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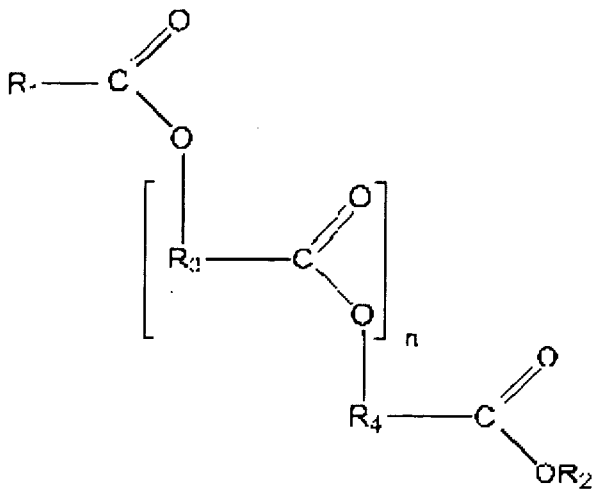
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(54) **Title**: HIGH-AND LOW-VISCOSITY ESTOLIDE BASE OILS AND LUBRICANTS



(57) **Abstract**: Provided herein are compounds of the formula: in which n is an integer equal to or greater than 1; R2 is selected from hydrogen and optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched; and R1, R3, and R4, independently for each occurrence, are selected from optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched, wherein compositions comprising the compounds are characterized by particular combinations of values for estolide number, kinematic viscosity, and pour point. Also provided are compositions containing the compounds and methods of making both the compounds and compositions thereof.

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HIGH- AND LOW-VISCOSITY ESTOLIDE BASE OILS AND LUBRICANTS

CROSS-REFERENCE TO RELATED APPLICATIONS

[001] This application claims the benefit under 35 U.S.C. § 119(e) of U.S. Provisional Patent Application No. 61/378,891, filed August 31, 2010, and U.S. Provisional Patent Application No. 61/498,499, filed June 17, 2011, both of which are incorporated herein by reference in their entireties for all purposes.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[002] The subject of this invention was made with support under U.S. Department of Agriculture – Agricultural Research Service Cooperative Research and Development Agreement (CRADA) Nos. 58-3K95-1-1508-M and 58-3K95-6-1147. Accordingly, the government may have certain rights in this invention.

FIELD

[003] The present disclosure relates to high- and low-viscosity base oil stocks and lubricants and methods of making the same. The estolides described herein may be suitable for use as biodegradable base oil stocks and lubricants.

BACKGROUND

[004] Synthetic esters such as polyol esters and adipates, low viscosity poly alpha olefins (PAO) such as PAO 2, and vegetable oils such as canola oil and oleates have been described for use industrially as biodegradable base stocks to formulate lubricants. Such base stocks may be used in the production of lubricating oils for automotives, industrial lubricants, and lubricating greases. Finished lubricants typically comprise the base oil and additives to help achieve desired viscometric properties, low temperature behavior, oxidative stability, corrosion protection, demulsibility and water rejection, friction coefficients, lubricities, wear protection, air release, color and other properties. However, it is generally understood that biodegradability cannot be improved by using common additives that are available in today's marketplace. For environmental, economical, and regulatory reasons, it is of interest to produce biodegradable lubricating oils, other biodegradable lubricants, and compositions including lubricating oils and/or lubricants, from renewable sources of biological origin.

[005] Estolides present a potential source of biobased, biodegradable oils that may be useful as lubricants and base stocks. Several estolide synthetic processes have been previously described, such as the homopolymerization of castor oil fatty acids or 12-hydroxystearic acid

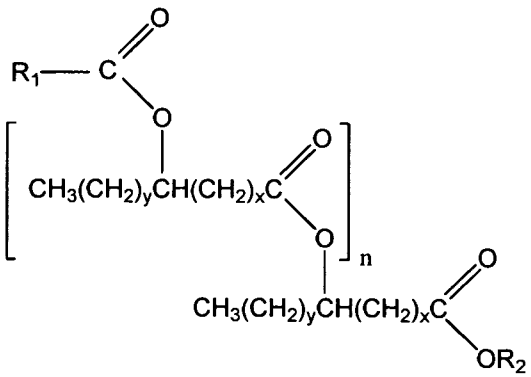
under thermal or acid catalyzed conditions, as well as the production of estolides from unsaturated fatty acids using a high temperature and pressure condensation over clay catalysts. Processes for the enzymatic production of estolides from hydroxy fatty acids present in castor oil using lipase have also been described.

[006] In U.S. Pat. No. 6,018,063, Isbell et al. described estolide compounds derived from oleic acids under acidic conditions and having properties for use as lubricant base stocks, wherein the "capping" fatty acid comprises oleic or stearic acid. In U.S. Patent No. 6,316,649, Cermak et al. reported estolides derived from oleic acids and having capping materials derived from C_6 to C_{14} fatty acids. According to Cermak et al., larger capping materials such as stearic acid adversely affect the properties of the estolide, such that having a greater percentage of stearic acid as the capping moiety generally increases pour point temperatures.

SUMMARY

[007] Described herein are estolide compounds, estolide-containing compositions, and methods of making the same. In certain embodiments, such compounds and/or compositions may be useful as base oils and lubricants.

[008] In certain embodiments, the estolides comprise at least one compound of Formula I:



Formula I

wherein

x is, independently for each occurrence, an integer selected from 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, and 20;

y is, independently for each occurrence, an integer selected from 0, 1, 2, 3, 4, 5, 6, 7, 8, 9,

10, 11, 12, 13, 14, 15, 16, 17, 18, 19, and 20;

n is an integer selected from 0 to 12;

R_1 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched; and

R_2 is selected from hydrogen and optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched;

wherein each fatty acid chain residue of said at least one compound is independently optionally substituted; and

wherein said composition has:

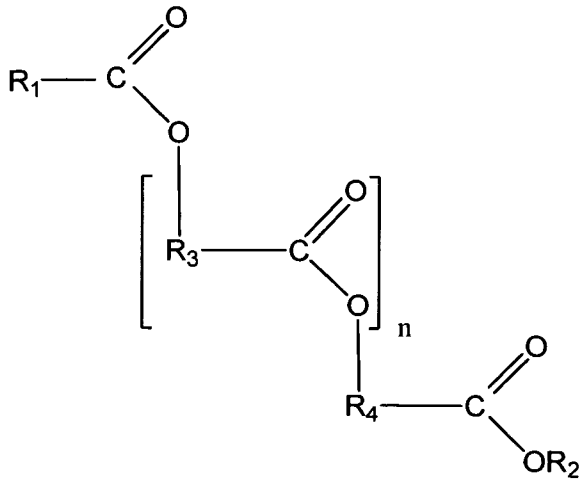
an EN selected from an integer that is equal to or greater than about 4, a kinematic viscosity equal to or greater than about 200 cSt when measured at 40 °C, and a pour point equal to or lower than about -40 °C;

an EN selected from an integer or fraction of an integer that is equal to or greater than about 3, a kinematic viscosity equal to or greater than about 130 cSt when measured at 40 °C, and a pour point equal to or lower than about -30 °C;

an EN selected from an integer or fraction of an integer that is equal to or less than about 2, a kinematic viscosity equal to or less than about 55 cSt when measured at 40 °C, and a pour point equal to or lower than about -25 °C; or

an EN selected from an integer or fraction of an integer that is equal to or less than about 2, a kinematic viscosity equal to or less than about 45 cSt when measured at 40 °C, and a pour point equal to or lower than about -25 °C.

[009] In certain embodiments, the estolide-containing compositions comprise at least one compound of Formula II:



Formula II

wherein

n is an integer equal to or greater than 0;

R_1 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched; and

R_2 is selected from hydrogen and optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched; and

R_3 and R_4, independently for each occurrence, are selected from optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched;

wherein said composition has:

an EN selected from an integer that is equal to or greater than about 4, a kinematic viscosity equal to or greater than about 200 cSt when measured at 40 °C, and a pour point equal to or lower than about -40 °C;

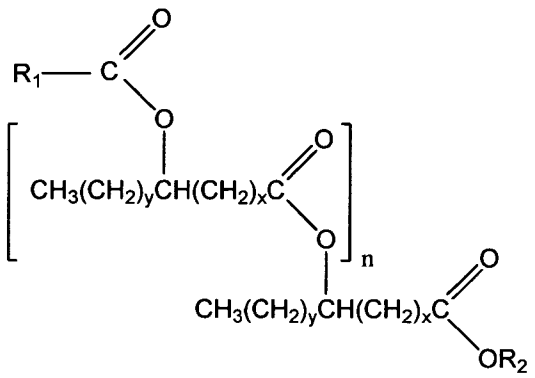
an EN selected from an integer or fraction of an integer that is equal to or greater than about 3, a kinematic viscosity equal to or greater than about 130 cSt when measured at 40 °C, and a pour point equal to or lower than about -30 °C;

an EN selected from an integer or fraction of an integer that is equal to or less than about 2, a kinematic viscosity equal to or less than about 55 cSt when measured at 40

°C, and a pour point equal to or lower than about -25 °C; or

an EN selected from an integer or fraction of an integer that is equal to or less than about 2, a kinematic viscosity equal to or less than about 45 cSt when measured at 40 °C, and a pour point equal to or lower than about -25 °C.

