{33}$
n-C_7H_{15}	n-C_9H_{19}	CH_3	n-$C_{17}H_{35}$

n-C_8H_{13}	n-$C_{10}H_{21}$	n-C_9H_{19}	n-$C_{10}H_{21}$
n-C_5H_{11}	n-$C_{11}H_{23}$	n-C_8H_{17}	n-$C_{11}H_{23}$
n-C_4H_9	n-$C_{12}H_{25}$	n-C_7H_{15}	n-$C_{12}H_{25}$
n-C_3H_7	n-$C_{13}H_{27}$	n-C_6H_{13}	n-$C_{13}H_{27}$
C_2H_5	n-$C_{14}H_{29}$	n-C_5H_{11}	n-$C_{14}H_{29}$
CH_3	n-$C_{15}H_{31}$	n-C_4H_9	n-$C_{15}H_{31}$
n-C_8H_{17}	n-C_9H_{19}	n-C_3H_7	n-$C_{16}H_{33}$
n-C_7H_{15}	n-$C_{10}H_{21}$	C_2H_5	n-$C_{17}H_{35}$
CH_3	n-$C_{18}H_{37}$	n-$C_{10}H_{21}$	n-$C_{12}H_{25}$
n-$C_{10}H_{21}$	n-$C_{10}H_{21}$	n-C_9H_{19}	n-$C_{13}H_{27}$
n-C_9H_{19}	n-$C_{11}H_{23}$	n-C_8H_{17}	n-$C_{14}H_{29}$
n-C_8H_{17}	n-$C_{12}H_{25}$	n-C_7H_{15}	n-$C_{15}H_{31}$
n-C_7H_{15}	n-$C_{13}H_{27}$	n-C_6H_{13}	n-$C_{16}H_{33}$
n-C_6H_{13}	n-$C_{14}H_{29}$	C_2H_5	n-$C_{20}H_{41}$
n-C_5H_{11}	n-$C_{15}H_{31}$	CH3	n-$C_{21}H_{43}$
n-C_4H_9	n-$C_{16}H_{33}$	n-$C_{11}H_{23}$	n-$C_{12}H_{25}$
n-C_3H_7	n-$C_{17}H_{35}$	n-$C_{10}H_{21}$	n-$C_{13}H_{27}$
C_2H_5	n-$C_{18}H_{37}$	n-C_4H_9	n-C_4H_9
CH_3	n-$C_{19}H_{39}$	n-C_5H_{11}	n-C_5H_{11}
n-$C_{10}H_{21}$	n-$C_{11}H_{23}$	n-C_6H_{13}	n-C_9H_{13}
n-C_9H_{19}	n-$C_{12}H_{25}$	n-C_7H_{15}	n-C_7H_{15}
n-C_8H_{17}	n-$C_{13}H_{27}$	n-$C_{12}H_{25}$	n-$C_{12}H_{25}$
n-C_7H_{15}	n-$C_{14}H_{28}$	n-$C_{13}H_{27}$	n-$C_{13}H_{27}$
n-C_6H_{13}	n-$C_{15}H_{31}$	n-$C_{14}H_{29}$	n-$C_{14}H_{29}$
n-C_5H_{11}	n-$C_{16}H_{33}$	n-$C_{15}H_{31}$	n-$C_{15}H_{31}$
n-C_4H_9	n-$C_{17}H_{35}$	n-$C_{16}H_{33}$	n-$C_{16}H_{33}$
n-C_3H_7	n-$C_{18}H_{37}$	n-$C_{17}H_{36}$	n-$C_{17}H_{35}$
C_2H_5	n-$C_{19}H_{39}$	n-$C_{18}H_{37}$	n-$C_{18}H_{37}$
CH_3	n-$C_{20}H_{41}$	n-$C_{19}H_{39}$	n-$C_{19}H_{39}$
n-$C_{11}H_{23}$	n-$C_{11}H_{23}$	n-$C_{20}H_{41}$	n-$C_{20}H_{41}$

[0037] In some embodiments, the hydroxy-fatty acids can also be unsaturated fatty acids including one or more of 2-hydroxy-3-pentenoic acid, 4-hydroxy-3-pentenoic acid, 4-hydroxy-4-pentenoic acid, 5-hydroxy-2,4-pentadienoic acid, 4-hydroxy-2-hexenoic acid, 3-hydroxy-4-hexenoic acid, 4-hydroxy-13-tetradecenoic acid, 16-hydroxy-6-hexadecenoic acid, 16-hydroxy-7-hexadecenoic acid, 9-hydroxy-

12-octadecenoic acid, (+)-12-hydroxy-cis-9-octadecenoic acid, (+)- 12-hydroxy-trans-9-octadecenoic acid, 4-hydroxyheneicosenoic acid, 2-hydroxy-15-tetracosenic acid, and 18-hydroxy-9, 11,13-octadecatrienoic acid.

[0038] Specific examples of polyhydroxy-fatty acids having 2 or more hydroxyl groups may include 2,3-dihydroxycaproic acid, 2,3-dihydroxyenanthic acid, 2,3-dihydroxycaprylic acid, 2,3-dihydroxypelargonic acid, 2,3-dihydroxycapric acid, 2,3-dihydroxyundecanoic acid, 2,3-dihydroxylauric acid, 2,3-dihydroxymyristic acid, 3, 11-dihydroxymyristic acid, 15-dihydroxypentadecanoic acid, 2,3-dihydroxypalmitic acid, 15,16-dihydroxypalmitic acid, 2,3-dihydroxystearic ac id, 6,7-dihydroxystearic acid, 7,8-dihydroxystearic acid, 8,9-dihydroxystearic acid, 9,10-dihydroxystearic acid, 10,11-di- hydroxystearic acid, 11,12-dihydroxystearic acid, 12,13-dihydroxystearic acid, 11,12-dihydroxyarachic acid; various dihydroxytriacontanoic acids, 2,5, 16-trihydroxyhexadecanoic acid, 8,9, 16-trihydroxyhexadecanoic acid, 9,10,16-trihyhdroxyhexadecanoic acid, 11,12,15-trihydroxyhexadecanoic acid, various tetrahydroxyhexadecanoic acids, and 9,14-di-hydroxy-10, 12-octadecadienoic acid.

[0039] In some embodiments, the hydroxy fatty acid may be 2-hydroxylinolenic acid, 2-hydroxyoleic acid, 2-hydroxytetraconsanic acid, 2-hydroxy-15-tetracosenic acid, 2-hydroxy palmitic acid, 3-hydroxyolylipins, 10-hydroxy-2-decenoic acid, 10-hydroxy-20decanoic acid, 9,10-hydroxy-2-decenoic acid, 3,10-dihydroxydecanoic acid, 8-hydroxotanoic acid, w-hydroxy octadecenoic acid, 15-hydroxylinoleate, 12-hydroxy-9-octadecenoic acid, 12-hydroxy stearic acid, 14-hydroxy-11-eicosenoic acid, 11-hydroxy hexadecanoic acid, 15-hydroxy-hexadecanoic acid, or 17-hydroxy-octadecanoic acid. In some embodiments, the hydroxy fatty acid may be 12-hydroxy-9-octadecenoic acid (ricinoleic acid) or 12-hydroxy stearic acid. In one embodiment the hydroxy fatty acid is 12-hydroxy-9-octadecenoic acid.

The Dicarboxylic Acid Component

[0040] Dicarboxylic acids suitable for use in invention may be aliphatic, aromatic, or combinations thereof. Suitable acids may contain from 2, 4, or 6 to 20, 15, 8, or 6 carbon atoms, and in some embodiments may contain 2 to 15, 4 to 15, 4 to 8, or even 6 carbon atoms. In some embodiments, the dicarboxylic acids include oxalic acid,

malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic, dodecanedioic acid, maleic acid, fumaric acid, glutatonic acid, traumatic acid, muconic acid, phthalic acid, isophthalic acid, terephthalic acid, cyclohexane dicarboxylic acid, or combinations thereof. In other embodiments, one or more of the dicarboxylic acids listed may be excluded from the invention.

[0041] In some embodiments, the dicarboxylic acid of the invention may also be derived from an ester or anhydride of one or more acids described above or combinations of such materials. Suitable esters include, in one embodiment, lower alkyl esters such as methyl acetate or ethyl acetate. Suitable anhydrides include succinic anhydride, alkyl and/or alkenyl succinic anhydride, phthalic anhydride and tetrahydrophthalic anhydride. In some embodiments, the acid is adipic acid. Blends of two or more acids may be used. In some embodiments the dicarboxylic acid includes a dimer acid, a trimer acid, or a fatty dimer acid. Dimer and trimer acids is the general term applied to products obtained by the reaction of two or more molecules of unsaturated fatty acids or unsaturated fatty acid esters, obtained from tall oil, oleic acid, canola oil or cottonseed oil, usually on clay catalysts. Examples of commercially available dimer, trimer and fatty dimer acids include Empol® available from BASF, and Pripol™ available from Croda.

The Polyalkylene Glycol Component

[0042] The drilling or completion fluid compositions described herein are made using ii) a polyalkylene glycol component.