[010] In certain embodiments, the estolides-containing compositions comprise at least one compound represented of Formula III:



Formula III

wherein

x is, independently for each occurrence, an integer selected from 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, and 20;

y is, independently for each occurrence, an integer selected from 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, and 20;

n is an integer equal to or greater than 0;

R_1 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched; and

R_2 is selected from hydrogen and optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched;

wherein each fatty acid chain residue of said at least one compound is independently optionally substituted; and

wherein said composition has:

an EN selected from an integer that is equal to or greater than about 4, a kinematic viscosity equal to or greater than about 200 cSt when measured at 40 °C, and a pour point equal to or lower than about -40 °C;

an EN selected from an integer or fraction of an integer that is equal to or greater than about 3, a kinematic viscosity equal to or greater than about 130 cSt when measured at 40 °C, and a pour point equal to or lower than about -30 °C;

an EN selected from an integer or fraction of an integer that is equal to or less than about 2, a kinematic viscosity equal to or less than about 55 cSt when measured at 40 °C, and a pour point equal to or lower than about -25 °C; or

an EN selected from an integer or fraction of an integer that is equal to or less than about 2, a kinematic viscosity equal to or less than about 45 cSt when measured at 40 °C, and a pour point equal to or lower than about -25 °C.

DETAILED DESCRIPTION

[011] As used in the present specification, the following words, phrases and symbols are generally intended to have the meanings as set forth below, except to the extent that the context in which they are used indicates otherwise. The following abbreviations and terms have the indicated meanings throughout:

[012] A dash ("–") that is not between two letters or symbols is used to indicate a point of attachment for a substituent. For example, $-C(O)NH_2$ is attached through the carbon atom.

[013] "Alkoxy" by itself or as part of another substituent refers to a radical $-OR^{31}$ where R^{31} is alkyl, cycloalkyl, cycloalkylalkyl, aryl, or arylalkyl, which can be substituted, as defined herein. In some embodiments, alkoxy groups have from 1 to 8 carbon atoms. In some embodiments, alkoxy groups have 1, 2, 3, 4, 5, 6, 7, or 8 carbon atoms. Examples of alkoxy groups include, but are not limited to, methoxy, ethoxy, propoxy, butoxy, cyclohexyloxy, and the like.

[014] "Alkyl" by itself or as part of another substituent refers to a saturated or unsaturated, branched, or straight-chain monovalent hydrocarbon radical derived by the removal of one hydrogen atom from a single carbon atom of a parent alkane, alkene, or alkyne. Examples of alkyl groups include, but are not limited to, methyl; ethyls such as ethanyl, ethenyl, and ethynyl;

propyls such as propan-1-yl, propan-2-yl, prop-1-en-1-yl, prop-1-en-2-yl, prop-2-en-1-yl (allyl), prop-1-yn-1-yl, prop-2-yn-1-yl, *etc.*; butyls such as butan-1-yl, butan-2-yl, 2-methyl-propan-1-yl, 2-methyl-propan-2-yl, but-1-en-1-yl, but-1-en-2-yl, 2-methyl-prop-1-en-1-yl, but-2-en-1-yl, but-2-en-2-yl, buta-1,3-dien-1-yl, buta-1,3-dien-2-yl, but-1-yn-1-yl, but-1-yn-3-yl, but-3-yn-1-yl, *etc.*; and the like.

[015] Unless otherwise indicated, the term "alkyl" is specifically intended to include groups having any degree or level of saturation, *i.e.*, groups having exclusively single carbon-carbon bonds, groups having one or more double carbon-carbon bonds, groups having one or more triple carbon-carbon bonds, and groups having mixtures of single, double, and triple carbon-carbon bonds. Where a specific level of saturation is intended, the terms "alkanyl," "alkenyl," and "alkynyl" are used. In certain embodiments, an alkyl group comprises from 1 to 40 carbon atoms, in certain embodiments, from 1 to 22 or 1 to 18 carbon atoms, in certain embodiments, from 1 to 16 or 1 to 8 carbon atoms, and in certain embodiments from 1 to 6 or 1 to 3 carbon atoms. In certain embodiments, an alkyl group comprises from 8 to 22 carbon atoms, in certain embodiments, from 8 to 18 or 8 to 16. In some embodiments, the alkyl group comprises from 3 to 20 or 7 to 17 carbons. In some embodiments, the alkyl group comprises 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, or 22 carbon atoms.

[016] "Aryl" by itself or as part of another substituent refers to a monovalent aromatic hydrocarbon radical derived by the removal of one hydrogen atom from a single carbon atom of a parent aromatic ring system. Aryl encompasses 5- and 6-membered carbocyclic aromatic rings, for example, benzene; bicyclic ring systems wherein at least one ring is carbocyclic and aromatic, for example, naphthalene, indane, and tetralin; and tricyclic ring systems wherein at least one ring is carbocyclic and aromatic, for example, fluorene. Aryl encompasses multiple ring systems having at least one carbocyclic aromatic ring fused to at least one carbocyclic aromatic ring, cycloalkyl ring, or heterocycloalkyl ring. For example, aryl includes 5- and 6-membered carbocyclic aromatic rings fused to a 5- to 7-membered non-aromatic heterocycloalkyl ring containing one or more heteroatoms chosen from N, O, and S. For such fused, bicyclic ring systems wherein only one of the rings is a carbocyclic aromatic ring, the point of attachment may be at the carbocyclic aromatic ring or the heterocycloalkyl ring. Examples of aryl groups include, but are not limited to, groups derived from aceanthrylene, acenaphthylene, acephenanthrylene, anthracene, azulene, benzene, chrysene, coronene, fluoranthene, fluorene, hexacene, hexaphene, hexalene, as-indacene, s-indacene, indane, indene, naphthalene, octacene, octaphene, octalene,

ovalene, penta-2,4-diene, pentacene, pentalene, pentaphene, perylene, phenalene, phenanthrene, picene, pleiadene, pyrene, pyranthrene, rubicene, triphenylene, trinaphthalene, and the like. In certain embodiments, an aryl group can comprise from 5 to 20 carbon atoms, and in certain embodiments, from 5 to 12 carbon atoms. In certain embodiments, an aryl group can comprise 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 carbon atoms. Aryl, however, does not encompass or overlap in any way with heteroaryl, separately defined herein. Hence, a multiple ring system in which one or more carbocyclic aromatic rings is fused to a heterocycloalkyl aromatic ring, is heteroaryl, not aryl, as defined herein.

[017] "Arylalkyl" by itself or as part of another substituent refers to an acyclic alkyl radical in which one of the hydrogen atoms bonded to a carbon atom, typically a terminal or sp^3 carbon atom, is replaced with an aryl group. Examples of arylalkyl groups include, but are not limited to, benzyl, 2-phenylethan-1-yl, 2-phenylethen-1-yl, naphthylmethyl, 2-naphthylethan-1-yl, 2-naphthylethen-1-yl, naphthobenzyl, 2-naphthophenylethan-1-yl, and the like. Where specific alkyl moieties are intended, the nomenclature arylalkanyl, arylalkenyl, or arylalkynyl is used. In certain embodiments, an arylalkyl group is C_{7-30} arylalkyl, *e.g.*, the alkanyl, alkenyl, or alkynyl moiety of the arylalkyl group is C_{1-10} and the aryl moiety is C_{6-20}, and in certain embodiments, an arylalkyl group is C_{7-20} arylalkyl, *e.g.*, the alkanyl, alkenyl, or alkynyl moiety of the arylalkyl group is C_{1-8} and the aryl moiety is C_{6-12}.

[018] Estolide "base oil" and "base stock", unless otherwise indicated, refer to any composition comprising one or more estolide compounds. It should be understood that an estolide "base oil" or "base stock" is not limited to compositions for a particular use, and may generally refer to compositions comprising one or more estolides, including mixtures of estolides. Estolide base oils and base stocks can also include compounds other than estolides.

[019] "Compounds" refers to compounds encompassed by structural Formula I, II, and III herein and includes any specific compounds within the formula whose structure is disclosed herein. Compounds may be identified either by their chemical structure and/or chemical name. When the chemical structure and chemical name conflict, the chemical structure is determinative of the identity of the compound. The compounds described herein may contain one or more chiral centers and/or double bonds and therefore may exist as stereoisomers such as double-bond isomers (*i.e.*, geometric isomers), enantiomers, or diastereomers. Accordingly, any chemical structures within the scope of the specification depicted, in whole or in part, with a relative configuration encompass all possible enantiomers and stereoisomers of the illustrated compounds

including the stereoisomerically pure form (*e.g.*, geometrically pure, enantiomerically pure, or diastereomerically pure) and enantiomeric and stereoisomeric mixtures. Enantiomeric and stereoisomeric mixtures may be resolved into their component enantiomers or stereoisomers using separation techniques or chiral synthesis techniques well known to the skilled artisan.

[020] For the purposes of the present disclosure, "chiral compounds" are compounds having at least one center of chirality (i.e. at least one asymmetric atom, in particular at least one asymmetric C atom), having an axis of chirality, a plane of chirality or a screw structure. "Achiral compounds" are compounds which are not chiral.

[021] Compounds of Formula I, II, and III include, but are not limited to, optical isomers of compounds of Formula I, II, and III, racemates thereof, and other mixtures thereof. In such embodiments, the single enantiomers or diastereomers, *i.e.*, optically active forms, can be obtained by asymmetric synthesis or by resolution of the racemates. Resolution of the racemates may be accomplished by, for example, chromatography, using, for example a chiral high-pressure liquid chromatography (HPLC) column. However, unless otherwise stated, it should be assumed that Formula I, II, and III cover all asymmetric variants of the compounds described herein, including isomers, racemates, enantiomers, diastereomers, and other mixtures thereof. In addition, compounds of Formula I, II and III include Z- and E-forms (*e.g.*, cis- and trans-forms) of compounds with double bonds. The compounds of Formula I, II, and III may also exist in several tautomeric forms including the enol form, the keto form, and mixtures thereof. Accordingly, the chemical structures depicted herein encompass all possible tautomeric forms of the illustrated compounds.