[0043] Suitable polyalkylene glycols include polyether polyols derived from a diol or polyol having a total of from 2 to 15 carbon atoms, in some embodiments an alkyl diol or glycol which is reacted with an ether comprising an alkylene oxide having from 2 to 6 carbon atoms, typically ethylene oxide or propylene oxide or mixtures thereof. For example, hydroxyl functional polyethers can be produced by first reacting propylene glycol with propylene oxide followed by subsequent reaction with ethylene oxide. Primary hydroxyl groups resulting from ethylene oxide are more reactive than secondary hydroxyl groups and thus are preferred. Useful commercial polyalkylene oxides include poly(ethylene glycol) comprising ethylene oxide reacted

with ethylene glycol, and poly(propylene glycol) comprising propylene oxide reacted with propylene glycol. The various polyalkylene glycols generally have a number average molecular weight (Mn) as determined by assay of the terminal functional groups which is an average molecular weight of at least about 150, or about 600, such as from about 700 to about 10,000, from about 1,450 to about 5,000, or from about 1,450 to about 2,500 or about 1,000, or even 2,000.

[0044] In some embodiments, the polyalkylene glycol component includes poly(propylene glycol), poly(ethylene glycol), copolymers of poly(ethylene glycol) and poly(propylene glycol), and the like, or combinations thereof. In some embodiments, the polyalkylene glycol component includes poly(ethylene glycol).

The Sulfurized Olefin

[0045] The additive composition described herein further includes iii) a sulfurized olefin. Sulfurized olefins are well known commercial materials prepared by reacting a single reactant or a mixture of appropriate reactants with a source of sulfur. The sulfurization reaction generally is effected at an elevated temperature, e.g., 50-350°C or 100-200°C, with efficient agitation and often in an inert atmosphere such as nitrogen, optionally in the presence of an inert solvent. The sulfurizing agents can include elemental sulfur, which is preferred, hydrogen sulfide, sulfur halide, sodium sulfide and a mixture of hydrogen sulfide and sulfur or sulfur dioxide. Usually, the amount of sulfur or sulfurizing agent employed is calculated based on the total olefinic unsaturation of the mixture. Typically 0.5 to 3 moles of sulfur are employed per mole of olefinic bonds. One type of sulfurized olefin can be prepared in accordance with the detailed teachings of U.S. Pat. No. 4,957,651.

[0046] In the case of sulfurized olefins, the reactant can be an olefinic compound. Olefinic compounds which may be sulfurized are diverse in nature, and broadly speaking are those that contain at least one olefinic double bond, which is defined as a non-aromatic double bond; that is, a double bond connecting two aliphatic carbon atoms. In its broadest sense, the olefin may be defined by the formula $R^3R^4C=CR^5R^6$, wherein each of R^3, R^4, R^5 and R^6 can be hydrogen or an organic group. In general, the R groups in the above formula which are not hydrogen may be satisfied by such groups as $--C(R^7)_3$, $--COOR^7$, --COOM, --X, $--YR^7$ or --Ar, wherein

each R^7 is independently hydrogen, alkyl, alkenyl, aryl, substituted alkyl, substituted alkenyl or substituted aryl, with the proviso that any two R^7 groups can be alkylene or substituted alkylene whereby a ring of up to 12 carbon atoms is formed; M is one equivalent of a metal cation (preferably Group I or II, e.g., sodium, potassium, barium, calcium); X is halogen (e.g., chloro, bromo, or iodo); Y is oxygen or divalent sulfur; Ar is an aryl or substituted aryl group of up to 12 carbon atoms. Any two of R^3, R^4, R^5 and R^6 may also together form an alkylene or substituted alkylene group; i.e., the olefinic compound may be alicyclic.

[0047] The olefinic compound is usually one in which each R group, above, which is not hydrogen is independently alkyl, alkenyl or aryl group. Monoolefinic and diolefinic compounds, particularly the former, are preferred, and especially terminal monoolefinic hydrocarbons; that is, those compounds in which R^5 and R^6 are hydrogen and R^3 and R^4 are alkyl or aryl, especially alkyl (that is, the olefin is aliphatic) having 1 to 30, or 1 to 16, or 1 to 8, or 1 to 4 carbon atoms. Olefinic compounds having 3 to 30 or 3 to 16 (often fewer than 9) carbon atoms can be used.

[0048] Isobutene, di-isobutylene, butylene, propylene and their dimers, trimers and tetramers, and mixtures thereof are useful as olefinic compounds for sulfurization, as are terpene compounds, that is, various isomeric terpene hydrocarbons having the empirical formula $C_{10}H_{16}$, as well as various synthetic and naturally occurring oxygen-containing derivatives thereof.

[0049] Other sulfurized olefins include those derived from natural sources, such as sulfurized vegetable oils and sulfurized lard oil (that is, sulfurized oils of animal sources generally). Example of natural oils from which such sulfurized olefins may be derived can include, but not be limited to, coconut oil, corn oil, cottonseed oil, sunflower oil, olive oil, palm oil, peanut oil, rapeseed oil, safflower oil, sesame oil, soybean oil, tallow, lard, fatty acids, and mixtures thereof. Preferred organic portions for the sulfurized vegetable oil are those derived from sunflower oil, olive oil, and rapeseed oil.