[022] "Cycloalkyl" by itself or as part of another substituent refers to a saturated or unsaturated cyclic alkyl radical. Where a specific level of saturation is intended, the nomenclature "cycloalkanyl" or "cycloalkenyl" is used. Examples of cycloalkyl groups include, but are not limited to, groups derived from cyclopropane, cyclobutane, cyclopentane, cyclohexane, and the like. In certain embodiments, a cycloalkyl group is C_{3-15} cycloalkyl, and in certain embodiments, C_{3-12} cycloalkyl or C_{5-12} cycloalkyl. In certain embodiments, a cycloalkyl group is a C_5, C_6, C_7, C_8, C_9, C_{10}, C_{11}, C_{12}, C_{13}, C_{14}, or C_{15} cycloalkyl.

[023] "Cycloalkylalkyl" by itself or as part of another substituent refers to an acyclic alkyl radical in which one of the hydrogen atoms bonded to a carbon atom, typically a terminal or sp^3 carbon atom, is replaced with a cycloalkyl group. Where specific alkyl moieties are intended, the

nomenclature cycloalkylalkanyl, cycloalkylalkenyl, or cycloalkylalkynyl is used. In certain embodiments, a cycloalkylalkyl group is C_{7-30} cycloalkylalkyl, *e.g.*, the alkanyl, alkenyl, or alkynyl moiety of the cycloalkylalkyl group is C_{1-10} and the cycloalkyl moiety is C_{6-20}, and in certain embodiments, a cycloalkylalkyl group is C_{7-20} cycloalkylalkyl, *e.g.*, the alkanyl, alkenyl, or alkynyl moiety of the cycloalkylalkyl group is C_{1-8} and the cycloalkyl moiety is C_{4-20} or C_{6-12}.

[024] "Halogen" refers to a fluoro, chloro, bromo, or iodo group.

[025] "Heteroaryl" by itself or as part of another substituent refers to a monovalent heteroaromatic radical derived by the removal of one hydrogen atom from a single atom of a parent heteroaromatic ring system. Heteroaryl encompasses multiple ring systems having at least one aromatic ring fused to at least one other ring, which can be aromatic or non-aromatic in which at least one ring atom is a heteroatom. Heteroaryl encompasses 5- to 12-membered aromatic, such as 5- to 7-membered, monocyclic rings containing one or more, for example, from 1 to 4, or in certain embodiments, from 1 to 3, heteroatoms chosen from N, O, and S, with the remaining ring atoms being carbon; and bicyclic heterocycloalkyl rings containing one or more, for example, from 1 to 4, or in certain embodiments, from 1 to 3, heteroatoms chosen from N, O, and S, with the remaining ring atoms being carbon and wherein at least one heteroatom is present in an aromatic ring. For example, heteroaryl includes a 5- to 7-membered heterocycloalkyl, aromatic ring fused to a 5- to 7-membered cycloalkyl ring. For such fused, bicyclic heteroaryl ring systems wherein only one of the rings contains one or more heteroatoms, the point of attachment may be at the heteroaromatic ring or the cycloalkyl ring. In certain embodiments, when the total number of N, S, and O atoms in the heteroaryl group exceeds one, the heteroatoms are not adjacent to one another. In certain embodiments, the total number of N, S, and O atoms in the heteroaryl group is not more than two. In certain embodiments, the total number of N, S, and O atoms in the aromatic heterocycle is not more than one. Heteroaryl does not encompass or overlap with aryl as defined herein.

[026] Examples of heteroaryl groups include, but are not limited to, groups derived from acridine, arsindole, carbazole, β-carboline, chromane, chromene, cinnoline, furan, imidazole, indazole, indole, indoline, indolizine, isobenzofuran, isochromene, isoindole, isoindoline, isoquinoline, isothiazole, isoxazole, naphthyridine, oxadiazole, oxazole, perimidine, phenanthridine, phenanthroline, phenazine, phthalazine, pteridine, purine, pyran, pyrazine, pyrazole, pyridazine, pyridine, pyrimidine, pyrrole, pyrrolizine, quinazoline, quinoline, quinolizine, quinoxaline, tetrazole, thiadiazole, thiazole, thiophene, triazole, xanthene, and the

like. In certain embodiments, a heteroaryl group is from 5- to 20-membered heteroaryl, and in certain embodiments from 5- to 12-membered heteroaryl or from 5- to 10-membered heteroaryl. In certain embodiments, a heteroaryl group is a 5-, 6-, 7-, 8-, 9-, 10-, 11-, 12-, 13-, 14-, 15-, 16-, 17-, 18-, 19-, or 20-membered heteroaryl. In certain embodiments heteroaryl groups are those derived from thiophene, pyrrole, benzothiophene, benzofuran, indole, pyridine, quinoline, imidazole, oxazole, and pyrazine.

[027] "Heteroarylalkyl" by itself or as part of another substituent refers to an acyclic alkyl radical in which one of the hydrogen atoms bonded to a carbon atom, typically a terminal or sp^3 carbon atom, is replaced with a heteroaryl group. Where specific alkyl moieties are intended, the nomenclature heteroarylalkanyl, heteroarylalkenyl, or heteroarylalkynyl is used. In certain embodiments, a heteroarylalkyl group is a 6- to 30-membered heteroarylalkyl, *e.g.*, the alkanyl, alkenyl, or alkynyl moiety of the heteroarylalkyl is 1- to 10-membered and the heteroaryl moiety is a 5- to 20-membered heteroaryl, and in certain embodiments, 6- to 20-membered heteroarylalkyl, *e.g.*, the alkanyl, alkenyl, or alkynyl moiety of the heteroarylalkyl is 1- to 8-membered and the heteroaryl moiety is a 5- to 12-membered heteroaryl.

[028] "Heterocycloalkyl" by itself or as part of another substituent refers to a partially saturated or unsaturated cyclic alkyl radical in which one or more carbon atoms (and any associated hydrogen atoms) are independently replaced with the same or different heteroatom. Examples of heteroatoms to replace the carbon atom(s) include, but are not limited to, N, P, O, S, Si, *etc.* Where a specific level of saturation is intended, the nomenclature "heterocycloalkanyl" or "heterocycloalkenyl" is used. Examples of heterocycloalkyl groups include, but are not limited to, groups derived from epoxides, azirines, thiiranes, imidazolidine, morpholine, piperazine, piperidine, pyrazolidine, pyrrolidine, quinuclidine, and the like.

[029] "Heterocycloalkylalkyl" by itself or as part of another substituent refers to an acyclic alkyl radical in which one of the hydrogen atoms bonded to a carbon atom, typically a terminal or sp^3 carbon atom, is replaced with a heterocycloalkyl group. Where specific alkyl moieties are intended, the nomenclature heterocycloalkylalkanyl, heterocycloalkylalkenyl, or heterocycloalkylalkynyl is used. In certain embodiments, a heterocycloalkylalkyl group is a 6- to 30-membered heterocycloalkylalkyl, *e.g.*, the alkanyl, alkenyl, or alkynyl moiety of the heterocycloalkylalkyl is 1- to 10-membered and the heterocycloalkyl moiety is a 5- to 20-membered heterocycloalkyl, and in certain embodiments, 6- to 20-membered

heterocycloalkylalkyl, *e.g.*, the alkanyl, alkenyl, or alkynyl moiety of the heterocycloalkylalkyl is 1- to 8-membered and the heterocycloalkyl moiety is a 5- to 12-membered heterocycloalkyl.

[030] "Mixture" refers to a collection of molecules or chemical substances. Each component in a mixture can be independently varied. A mixture may contain, or consist essentially of, two or more substances intermingled with or without a constant percentage composition, wherein each component may or may not retain its essential original properties, and where molecular phase mixing may or may not occur. In mixtures, the components making up the mixture may or may not remain distinguishable from each other by virtue of their chemical structure.

[031] "Parent aromatic ring system" refers to an unsaturated cyclic or polycyclic ring system having a conjugated π (pi) electron system. Included within the definition of "parent aromatic ring system" are fused ring systems in which one or more of the rings are aromatic and one or more of the rings are saturated or unsaturated, such as, for example, fluorene, indane, indene, phenalene, *etc.* Examples of parent aromatic ring systems include, but are not limited to, aceanthrylene, acenaphthylene, acephenanthrylene, anthracene, azulene, benzene, chrysene, coronene, fluoranthene, fluorene, hexacene, hexaphene, hexalene, *as*-indacene, *s*-indacene, indane, indene, naphthalene, octacene, octaphene, octalene, ovalene, penta-2,4-diene, pentacene, pentalene, pentaphene, perylene, phenalene, phenanthrene, picene, pleiadene, pyrene, pyranthrene, rubicene, triphenylene, trinaphthalene, and the like.

[032] "Parent heteroaromatic ring system" refers to a parent aromatic ring system in which one or more carbon atoms (and any associated hydrogen atoms) are independently replaced with the same or different heteroatom. Examples of heteroatoms to replace the carbon atoms include, but are not limited to, N, P, O, S, Si, *etc.* Specifically included within the definition of "parent heteroaromatic ring systems" are fused ring systems in which one or more of the rings are aromatic and one or more of the rings are saturated or unsaturated, such as, for example, arsindole, benzodioxan, benzofuran, chromane, chromene, indole, indoline, xanthene, *etc.* Examples of parent heteroaromatic ring systems include, but are not limited to, arsindole, carbazole, β-carboline, chromane, chromene, cinnoline, furan, imidazole, indazole, indole, indoline, indolizine, isobenzofuran, isochromene, isoindole, isoindoline, isoquinoline, isothiazole, isoxazole, naphthyridine, oxadiazole, oxazole, perimidine, phenanthridine, phenanthroline, phenazine, phthalazine, pteridine, purine, pyran, pyrazine, pyrazole, pyridazine,

pyridine, pyrimidine, pyrrole, pyrrolizine, quinazoline, quinoline, quinolizine, quinoxaline, tetrazole, thiadiazole, thiazole, thiophene, triazole, xanthene, and the like.

[033] "Substituted" refers to a group in which one or more hydrogen atoms are independently replaced with the same or different substituent(s). Examples of substituents include, but are not limited to, $-R^{64}$, $-R^{60}$, $-O^-$, $-OH$, $=O$, $-OR^{60}$, $-SR^{60}$, $-S^-$, $=S$, $-NR^{60}R^{61}$, $=NR^{60}$, $-CN$, $-CF_3$, $-OCN$, $-SCN$, $-NO$, $-NO_2$, $=N_2$, $-N_3$, $-S(O)_2O^-$, $-S(O)_2OH$, $-S(O)_2R^{60}$, $-OS(O_2)O^-$, $-OS(O)_2R^{60}$, $-P(O)(O^-)_2$, $-P(O)(OR^{60})(O^-)$, $-OP(O)(OR^{60})(OR^{61})$, $-C(O)R^{60}$, $-C(S)R^{60}$, $-C(O)OR^{60}$, $-C(O)NR^{60}R^{61}$, $-C(O)O^-$, $-C(S)OR^{60}$, $-NR^{62}C(O)NR^{60}R^{61}$, $-NR^{62}C(S)NR^{60}R^{61}$, $-NR^{62}C(NR^{63})NR^{60}R^{61}$, $-C(NR^{62})NR^{60}R^{61}$, $-S(O)_2$, $NR^{60}R^{61}$, $-NR^{63}S(O)_2R^{60}$, $-NR^{63}C(O)R^{60}$, and $-S(O)R^{60}$;

wherein each $-R^{64}$ is independently a halogen; each R^{60} and R^{61} are independently alkyl, substituted alkyl, alkoxy, substituted alkoxy, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, arylalkyl, substituted arylalkyl, heteroarylalkyl, or substituted heteroarylalkyl, or R^{60} and R^{61} together with the nitrogen atom to which they are bonded form a heterocycloalkyl, substituted heterocycloalkyl, heteroaryl, or substituted heteroaryl ring, and R^{62} and R^{63} are independently alkyl, substituted alkyl, aryl, substituted aryl, arylalkyl, substituted arylalkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, heteroaryl, substituted heteroaryl, heteroarylalkyl, or substituted heteroarylalkyl, or R^{62} and R^{63} together with the atom to which they are bonded form one or more heterocycloalkyl, substituted heterocycloalkyl, heteroaryl, or substituted heteroaryl rings;

wherein the "substituted" substituents, as defined above for R^{60}, R^{61}, R^{62}, and R^{63}, are substituted with one or more, such as one, two, or three, groups independently selected from alkyl, -alkyl-OH, -O-haloalkyl, -alkyl-NH_2, alkoxy, cycloalkyl, cycloalkylalkyl, heterocycloalkyl, heterocycloalkylalkyl, aryl, heteroaryl, arylalkyl, heteroarylalkyl, $-O^-$, $-OH$, $=O$, -O-alkyl, -O-aryl, -O-heteroarylalkyl, -O-cycloalkyl, -O-heterocycloalkyl, $-SH$, $-S^-$, $=S$, -S-alkyl, -S-aryl, -S-heteroarylalkyl, -S-cycloalkyl, -S-heterocycloalkyl, $-NH_2$, $=NH$, $-CN$, $-CF_3$, $-OCN$, $-SCN$, $-NO$, $-NO_2$, $=N_2$, $-N_3$, $-S(O)_2O^-$, $-S(O)_2$, $-S(O)_2OH$, $-OS(O_2)O^-$, -SO_2(alkyl), -SO_2(phenyl), -SO_2(haloalkyl), -SO_2NH_2, -SO_2NH(alkyl), -SO_2NH(phenyl), $-P(O)(O^-)_2$, $-P(O)$(O-alkyl)(O^-), $-OP(O)$(O-alkyl)(O-alkyl), -CO_2H, -C(O)O(alkyl), -CON(alkyl)(alkyl), -CONH(alkyl), -$CONH_2$, -C(O)(alkyl), -C(O)(phenyl), -C(O)(haloalkyl), -OC(O)(alkyl), -N(alkyl)(alkyl), -NH(alkyl), -N(alkyl)(alkylphenyl), -NH(alkylphenyl), -NHC(O)(alkyl), -NHC(O)(phenyl),

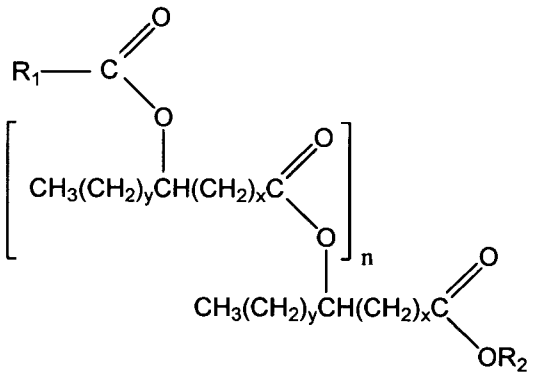
-N(alkyl)C(O)(alkyl), and -N(alkyl)C(O)(phenyl).

[034] As used in this specification and the appended claims, the articles "a," "an," and "the" include plural referents unless expressly and unequivocally limited to one referent.

[035] All numerical ranges herein include all numerical values and ranges of all numerical values within the recited range of numerical values.

[036] The present disclosure relates to estolide compounds, compositions and methods of making the same. In certain embodiments, the present disclosure also relates to estolide compounds, compositions comprising estolide compounds, for high- and low-viscosity base oil stocks and lubricants, the synthesis of such compounds, and the formulation of such compositions. In certain embodiments, the present disclosure relates to biosynthetic estolides having desired viscometric properties, while retaining or even improving other properties such as oxidative stability and pour point. In certain embodiments, new methods of preparing estolide compounds exhibiting such properties are provided. The present disclosure also relates to compositions comprising certain estolide compounds exhibiting such properties.

[037] In certain embodiments the composition comprises at least one estolide compound of Formula I:



Formula I

wherein

x is, independently for each occurrence, an integer selected from 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, and 20;

y is, independently for each occurrence, an integer selected from 0, 1, 2, 3, 4, 5, 6, 7, 8, 9,

10, 11, 12, 13, 14, 15, 16, 17, 18, 19, and 20;

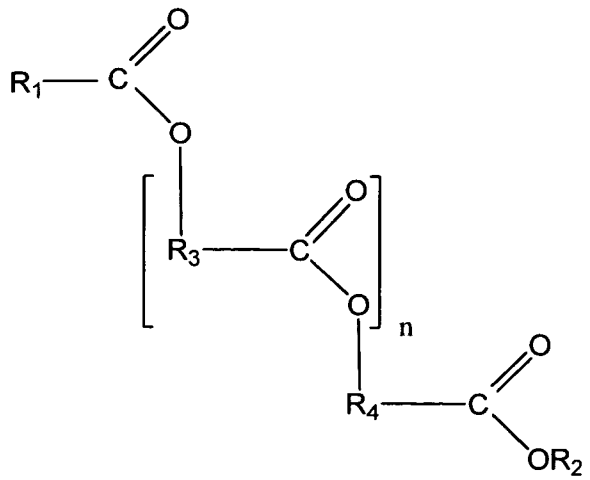
n is an integer selected from 0 to 12;

R_1 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched; and

R_2 is selected from hydrogen and optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched;

wherein each fatty acid chain residue of said at least one compound is independently optionally substituted.

[038] In certain embodiments the composition comprises at least one estolide compound of Formula II:



Formula II

wherein

n is an integer greater than or equal to 0;

R_1 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched;

R_2 is selected from hydrogen and optionally substituted alkyl that is saturated or

unsaturated, and branched or unbranched; and

R_3 and R_4, independently for each occurrence, are selected from optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched.

[039] In certain embodiments, the composition comprises at least one estolide of Formula I, II, or III where R_1 is hydrogen.

[040] The terms "chain" or "fatty acid chain" or "fatty acid chain residue," as used with respect to the estolide compounds of Formula I, II, and III, refer to one or more of the fatty acid residues incorporated in estolide compounds, e.g., R_3 or R_4 of Formula II, or the structures represented by $CH_3(CH_2)_yCH(CH_2)_xC(O)O$- in Formula I and III.

[041] The R_1 in Formula I, II, and III at the top of each Formula shown is an example of what may be referred to as a "cap" or "capping material," as it "caps" the top of the estolide. Similarly, the capping group may be an organic acid residue of general formula -OC(O)-alkyl, i.e., a carboxylic acid with a substituted or unsubstituted, saturated or unsaturated, and/or branched or unbranched alkyl as defined herein, or a formic acid residue. In certain embodiments, the "cap" or "capping group" is a fatty acid. In certain embodiments, the capping group, regardless of size, is substituted or unsubstituted, saturated or unsaturated, and/or branched or unbranched. The cap or capping material may also be referred to as the primary or alpha (α) chain.

[042] Depending on the manner in which the estolide is synthesized, the cap or capping group alkyl may be the only alkyl from an organic acid residue in the resulting estolide that is unsaturated. In certain embodiments, it may be desirable to use a saturated organic or fatty-acid cap to increase the overall saturation of the estolide and/or to increase the resulting estolide's stability. For example, in certain embodiments, it may be desirable to provide a method of providing a saturated capped estolide by hydrogenating an unsaturated cap using any suitable methods available to those of ordinary skill in the art. Hydrogenation may be used with various sources of the fatty-acid feedstock, which may include mono- and/or polyunsaturated fatty acids. Without being bound to any particular theory, in certain embodiments, hydrogenating the estolide may help to improve the overall stability of the molecule. However, a fully-hydrogenated estolide, such as an estolide with a larger fatty acid cap, may exhibit increased pour point

temperatures. In certain embodiments, it may be desirable to offset any loss in desirable pour-point characteristics by using shorter, saturated capping materials.