[0050] In embodiments which include the sulfurized olefin, it will be present in the additive composition at a ratio of from about 1:1 to about 15:1 of polymeric ester

to sulfurized olefin, and in another embodiment from about 1:1 to 10:1, and in a further embodiment from about 2:1 to about 9:1.

The Metal Thiophosphate Compound

[0051] In some embodiments, the additive composition will further include a metal thiophosphate compound. Zinc dialkyldithiophosphates may be described as primary zinc dialkyldithiophosphates or as secondary zinc dialkyldithiophosphates, depending on the structure of the alcohol used in its preparation. In some embodiments, the compositions of the invention include primary zinc dialkyldithiophosphates. In some embodiments, the compositions of the invention include secondary zinc dialkyldithiophosphates. In some embodiments, the compositions of the invention include a mixture of primary and secondary zinc dialkyldithiophosphates. In some embodiments, component (b) is a mixture of primary and secondary zinc dialkyldithiophosphates where the ratio of primary zinc dialkyldithiophosphates to secondary zinc dialkyldithiophosphates (one a weight basis) is at least 1:1, or even at least 1:1.2, or even at least 1:1.5 or 1:2, or 1:10. In some embodiments, component (b) is a mixture of primary and secondary zinc dialkyldithiophosphates that is at least 50 percent by weight primary, or even at least 60, 70, 80, or even 90 percent by weight primary. In some embodiments, component (b) is free of primary zinc dialkyldithiophosphates.

[0052] In embodiments which include the metal dithiophosphate, it will be present in the additive composition at a ratio of from about 1:1 to about 15:1 of polymeric ester to metal dithiophosphate, and in another embodiment from about 1:1 to 10:1, and in a further embodiment from about 2:1 to about 9:1.

Additional Additives

[0053] In some embodiments, additional additives may be added to the well treatments fluids. Such additives include the clays bentonite, attapulgite, hectorite, sepiolite, and the synthetic minerals Laponite™ (a synthetic hectorite ex Rockwood Additives Limited) and mixed metal hydroxides. Other clays which may be present in the fluids include kaolinite and illite which can be contaminants arising from drilled shale formations. Some of the shale cuttings inevitably become dispersed in a wellbore fluid as fine illite and kaolinite clay particles.

[0054] The well treatment fluids may additionally comprise a particulate bridging agent, for example acid-soluble materials such as calcium carbonate, water-soluble particles such as alkali metal halides; and sparingly water-soluble materials such as Ulexite (a sodium calcium borate salt) and magnesium salts of carboxylic acids. Where the particulate bridging agent is comprised of a water-soluble or sparingly water-soluble material, it is employed in an aqueous based fluid in amounts above the saturation concentration of the water-soluble or sparingly water-soluble material in water at the conditions encountered downhole so as to provide suspended particles of the conventional particulate bridging agent. Other suspended solids can include graphite particles, cellulose fibers, and mica flakes.

[0055] The well treatment fluid may comprise additional additives for improving the performance of the wellbore fluid with respect to one or more properties. Examples include: pH control agents such as calcium hydroxide, magnesium hydroxide, magnesium oxide, potassium hydroxide, sodium hydroxide and citric acid; clay or shale hydration inhibitors (such as polyalkylene glycols), bactericides, detergents and emulsifiers, solid and liquid lubricants, gas-hydrate inhibitors, corrosion inhibitors, oxygen scavengers, defoamers, scale inhibitors, enzymes, oxidising polymer-breakers, emulsified hydrophobic liquids such as oils, acid gas-scavengers (such as hydrogen sulfide scavengers), thinners (such as lignosulfonates), demulsifiers and surfactants designed to assist the clean-up of invaded fluid from producing formations.

[0056] Other water-soluble polymers may be added to the well treatment fluid to impart viscous properties, solids-dispersion and/or filtration control to the fluid. A wide range of water-soluble polymers may be used including cellulose derivatives such as carboxymethyl cellulose, hydroxyethylcellulose, carboxymethylhydroxyethyl cellulose, sulphoethylcellulose; starch derivatives (which may be cross-linked) including carboxymethyl starch, hydroxyethylstarch, hydroxypropyl starch; bacterial gums including xanthan, welan, diutan, succinoglycan, scleroglucan, dextran, pullulan; plant derived gums such as guar gum, locust-bean gum, tara gum and their derivatives; synthetic polymers and copolymers.

[0057] Synthetic water-soluble homopolymers and copolymers can be used to viscosify a fluid and/or as a fluid loss reducer, or as an encapsulating polymer to reduce the rate of shale hydration and cuttings dispersion. Such synthetic (co)polymers are typically based on one or more monomers selected from the group consisting of acrylic acid, methacrylic acid, hydroxyethylmethacrylic acid, hydroxypropylmethacrylic acid; acrylamide, N,N-dimethylacrylamide, maleic acid or maleic anhydride, fumaric acid, itaconic acid, vinyl acetate, 2-acrylamido-2-methyl propane sulfonic acid (AMPS), 2-acrylamidoethane sulfonic acid, 2-acrylamidopropane sulfonic acid, 3-methacrylamidopropane sulfonic acid, styrene sulphonic acid, vinylsulfonic acid, allyl sulfonic acid, methallyl sulfonic acid, vinylbenzyl sulfonic acid, N-vinyl formamide, N-vinyl acetamide, N-vinyl pyrrolidone, N-vinyl caprolactone and N,N-dimethylacrylamide, N-vinylpyridine and other cationic vinylic monomers (for example, diallyldimethylammonium chloride, DADMAC). Typically, alkali metal, ammonium or amine salts of the acidic functional groups in the (co)polymer are used in the well treatment fluids. These synthetic (co)polymers have a number average molecular weight in the range 100,000 to 20,000,000 daltons, although molecular weights lower than 100,000 are of value where it is desired that the (co)polymer exert a useful solids-dispersing effect.

[0058] Another class of viscosifying agents that may be used is that of viscoelastic surfactants (VESs). VESs are used in wellbore fluids where easy clean-up of the fluid after use is needed. Examples include a gravel-pack carrier fluid and a fracturing fluid.

[0059] Other examples of fluid loss reducers that can be used include asphalts (for example sulfonated asphalts); gilsonite; lignite (humic acid) and its derivatives such as sulfomethylated lignite; lignin derivatives such as lignin sulfonates and condensed polymeric lignin sulfonates.

[0060] Dispersants for solids suspended in the fluid (also known as thinners) can be used. Such dispersants include lignosulfonates, polyphosphates, tannins and/or quebracho extract, sulfomethylated tannins. Other useful dispersants include synthetic water-soluble polyanionic polymers such as sodium polyacrylate and other largely anionic (co)polymers produced from the monomers listed above and having a

number average molecular weight, Mn, in the range 1,000 to 100,000, more typically 3,000 to 30,000.

[0061] Shale hydration inhibitors will often be used as an additional additive in the well treatment fluid. These include partially hydrolyzed polyacrylamide or copolymers of acrylamide and acrylic acid, polyalkyleneglycols, polyinylpyrrolidone or N-vinylpyrrolidone copolymers, polyamines, amine end-capped polyalkyleneglycols, at least partially cationic polymers derived from cationic monomers such as diallyl dimethyl ammonium chloride, and organic cations such as tetramethylammonium and choline cations.

[0062] The invention provides a method of lubricating a well treatment fluid. The method includes the step of: adding to the well treatment fluid the reaction product of i) at least one triglyceride of an hydroxy fatty acid; ii) at least one dicarboxylic acid or ester or anhydride thereof; and iii) at least one polyalkylene glycol.

[0063] The invention further provides a method for the preparation of an additive composition for increasing the lubricity and decreasing the coefficient of friction of a well treatment fluid. The method includes the steps of mixing the components until they are substantially or wholly dissolved. The order of addition of the composition components is not overly limited. The optional additives may be mixed in at the same time as the other components or at a later time. In one embodiment the components of the additive composition are present such that the total ratio of equivalent acid groups of hydroxy fatty acid and dicarboxylic acid to the hydroxyl groups in the polyalkylene glycol is from about 0.3 to about 2.5, and in one embodiment from about 0.4 to about 1.5.

[0064] In some embodiments, optional additives include any of those described above. In some embodiments, these optional additives may be added such that they are present in the overall compositions in the range about 0, 0.01, 0.1 or even 0.25 wt%.

[0065] The invention further provides a method of increasing the lubricity and decreasing the coefficient of friction of a well treatment fluid containing a brine on which the additive composition described herein is added to the brine. In the

method, in some embodiments, the coefficient of friction may be reduced by at least 5%, or by at least 10%, or by at least 20%, or from about 5% to about 95%, or from 10% to about 85%, or even from about 25% to about 75%.

Industrial application

[0066] The additive composition described herein can be, in some embodiments, utilized in well treatment fluids to increase the lubricity of the well treatment fluid, and in some embodiments, to reduce the coefficient of friction of the well treatment fluid. The additive composition may also clean debris and residue, including but not limited to residual water-based, oil-based and invert emulsion-based drilling muds, from the formation after drilling the wellbore so that the well can be completed and prepared for production. Well cleanup and completion fluids are often water-based or brine-based, and include but are not limited to preflush fluids, spacer fluids and tubular wash fluids. Adding the additive composition to an aqueous well cleanup fluid can improve the cleaning performance by allowing sticky oil, tar and other hydrophobic residue to be cleaned from solid debris and from the wellbore, allowing the debris to be more readily removed from the wellbore. In addition, the removal of residual water-based, oil-based and invert-based drilling muds from the wellbore when drilling is completed can be facilitated by well cleanup and completion fluids containing the additive composition.