[043] The $R_4C(O)O$- of Formula II or structure $CH_3(CH_2)_yCH(CH_2)_xC(O)O$- of Formula I and III serve as the "base" or "base chain residue" of the estolide. Depending on the manner in which the estolide is synthesized, the base organic acid or fatty acid residue may be the only residue that remains in its free-acid form after the initial synthesis of the estolide. However, in certain embodiments, in an effort to alter or improve the properties of the estolide, the free acid may be reacted with any number of substituents. For example, it may be desirable to react the free acid estolide with alcohols, glycols, amines, or other suitable reactants to provide the corresponding ester, amide, or other reaction products. The base or base chain residue may also be referred to as tertiary or gamma (γ) chains.

[044] The $R_3C(O)O$- of Formula II or structure $CH_3(CH_2)_yCH(CH_2)_xC(O)O$- of Formula I and III are linking residues that link the capping material and the base fatty-acid residue together. There may be any number of linking residues in the estolide, including when n=0 and the estolide is in its dimer form. Depending on the manner in which the estolide is prepared, a linking residue may be a fatty acid and may initially be in an unsaturated form during synthesis. In some embodiments, the estolide will be formed when a catalyst is used to produce a carbocation at the fatty acid's site of unsaturation, which is followed by nucleophilic attack on the carbocation by the carboxylic group of another fatty acid. In some embodiments, it may be desirable to have a linking fatty acid that is monounsaturated so that when the fatty acids link together, all of the sites of unsaturation are eliminated. The linking residue(s) may also be referred to as secondary or beta (β) chains.

[045] In certain embodiments, the cap is an acetyl group, the linking residue(s) is one or more fatty acid residues, and the base chain residue is a fatty acid residue. In certain embodiments, the linking residues present in an estolide differ from one another. In certain embodiments, one or more of the linking residues differs from the base chain residue.

[046] As noted above, in certain embodiments, suitable unsaturated fatty acids for preparing the estolides may include any mono- or polyunsaturated fatty acid. For example, monounsaturated fatty acids, along with a suitable catalyst, will form a single carbocation that allows for the addition of a second fatty acid, whereby a single link between two fatty acids is formed. Suitable monounsaturated fatty acids may include, but are not limited to, palmitoleic

acid (16:1), vaccenic acid (18:1), oleic acid (18:1), eicosenoic acid (20:1), erucic acid (22:1), and nervonic acid (24:1). In addition, in certain embodiments, polyunsaturated fatty acids may be used to create estolides. Suitable polyunsaturated fatty acids may include, but are not limited to, hexadecatrienoic acid (16:3), alpha-linolenic acid (18:3), stearidonic acid (18:4), eicosatrienoic acid (20:3), eicosatetraenoic acid (20:4), eicosapentaenoic acid (20:5), heneicosapentaenoic acid (21:5), docosapentaenoic acid (22:5), docosahexaenoic acid (22:6), tetracosapentaenoic acid (24:5), tetracosahexaenoic acid (24:6), linoleic acid (18:2), gamma-linoleic acid (18:3), eicosadienoic acid (20:2), dihomo-gamma-linolenic acid (20:3), arachidonic acid (20:4), docosadienoic acid (20:2), adrenic acid (22:4), docosapentaenoic acid (22:5), tetracosatetraenoic acid (22:4), tetracosapentaenoic acid (24:5), pinolenic acid (18:3), podocarpic acid (20:3), rumenic acid (18:2), alpha-calendic acid (18:3), beta-calendic acid (18:3), jacaric acid (18:3), alpha-eleostearic acid (18:3), beta-eleostearic (18:3), catalpic acid (18:3), punicic acid (18:3), rumelenic acid (18:3), alpha-parinaric acid (18:4), beta-parinaric acid (18:4), and bosseopentaenoic acid (20:5).

[047] The process for preparing the estolide compounds described herein may include the use of any natural or synthetic fatty acid source. However, it may be desirable to source the fatty acids from a renewable biological feedstock. Suitable starting materials of biological origin may include plant fats, plant oils, plant waxes, animal fats, animal oils, animal waxes, fish fats, fish oils, fish waxes, algal oils and mixtures thereof. Other potential fatty acid sources may include waste and recycled food-grade fats and oils, fats, oils, and waxes obtained by genetic engineering, fossil fuel-based materials and other sources of the materials desired.

[048] In some embodiments, the estolide comprises fatty-acid chains of varying lengths. In some embodiments, x is, independently for each occurrence, an integer selected from 0 to 20, 0 to 18, 0 to 16, 0 to 14, 1 to 12, 1 to 10, 2 to 8, 6 to 8, or 4 to 6. In some embodiments, x is, independently for each occurrence, an integer selected from 7 and 8. In some embodiments, x is, independently for each occurrence, an integer selected from 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, and 20.

[049] In some embodiments, y is, independently for each occurrence, an integer selected from 0 to 20, 0 to 18, 0 to 16, 0 to 14, 1 to 12, 1 to 10, 2 to 8, 6 to 8, or 4 to 6. In some embodiments, y is, independently for each occurrence, an integer selected from 7 and 8. In some embodiments, y is, independently for each occurrence, an integer selected from 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, and 20.

[050] In some embodiments, x+y is, independently for each chain, an integer selected from 0 to 40, 0 to 20, 10 to 20, or 12 to 18. In some embodiments, x+y is, independently for each chain, an integer selected from 13 to 15. In some embodiments, x+y is 15. In some embodiments, x+y is, independently for each chain, an integer selected from 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, and 24.

[051] In some embodiments, the estolide compound of Formula I, II, or III may comprise any number of fatty acid residues to form an "*n*-mer" estolide. For example, the estolide may be in its dimer (n=0), trimer (n=1), tetramer (n=2), pentamer (n=3), hexamer (n=4), heptamer (n=5), octamer (n=6), nonamer (n=7), or decamer (n=8) form. In some embodiments, n is an integer selected from 0 to 20, 0 to 18, 0 to 16, 0 to 14, 0 to 12, 0 to 10, 0 to 8, or 0 to 6. In some embodiments, n is an integer selected from 0 to 4. In some embodiments, n is 1, wherein said at least one compound of Formula I, II, or III comprises the trimer. In some embodiments, n is greater than 1. In some embodiments, n is an integer selected from 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, and 20.

[052] In some embodiments, R_1 of Formula I, II, or III is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched. In some embodiments, the alkyl group is a C_1 to C_{40} alkyl, C_1 to C_{22} alkyl or C_1 to C_{18} alkyl. In some embodiments, the alkyl group is selected from C_7 to C_{17} alkyl. In some embodiments, R_1 is selected from C_7 alkyl, C_9 alkyl, C_{11} alkyl, C_{13} alkyl, C_{15} alkyl, and C_{17} alkyl. In some embodiments, R_1 is selected from C_{13} to C_{17} alkyl, such as from C_{13} alkyl, C_{15} alkyl, and C_{17} alkyl. In some embodiments, R_1 is a C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9, C_{10}, C_{11}, C_{12}, C_{13}, C_{14}, C_{15}, C_{16}, C_{17}, C_{18}, C_{19}, C_{20}, C_{21}, or C_{22} alkyl.

[053] In some embodiments, R_2 of Formula I, II, or III is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched. In some embodiments, the alkyl group is a C_1 to C_{40} alkyl, C_1 to C_{22} alkyl or C_1 to C_{18} alkyl. In some embodiments, the alkyl group is selected from C_7 to C_{17} alkyl. In some embodiments, R_2 is selected from C_7 alkyl, C_9 alkyl, C_{11} alkyl, C_{13} alkyl, C_{15} alkyl, and C_{17} alkyl. In some embodiments, R_2 is selected from C_{13} to C_{17} alkyl, such as from C_{13} alkyl, C_{15} alkyl, and C_{17} alkyl. In some embodiments, R_2 is a C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9, C_{10}, C_{11}, C_{12}, C_{13}, C_{14}, C_{15}, C_{16}, C_{17}, C_{18}, C_{19}, C_{20}, C_{21}, or C_{22} alkyl.

[054] In some embodiments, R_3 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched. In some embodiments, the alkyl group is a C_1 to C_{40} alkyl, C_1 to C_{22} alkyl or C_1 to C_{18} alkyl. In some embodiments, the alkyl group is selected from

C_7 to C_{17} alkyl. In some embodiments, R_3 is selected from C_7 alkyl, C_9 alkyl, C_{11} alkyl, C_{13} alkyl, C_{15} alkyl, and C_{17} alkyl. In some embodiments, R_3 is selected from C_{13} to C_{17} alkyl, such as from C_{13} alkyl, C_{15} alkyl, and C_{17} alkyl. In some embodiments, R_3 is a C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9, C_{10}, C_{11}, C_{12}, C_{13}, C_{14}, C_{15}, C_{16}, C_{17}, C_{18}, C_{19}, C_{20}, C_{21}, or C_{22} alkyl.

[055] In some embodiments, R_4 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched. In some embodiments, the alkyl group is a C_1 to C_{40} alkyl, C_1 to C_{22} alkyl or C_1 to C_{18} alkyl. In some embodiments, the alkyl group is selected from C_7 to C_{17} alkyl. In some embodiments, R_4 is selected from C_7 alkyl, C_9 alkyl, C_{11} alkyl, C_{13} alkyl, C_{15} alkyl, and C_{17} alkyl. In some embodiments, R_4 is selected from C_{13} to C_{17} alkyl, such as from C_{13} alkyl, C_{15} alkyl, and C_{17} alkyl. In some embodiments, R_4 is a C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9, C_{10}, C_{11}, C_{12}, C_{13}, C_{14}, C_{15}, C_{16}, C_{17}, C_{18}, C_{19}, C_{20}, C_{21}, or C_{22} alkyl.