[0067] The additive composition of the invention described herein may be present in a well treatment fluid in an amount, in one embodiment, from about 0.1 wt% to about 5 wt%, and in one embodiment from about 1 wt% to about 3 wt%.

[0068] The amount of each chemical component described is presented exclusive of any solvent, which may be customarily present in the commercial material, that is, on an active chemical basis, unless otherwise indicated. However, unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade.

[0069] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different

from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic or anionic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

EXAMPLES

[0070] The invention will be further illustrated by the following examples, which sets forth particularly advantageous embodiments. While the examples are provided to illustrate the present invention, they are not intended to limit it.

[0071] Lubricating fluids were prepared according to the formulations set forth in the Tables below. The lubricity of the lubricating fluids was evaluated using an EP Lubricity Tester, manufactured by OFI Testing Equipment, Inc., wherein fluid resistance of the fluids was measured by application of 150 inch-pounds of force (the equivalent of 5,000 to 10,000 psi- 34,500 to 69,000 kPa) – pressure on the fluid) between two hardened steel surfaces, a block and a ring rotating at 60 rpm for 5 minutes. Tables 1 through 4 set forth the coefficients of friction of the various brines and water-based drilling mud and inventive formulations at 21°C.

Table 2

Coefficient of Friction in Brine with Inventive Composition A*			
Example No.	Sample Description	**CoF**	**% reduction in CoF**
	DI water	0.355	-----
1	KCl (12.5% solution) in DI water	0.316	-----
2	Example 1 + 0.37% Inventive A	0.094	70.3
1(a)	KCl (12.5% solution) in DI water	0.29	-----
3	Example 1 + 1.5% Inventive A	0.128	55.8
4	Example 1 +4.0% Inventive A	0.114	60.7

Coefficient of Friction in Brine with Inventive Composition A*			
Example No.	Sample Description	**CoF**	**% reduction in CoF**
5	potassium formate (31.3%) in DI water	0.318	-----
6	Example 5 + 0.4 % by weight Inventive A	0.261	17.9
5(a)	Potassium formate (31.3%) in DI water	0.283	-----
7	Example 5 + 1.5% Inventive A	0.087	69.2
8	Example 5 +4.0% Inventive A	0.07	75.2
9	NaCl (10.7%) in DI water	0.304	-----
10	NaCl (10.7%) in DI water + 0.4wt% Inventive A	0.094	69.1%

*Inventive Composition A is the reaction product of i) a polymeric ester of castor oil, ii) adipic acid and iii) PEG

**All values are percent by weight

Table 3

Coefficient of Friction in Brine with Inventive Composition B*			
Example No.	Sample Description	**CoF**	**% reduction in CoF**
11	DI Water	0.323	-------
12	potassium formate (31.3%) in DI water	0.318	-------
13	Example 12 + 0.4 wt% Inventive A	0.261	17.9%
14	Example 12 + 0.4 % by weight sulfurized olefin	0.274	13.8%
15	Example 12 + 0.4 % by weight - Inventive B 2:1	0.107	66.3%
16	Example 12 + 0.4 % by weight Inventive B 9:1	0.108	66.0%
17	NaCl (10.7%) in DI water	0.304	

Coefficient of Friction in Brine with Inventive Composition B*			
Example No.	Sample Description	**CoF**	**% reduction in CoF**
18	Example 17 + 0.4% Inventive A	0.094	69.1%
19	Example 17 + 0.4% sulfurized olefin	0.267	12.2%
20	Example 17 + 0.4% Inventive B 2:1	0.078	74.3%
21	Example 17 + 0.4% Inventive B 9:1	0.071	76.6%

*Inventive Composition B is the same as Inventive Composition A but further includes an isobutylene-based sulfurized olefin manufactured under a no pressure process in a ratio of Composition A:olefin of 2:1 and 9:1
**All values are percent by weight

Table 4

Coefficient of Friction in Brine with Inventive Composition C*			
Example	Sample Description	**CoF**	**% reduction in CoF**
22	DI water	0.355	-------
23	KCl (12.5% solution) in DI water	0.311	-------
24	Example 23 + 0.37% Inventive C 2:1	0.023	92.6%
25	Example 23 + 0.37% Inventive C 9:1	0.079	75.0%
26	NaCl (10.74%) in DI water	0.316	
27	Example 26 + 0.37% Inventive C 9:1	0.054	82.9%

*Inventive Composition C is the same as Inventive Composition A but includes an isobutylene – based sulfurized olefin made under a high pressure process in a ratio of Composition A:olefin of 2:1 and 9:1
**All values are percent by weight

[0072] As illustrated in Tables 3 and 4, it can be seen that the addition of a sulfurized olefin to the additive composition provides a synergistic effect, thereby lowering the coefficient of friction as well as increasing the percent reduction in coefficient of friction in an amount greater than a composition containing only the sulfurized olefin or only the additive composition.

Table 5

	Coefficient of Friction in Brine with Inventive Composition D*		
Example No.	Sample Description	**CoF**	**% reduction in CoF**
28	DI water	0.326	-----
29	NaCl (10.7%) in DI water	0.298	-----
30	Example 29 + 0.4% Inventive A	0.127	57.4%
31	Example 29 + 0.4% ZDDP	0.201	32.5%
32	Example 29 + 0.4% Inventive D 2:1	0.102	65.8%
33	Example 29 + 0.4% Inventive D 9:1	0.11	63.1%

*Inventive Composition D is the same as Inventive Composition A but includes zinc dialkyldithiophosphate (ZDDP) in a ratio of Composition A:ZDDP of 2:1 and 9:1

[0073] As illustrated in Table 5, it can be seen that the addition of ZDDP to the additive composition provides a synergistic effect, thereby lowering the coefficient of friction, as well as increasing the percent reduction in coefficient of friction in an amount greater than a composition containing only ZDDP or only the additive composition.

Table 6

Coefficient of Friction in Brine with Inventive Composition E*			
Example No.	Sample Description	**CoF**	**% reduction in CoF**
34	DI Water	0.347	-------
35	Sodium silicate (3%) in DI water	0.519	-------
36	Example 35 + 1 wt% Inventive E	0.14	73.0%
37	Example 35 + 2 wt% Inventive E	0.119	77.0%
38	Potassium silicate (2.3%) in DI water	0.497	------
39	Example 38 + 1 % Inventive E	0.143	71.0%
40	Example 38 + 2 % Inventive E	0.13	74.0%

*Inventive Composition E is the same as Inventive Composition A but further includes an isobutylene-based sulfurized olefin manufactured under a no pressure process and PnB ether in a ratio of Composition E:olefin of 9:1.
**All values are percent by weight

[0074] As illustrated in Table 6, it can be seen that the addition of sulfurized olefin to the additive composition provides a synergistic effect, thereby lowering the coefficient of friction as well as increasing the percent reduction in coefficient of friction in an amount greater than a composition containing only the sulfurized olefin or only the additive composition.

Table 7

Coefficient of Friction in Drilling Mud with Inventive Composition E			
Example No.	Sample Description	**CoF**	**% reduction in CoF**
41	DI Water	0.364	-------
42	Sodium silicate drilling mud A*	0.431	-------
43	Example 42 + 1 wt% Inventive E	0.196	54.0%
44	Example 42 + 2 wt% Inventive E	0.127	70.0%
45	Potassium silicate drilling mud B**	0.496	------
46	Example 45 + 2 % Inventive E	0.124	75.0%

*Drilling Mud A is a 3% solution of sodium silicate containing xanthan gum, scleroglucan and rev dust
**Drilling Mud B is a 2.3% solution of potassium silicate containing xanthan gum, scleroglucan and rev dust
***All values are percent by weight

[0075] As illustrated in Table 7, it can be seen that the addition of the additive composition disclosed herein to a water-based drilling mud is effective to lower the coefficient of friction as well as increasing the percent reduction in coefficient of friction in an amount greater than a composition without the additive composition present

[0076] Each of the documents referred to above is incorporated herein by reference, including any prior applications, whether or not specifically listed above, from which priority is claimed. The mention of any document is not an admission that such document qualifies as prior art or constitutes the general knowledge of the skilled person in any jurisdiction. Except in the Examples, or where otherwise explicitly

indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements.

[0077] As used herein, the transitional term "comprising," which is synonymous with "including," "containing," or "characterized by," is inclusive or open-ended and does not exclude additional, un-recited elements or method steps. However, in each recitation of "comprising" herein, it is intended that the term also encompass, as alternative embodiments, the phrases "consisting essentially of" and "consisting of," where "consisting of" excludes any element or step not specified and "consisting essentially of" permits the inclusion of additional un-recited elements or steps that do not materially affect the essential or basic and novel characteristics of the composition or method under consideration.

What is claimed is:

1. An additive composition for a well treatment fluid, comprising the reaction product of:

i) at least one triglyceride of a hydroxy fatty acid;

ii) at least one dicarboxylic acid or an ester or anhydride thereof; and

iii) at least one polyalkylene glycol.