[056] As noted above, in certain embodiments, it may be possible to manipulate one or more of the estolides' properties by altering the length of R_1 and/or its degree of saturation. However, in certain embodiments, the level of substitution on R_1 may also be altered to change or even improve the estolides' properties. Without being bound to any particular theory, in certain embodiments, it is believed that the presence of polar substituents on R_1, such as one or more hydroxy groups, may increase the viscosity of the estolide, while increasing pour point. Accordingly, in some embodiments, R_1 will be unsubstituted or optionally substituted with a group that is not hydroxyl.

[057] In some embodiments, the estolide is in its free-acid form, wherein R_2 of Formula I, II, or III is hydrogen. In some embodiments, R_2 is selected from optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched. In certain embodiments, the R_2 residue may comprise any desired alkyl group, such as those derived from esterification of the estolide with the alcohols identified in the examples herein. In some embodiments, the alkyl group is selected from C_1 to C_{40}, C_1 to C_{22}, C_3 to C_{20}, C_1 to C_{18}, or C_6 to C_{12} alkyl. In some embodiments, R_2 may be selected from C_3 alkyl, C_4 alkyl, C_8 alkyl, C_{12} alkyl, C_{16} alkyl, C_{18} alkyl, and C_{20} alkyl. For example, in certain embodiments, R_2 may be branched, such as isopropyl, isobutyl, or 2-ethylhexyl. In some embodiments, R_2 may be a larger alkyl group, branched or unbranched, comprising C_{12} alkyl, C_{16} alkyl, C_{18} alkyl, or C_{20} alkyl. Such groups at the R_2 position may be derived from esterification of the free-acid estolide using the Jarcol™ line of alcohols marketed by Jarchem Industries, Inc. of Newark, New Jersey, including Jarcol™ I-18CG, I-20, I-12, I-16, I-18T, and 85BJ. In some cases, R_2 may be sourced from certain alcohols to provide branched

alkyls such as isostearyl and isopalmityl. It should be understood that such isopalmityl and isostearyl akyl groups may cover any branched variation of C_{16} and C_{18}, respectively. For example, the estolides described herein may comprise highly-branched isopalmityl or isostearyl groups at the R_2 position, derived from the Fineoxocol® line of isopalmityl and isostearyl alcohols marketed by Nissan Chemical America Corporation of Houston, Texas, including Fineoxocol® 180, 180N, and 1600. Without being bound to any particular theory, in embodiments, large, highly-branched alkyl groups (e.g., isopalmityl and isostearyl) at the R_2 position of the estolides canprovide at least one way to increase the lubricant's viscosity, while substantially retaining or even reducing its pour point.

[058] In some embodiments, the compounds described herein may comprise a mixture of two or more estolide compounds of Formula I, II, and III. It is possible to characterize the chemical makeup of an estolide, a mixture of estolides, or a composition comprising estolides, by using the compound's, mixture's, or composition's measured estolide number (EN) of compound or composition. The EN represents the average number of fatty acids added to the base fatty acid. The EN also represents the average number of estolide linkages per molecule:

$$EN = n+1$$

wherein n is the number of secondary (β) fatty acids. Accordingly, a single estolide compound will have an EN that is a whole number, for example for dimers, trimers, and tetramers:

$$\text{dimer EN} = 1$$

$$\text{trimer EN} = 2$$

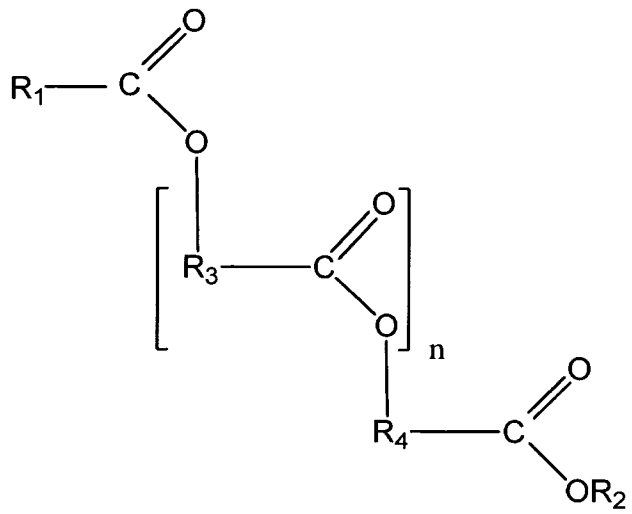
$$\text{tetramer EN} = 3$$

[059] However, a composition comprising two or more estolide compounds may have an EN that is a whole number or a fraction of a whole number. For example, a composition having a 1:1 molar ratio of dimer and trimer would have an EN of 1.5, while a composition having a 1:1 molar ratio of tetramer and trimer would have an EN of 2.5.

[060] In some embodiments, the compositions may comprise a mixture of two or more estolides having an EN that is an integer or fraction of an integer that is greater than 4.5, or even 5.0. In some embodiments, the EN may be an integer or fraction of an integer selected from about 1.0 to about 5.0. In some embodiments, the EN is an integer or fraction of an integer

selected from 1.2 to about 4.5. In some embodiments, the EN is selected from a value greater than 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, 3.6, 3.8, 4.0, 4.2, 4.4, 4.6, 4.8, 5.0, 5.2, 5.4, 5.6 and 5.8. In some embodiments, the EN is selected from a value less than 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, 3.6, 3.8, 4.0, 4.2, 4.4, 4.6, 4.8, and 5.0, 5.2, 5.4, 5.6, 5.8, and 6.0. In some embodiments, the EN is selected from 1, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, 3.6, 3.8, 4.0, 4.2, 4.4, 4.6, 4.8, 5.0, 5.2, 5.4, 5.6, 5.8, and 6.0.

[061] As noted above, it should be understood that the chains of the estolide compounds may be independently optionally substituted, wherein one or more hydrogens are removed and replaced with one or more of the substituents identified herein. Similarly, two or more of the hydrogen residues may be removed to provide one or more sites of unsaturation, such as a cis or trans double bond. Further, the chains may optionally comprise branched hydrocarbon residues. For example, in some embodiments the estolides described herein may comprise at least one compound of Formula II:



Formula II

wherein

n is an integer equal to or greater than 0;

R_1 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched

R_2 is selected from hydrogen and optionally substituted alkyl that is saturated or

unsaturated, and branched or unbranched; and

R_3 and R_4, independently for each occurrence, are selected from optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched.

[062] In some embodiments, n is an integer selected from 1 to 20. In some embodiments, n is an integer selected from 1 to 12. In some embodiments, n is an integer selected from 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 and 20. In some embodiments, one or more R_3 differs from one or more other R_3 in a compound of Formula II. In some embodiments, one or more R_3 differs from R_4 in a compound of Formula II. . In some embodiments, if the compounds of Formula II are prepared from one or more polyunsaturated fatty acids, it is possible that one or more of R_3 and R_4 will have one or more sites of unsaturation. In some embodiments, if the compounds of Formula II are prepared from one or more branched fatty acids, it is possible that one or more of R_3 and R_4 will be branched.

[063] In some embodiments, R_3 and R_4 can be $CH_3(CH_2)_yCH(CH_2)_x$-, where x is, independently for each occurrence, an integer selected from 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, and 20, and y is, independently for each occurrence, an integer selected from 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, and 20. Where both R_3 and R_4 are $CH_3(CH_2)_yCH(CH_2)_x$-, the compounds may be compounds according to Formula I and III.

[064] Without being bound to any particular theory, in certain embodiments, altering the EN produces estolides having desired viscometric properties while substantially retaining or even reducing pour point. For example, in some embodiments the estolides exhibit a decreased pour point upon increasing the EN value. Accordingly, in certain embodiments, a method is provided for retaining or decreasing the pour point of an estolide base oil by increasing the EN of the base oil, or a method is provided for retaining or decreasing the pour point of a composition comprising an estolide base oil by increasing the EN of the base oil. In some embodiments, the method comprises: selecting an estolide base oil having an initial EN and an initial pour point; and removing at least a portion of the base oil, said portion exhibiting an EN that is less than the initial EN of the base oil, wherein the resulting estolide base oil exhibits an EN that is greater than the initial EN of the base oil, and a pour point that is equal to or lower than the initial pour point of the base oil. In some embodiments, the selected estolide base oil is prepared by oligomerizing at least one first unsaturated fatty acid with at least one second unsaturated fatty acid and/or saturated fatty acid. In some embodiments, the removing at least a portion of the base

oil is accomplished by distillation, chromatography, membrane separation, phase separation, affinity separation, solvent extraction, or combinations thereof. In some embodiments, the distillation takes place at a temperature and/or pressure that is suitable to separate the estolide base oil into different "cuts" that individually exhibit different EN values. In some embodiments, this may be accomplished by subjecting the base oil temperature of at least about 250°C and an absolute pressure of no greater than about 25 microns. In some embodiments, the distillation takes place at a temperature range of about 250°C to about 310°C and an absolute pressure range of about 10 microns to about 25 microns.

[065] In some embodiments, estolide compounds and compositions exhibit an EN that is greater than or equal to 1, such as an integer or fraction of an integer selected from about 1.0 to about 2.0. In some embodiments, the EN is an integer or fraction of an integer selected from about 1.0 to about 1.6. In some embodiments, the EN is a fraction of an integer selected from about 1.1 to about 1.5. In some embodiments, the EN is selected from a value greater than 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, and 1.9. In some embodiments, the EN is selected from a value less than 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, and 2.0.