2. The additive composition of claim 1, wherein the hydroxy fatty acid comprises one or more of 2-hydroxylinolenic acid, 2-hydroxyoleic acid, 2-hydroxytetraconsanic acid, 2-hydroxy-15-tetracosenic acid, 2-hydroxy palmitic acid, 3-hydroxyolylipins, 10-hydroxy-2-decenoic acid, 10-hydroxy-2-decanoic acid, 9,10-hydroxy-2-decenoic acid, 3,10-dihydroxydecanoic acid, 8-hydroxotanoic acid, w-hydroxy octadecenoic acid, 15-hydroxylinoleate, 12-hydroxy-9-octadecenoic acid, 12-hydroxy stearic acid, 14-hydroxy-11-eicosenoic acid, 11-hydroxy hexadecanoic acid, 15-hydroxy-hexadecanoic acid, or 17-hydroxy-octadecanoic acid.

3. The additive composition of claims 1 or 2, wherein the at least one dicarboxylic acid comprises one or more of an aliphatic acid, an aromatic acid, a dimer acid, a trimer acid or a fatty dimer acid.

4. The additive composition of claim 3, wherein the dicarboxylic acid comprises oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, maleic acid, fumaric acid, glutaconic acid, traumatic acid and muconic acid, phthalic acid, isophthalic acid, terephthalic acid or diphenic acid.

5. The additive composition of any of claims 1 to 3, wherein the polyalkylene glycol comprises one or more of polyethylene glycol or polypropylene glycol.

6. The additive composition of claim 5, wherein the polyalkylene glycol comprises polyethylene glycol having a Mn of from 100 to 10,000.

7. The additive composition of claim 5, wherein the polyalkylene glycol comprises polypropylene glycol having a Mn of less than 2000.

8. The additive composition of claim 1, wherein the additive composition comprises the reaction product of a triglyceride of a hydroxy fatty acid, adipic acid and polyethylene glycol.

9. The additive composition of claim 8, wherein the ratio of equivalent acid groups of hydroxyl fatty acid and dicarboxylic acid to hydroxyl groups of the polyalkylene glycol is from 0.3 to 2.5.

10. The additive composition of claim 1, further comprising a sulfurized olefin.

11. The additive composition of claim 1, further comprising a metal thiophosphate compound.

12. The additive composition of claim 11, wherein the metal thiophosphate compound comprises zinc dialkyldithiophosphate.

13. A well treatment fluid including the additive composition as defined in claim 1.

14. The well treatment fluid according to claim 13 which is a completion fluid.

15. The well treatment fluid according to claim 13 which is a drilling fluid.

16. A well treatment fluid, comprising:

a) a brine; and

b) an additive composition comprising the reaction product of:

i) at least one triglyceride of a hydroxy fatty acid;

ii) at least one dicarboxylic acid or an ester or anhydride thereof; and

iii) at least one polyalkylene glycol.

17. The well treatment fluid of claim 16, wherein the brine comprises a sodium chloride, a potassium chloride, a calcium chloride, a sodium bromide, a calcium bromide, a sodium bromide, a zinc bromide, a potassium formate, a cesium formate, a sodium formate, a potassium silicate, or a sodium silicate.

18. The well treatment fluid of claim 16 or 17, wherein the additive composition is added to the well treatment fluid in an amount from 0.1 wt% to 5 wt%.

19. A method of lubricating a well treatment fluid, comprising:

adding to the completion fluid the reaction product of i) at least one triglyceride of a hydroxy fatty acid; ii) at least one dicarboxylic acid or an ester or anhydride thereof; and iii) at least one polyalkylene glycol.

20. A method of increasing the lubricity and decreasing the coefficient of friction of a well treatment fluid containing a brine comprising adding to the brine an additive composition comprising the reaction product of:

i) at least one triglyceride of a hydroxy fatty acid;

ii) at least one dicarboxylic acid or an ester or anhydride thereof; and

iii) at least one polyalkylene glycol.

20. The method of claim 19, wherein the coefficient of friction of the well treatment fluid is decreased in an amount of at least 5%.

21. A method of making an additive composition for increasing the lubricity and decreasing the coefficient of friction of a well treatment fluid comprising the step of mixing i) at least one triglyceride of a hydroxy fatty acid; ii) at least one dicarboxylic acid or an ester or anhydride thereof; and iii) at least one polyalkylene glycol to form the additive composition.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/043046

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/035
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 066 159 A (DE GROOTE MELVIN ET AL) 27 November 1962 (1962-11-27) columns 2,4 - column 6; examples 17a-28a; table I column 9 - column 12; claims	1-21
X	US 6 706 667 B1 (SMITH CARL KEITH [CA] ET AL) 16 March 2004 (2004-03-16) columns 1,3 - column 4; claims; examples	1-21
X	US 3 381 022 A (LE SUER WILLIAM M) 30 April 1968 (1968-04-30) column 1 - column 3; examples 3,5 column 11 - column 13	1-21

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

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Date of the actual completion of the international search	Date of mailing of the international search report
29 October 2015	09/11/2015

Name and mailing address of the ISA/	Authorized officer
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