[066] In some embodiments, the EN is greater than or equal to 1.5, such as an integer or fraction of an integer selected from about 1.8 to about 2.8. In some embodiments, the EN is an integer or fraction of an integer selected from about 2.0 to about 2.6. In some embodiments, the EN is a fraction of an integer selected from about 2.1 to about 2.5. In some embodiments, the EN is selected from a value greater than 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, and 2.7. In some embodiments, the EN is selected from a value less than 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, and 2.8. In some embodiments, the EN is about 1.8, 2.0, 2.2, 2.4, 2.6, or 2.8.

[067] In some embodiments, the EN is greater than or equal to about 4, such as an integer or fraction of an integer selected from about 4.0 to about 5.0. In some embodiments, the EN is a fraction of an integer selected from about 4.2 to about 4.8. In some embodiments, the EN is a fraction of an integer selected from about 4.3 to about 4.7. In some embodiments, the EN is selected from a value greater than 4.0, 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, 4.8, and 4.9. In some embodiments, the EN is selected from a value less than 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, 4.8, 4.9, and 5.0. In some embodiments, the EN is about 4.0, 4.2, 4.4, 4.6, 4.8, or 5.0.

[068] In some embodiments, the EN is greater than or equal to about 5, such as an integer or fraction of an integer selected from about 5.0 to about 6.0. In some embodiments, the EN is a

fraction of an integer selected from about 5.2 to about 5.8. In some embodiments, the EN is a fraction of an integer selected from about 5.3 to about 5.7. In some embodiments, the EN is selected from a value greater than 5.0, 5.1, 5.2, 5.3, 5.4, 5.5, 5.6, 5.7, 5.8, and 5.9. In some embodiments, the EN is selected from a value less than 5.1, 5.2, 5.3, 5.4, 5.5, 5.6, 5.7, 5.8, 5.9, and 6.0. In some embodiments, the EN is about 5.0, 5.2, 5.4, 5.4, 5.6, 5.8, or 6.0.

[069] In some embodiments, the EN is greater than or equal to 1, such as an integer or fraction of an integer selected from about 1.0 to about 2.0. In some embodiments, the EN is a fraction of an integer selected from about 1.1 to about 1.7. In some embodiments, the EN is a fraction of an integer selected from about 1.1 to about 1.5. In some embodiments, the EN is selected from a value greater than 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, or 1.9. In some embodiments, the EN is selected from a value less than 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, or 2.0. In some embodiments, the EN is about 1.0, 1.2, 1.4, 1.6, 1.8, or 2.0.In some embodiments, the EN is greater than or equal to 1, such as an integer or fraction of an integer selected from about 1.2 to about 2.2. In some embodiments, the EN is an integer or fraction of an integer selected from about 1.4 to about 2.0. In some embodiments, the EN is a fraction of an integer selected from about 1.5 to about 1.9. In some embodiments, the EN is selected from a value greater than 1.0, 1.1. 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, and 2.1. In some embodiments, the EN is selected from a value less than 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, and 2.2. In some embodiments, the EN is about 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, or 2.2.

[070] In some embodiments, the EN is greater than or equal to 2, such as an integer or fraction of an integer selected from about 2.8 to about 3.8. In some embodiments, the EN is an integer or fraction of an integer selected from about 2.9 to about 3.5. In some embodiments, the EN is an integer or fraction of an integer selected from about 3.0 to about 3.4. In some embodiments, the EN is selected from a value greater than 2.0, 2.1, 2.2., 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1, 3.4, 3.5, 3.6, and 3.7. In some embodiments, the EN is selected from a value less than 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, and 3.8. In some embodiments, the EN is about 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, 3.6, or 3.8.Typically, base stocks and lubricant compositions exhibit certain lubricity, viscosity, and/or pour point characteristics. For example, in certain embodiments, suitable viscosity characteristics of the base oil may range from about 10 cSt to about 250 cSt at 40 °C, and/or about 3 cSt to about 30 cSt at 100 °C. In some embodiments, the compounds and compositionsmay exhibit viscosities

within a range from about 50 cSt to about 150 cSt at 40 °C, and/or about 10 cSt to about 20 cSt at 100 °C.

[071] In some embodiments, the estolide compounds and compositions may exhibit viscosities less than about 55 cSt at 40 °C or less than about 45 cSt at 40 °C, and/or less than about 12 cSt at 100 °C or less than about 10 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may exhibit viscosities within a range from about 25 cSt to about 55 cSt at 40 °C, and/or about 5 cSt to about 11 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may exhibit viscosities within a range from about 35 cSt to about 45 cSt at 40 °C, and/or about 6 cSt to about 10 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may exhibit viscosities within a range from about 38 cSt to about 43 cSt at 40 °C, and/or about 7 cSt to about 9 cSt at 100 °C.

[072] In some embodiments, the estolide compounds and compositions may exhibit viscosities less than about 120 cSt at 40 °C or less than about 100 cSt at 40 °C, and/or less than about 18 cSt at 100 °C or less than about 17 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may exhibit a viscosity within a range from about 70 cSt to about 120 cSt at 40 °C, and/or about 12 cSt to about 18 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may exhibit viscosities within a range from about 80 cSt to about 100 cSt at 40 °C, and/or about 13 cSt to about 17 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may exhibit viscosities within a range from about 85 cSt to about 95 cSt at 40 °C, and/or about 14 cSt to about 16 cSt at 100 °C.

[073] In some embodiments, the estolide compounds and compositions may exhibit viscosities greater than about 180 cSt at 40 °C or greater than about 200 cSt at 40 °C, and/or greater than about 20 cSt at 100 °C or greater than about 25 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may exhibit a viscosity within a range from about 180 cSt to about 230 cSt at 40 °C, and/or about 25 cSt to about 31 cSt at 100 °C. In some embodiments, estolide compounds and compositions may exhibit viscosities within a range from about 200 cSt to about 250 cSt at 40 °C, and/or about 25 cSt to about 35 cSt at 100 °C. In some embodiments, estolide compounds and compositions may exhibit viscosities within a range from about 210 cSt to about 230 cSt at 40 °C, and/or about 28 cSt to about 33 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may exhibit viscosities within a range from about 200 cSt to about 220 cSt at 40 °C, and/or about 26 cSt to about 30 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may exhibit viscosities

within a range from about 205 cSt to about 215 cSt at 40 °C, and/or about 27 cSt to about 29 cSt at 100 °C.

[074] In some embodiments, the estolide compounds and compositions may exhibit viscosities less than about 45 cSt at 40 °C or less than about 38 cSt at 40 °C, and/or less than about 10 cSt at 100 °C or less than about 9 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may exhibit a viscosity within a range from about 20 cSt to about 45 cSt at 40 °C, and/or about 4 cSt to about 10 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may exhibit viscosities within a range from about 28 cSt to about 38 cSt at 40 °C, and/or about 5 cSt to about 9 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may exhibit viscosities within a range from about 30 cSt to about 35 cSt at 40 °C, and/or about 6 cSt to about 8 cSt at 100 °C.

[075] In some embodiments, the estolide compounds and compositions may exhibit viscosities less than about 80 cSt at 40 °C or less than about 70 cSt at 40 °C, and/or less than about 14 cSt at 100 °C or less than about 13 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may exhibit a viscosity within a range from about 50 cSt to about 80 cSt at 40 °C, and/or about 8 cSt to about 14 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may exhibit viscosities within a range from about 60 cSt to about 70 cSt at 40 °C, and/or about 9 cSt to about 13 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may exhibit viscosities within a range from about 63 cSt to about 68 cSt at 40 °C, and/or about 10 cSt to about 12 cSt at 100 °C.

[076] In some embodiments, the estolide compounds and compositions may exhibit viscosities greater than about 120 cSt at 40 °C or greater than about 130 cSt at 40 °C, and/or greater than about 15 cSt at 100 °C or greater than about 18 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may exhibit a viscosity within a range from about 120 cSt to about 150 cSt at 40 °C, and/or about 16 cSt to about 24 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may exhibit viscosities within a range from about 130 cSt to about 160 cSt at 40 °C, and/or about 17 cSt to about 28 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may exhibit viscosities within a range from about 130 cSt to about 145 cSt at 40 °C, and/or about 17 cSt to about 23 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may exhibit viscosities within a range from about 135 cSt to about 140 cSt at 40 °C, and/or about 19 cSt to about 21 cSt at 100 °C. In some embodiments, the estolide compounds and compositions may

exhibit viscosities of about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230, 240, 250, 260, 270, 280, 290, 300, 350, or 400 cSt. at 40 °C. In some embodiments, the estolide compounds and compositions may exhibit viscosities of about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, and 30 cSt at 100 °C. In certain embodiments, estolides may exhibit desirable low-temperature pour point properties. In some embodiments, the estolide compounds and compositions may exhibit a pour point lower than about -25 °C, about -35 °C, -40 °C, or even about -50 °C. In some embodiments, the estolide compounds and compositions have a pour point of about -25 °C to about -45 °C. In some embodiments, the pour point falls within a range of about -30 °C to about -40 °C, about -34 °C to about -38 °C, about -30 °C to about -45 °C, -35 °C to about -45 °C, 34 °C to about -42 °C, about -38 °C to about -42 °C, or about 36 °C to about -40 °C. In some embodiments, the pour point falls within the range of about -27 °C to about -37 °C, or about -30 °C to about -34 °C. In some embodiments, the pour point falls within the range of about -25 °C to about -35 °C, or about -28 °C to about -32 °C. In some embodiments, the pour point falls within the range of about -28 °C to about -38 °C, or about -31 °C to about -35 °C. In some embodiments, the pour point falls within the range of about -31 °C to about -41 °C, or about -34 °C to about -38 °C. In some embodiments, the pour point falls within the range of about -40 °C to about -50 °C, or about -42 °C to about -48 °C. In some embodiments, the pour point falls within the range of about -50 °C to about -60 °C, or about -52 °C to about -58 °C. In some embodiments, the upper bound of the pour point is less than about - 35 °C, about -36 °C, about -37 °C, about -38 °C, about -39 °C, about -40 °C, about -41 °C, about -42 °C, about -43 °C, about -44 °C, or about -45 °C. In some embodiments, the lower bound of the pour point is greater than about -70 °C, about -69 °C, about -68 °C, about -67 °C, about -66 °C, about -65 °C, about -64 °C, about -63 °C, about -62 °C, about -61 °C, about -60 °C, about -59 °C, about -58 °C, about -57 °C, about -56 °C, -55 °C, about -54 °C, about -53 °C, about -52 °C, -51, about -50 °C, about -49 °C, about -48 °C, about -47 °C, about -46 °C, or about -45 °C.

[077] In addition, in certain embodiments, the estolides may exhibit decreased Iodine Values (IV) when compared to estolides prepared by other methods. IV is a measure of the degree of total unsaturation of an oil, and is determined by measuring the amount of iodine per gram of estolide (cg/g). In certain instances, oils having a higher degree of unsaturation may be more susceptible to creating corrosiveness and deposits, and may exhibit lower levels of

oxidative stability. Compounds having a higher degree of unsaturation will have more points of unsaturation for iodine to react with, resulting in a higher IV. Thus, in certain embodiments, it may be desirable to reduce the IV of estolides in an effort to increase the oil's oxidative stability, while also decreasing harmful deposits and the corrosiveness of the oil.

[078] In some embodiments, estolide compounds and compositions described herein have an IV of less than about 40 cg/g or less than about 35 cg/g. In some embodiments, estolides have an IV of less than about 30 cg/g, less than about 25 cg/g, less than about 20 cg/g, less than about 15 cg/g, less than about 10 cg/g, or less than about 5 cg/g. The IV of a composition may be reduced by decreasing the estolide's degree of unsaturation. This may be accomplished by , for example, by increasing the amount of saturated capping materials relative to unsaturated capping materials when synthesizing the estolides. Alternatively, in certain embodiments, IV may be reduced by hydrogenating estolides having unsaturated caps.

[079] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{17} alkyl; n is 1; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[080] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{17} alkyl; n is 2; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[081] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{17} alkyl; n is 3; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[082] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{17} alkyl; n is 4; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[083] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{17} alkyl; n

is 5; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[084] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{17} alkyl; n is 6; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[085] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{17} alkyl; n is 7; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[086] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{17} alkyl; n is 8; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[087] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{21} alkyl; n is 1; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[088] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{21} alkyl; n is 2; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[089] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{21} alkyl; n is 3; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[090] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{21} alkyl; n

is 4; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[091] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{21} alkyl; n is 5; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[092] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{21} alkyl; n is 6; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[093] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{21} alkyl; n is 7; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[094] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{21} alkyl; n is 8; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[095] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{15} alkyl; n is 1; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[096] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{15} alkyl; n is 2; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[097] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{15} alkyl; n

is 3; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[098] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{15} alkyl; n is 4; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[099] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{15} alkyl; n is 5; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[0100] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{15} alkyl; n is 6; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[0101] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{15} alkyl; n is 7; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[0102] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{15} alkyl; n is 8; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[0103] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{19} alkyl; n is 1; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[0104] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{19} alkyl; n

is 2; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[0105] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{19} alkyl; n is 3; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[0106] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{19} alkyl; n is 4; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[0107] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{19} alkyl; n is 5; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[0108] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{19} alkyl; n is 6; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[0109] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{19} alkyl; n is 7; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

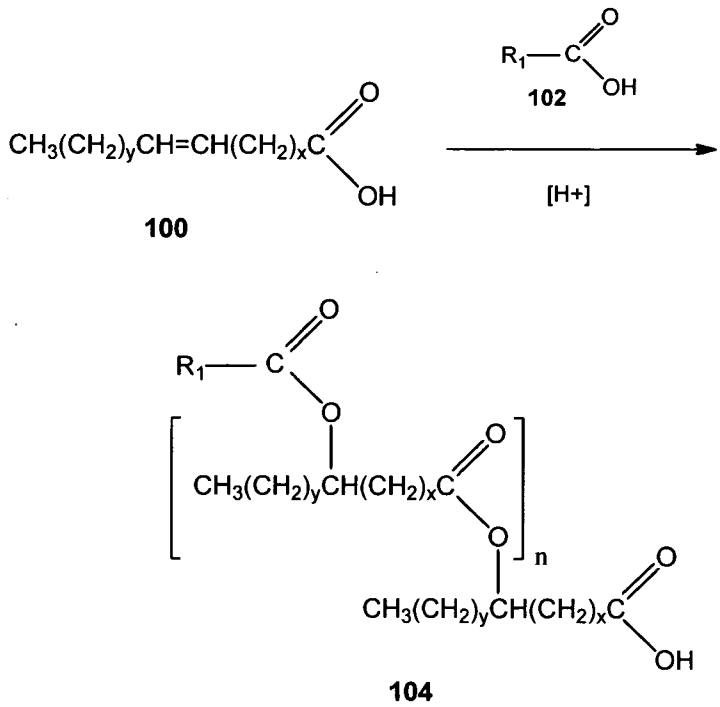
[0110] In some embodiments, estolides comprise at least one compound of Formula II, wherein: one or more of R_1, R_3 and R_4 are selected from a saturated and unbranched C_{19} alkyl; n is 8; and R_2 is an optionally substituted C_1-C_{40} alkyl that is saturated or unsaturated and branched or unbranched.

[0111] The present disclosure further relates to methods of making estolides according to Formula I, II, and III. By way of example, the reaction of an unsaturated fatty acid with an organic acid and the esterification of the resulting free acid estolide are illustrated and discussed

in the following Schemes 1 and 2. The particular structural formulas used to illustrate the reactions correspond to those for synthesis of compounds according to Formula I and III; however, the methods apply equally to the synthesis of compounds according to Formula II, with use of compounds having structure corresponding to R_3 and R_4 with a reactive site of unsaturation.

[0112] As illustrated below, compound **100** represents an unsaturated fatty acid that may serve as the basis for preparing the estolide compounds described herein.

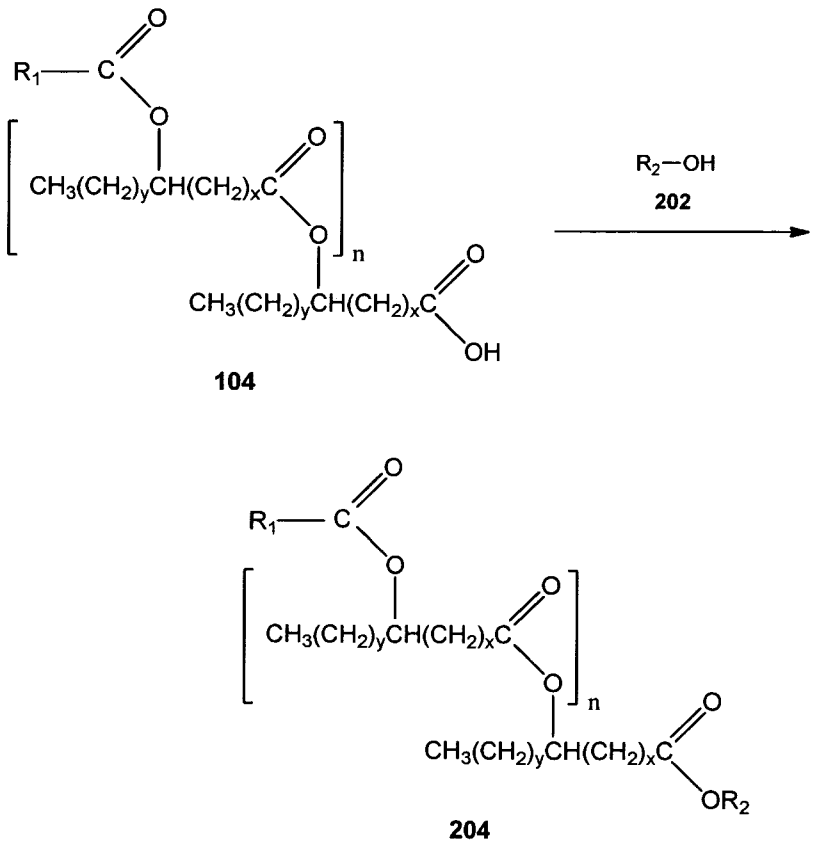
Scheme 1



[0113] In Scheme 1, wherein x is, independently for each occurrence, an integer selected from 0 to 20, y is, independently for each occurrence, an integer selected from 0 to 20, n is an integer greater than or equal to 1, and R_1 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched, unsaturated fatty acid 100 may be combined with compound 102 and a proton from a proton source to form free acid estolide 104. In certain embodiments, compound 102 is not included, and unsaturated fatty acid 100 may be exposed alone to acidic conditions to form free acid estolide 104, wherein R_1 would represent an unsaturated alkyl group. In certain embodiments, if compound 102 is included in the reaction, R_1 may represent one or more optionally substituted alkyl residues that are saturated or

unsaturated and branched or unbranched. Any suitable proton source may be implemented to catalyze the formation of free acid estolide 104, including but not limited to homogenous acids and/or strong acids like hydrochloric acid, sulfuric acid, perchloric acid, nitric acid, triflic acid, and the like.

Scheme 2



[0114] Similarly, in Scheme 2, wherein x is, independently for each occurrence, an integer selected from 0 to 20, y is, independently for each occurrence, an integer selected from 0 to 20, n is an integer greater than or equal to 1, and R_1 and R2 are each an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched, free acid estolide 104 may be esterified by any suitable procedure known to those of skilled in the art, such as acid-catalyzed reduction with alcohol 202, to yield esterified estolide 204. Other exemplary methods may include other types of Fischer esterification, such as those using Lewis acid catalysts such as BF_3.

[0115] As discussed above, in certain embodiments, the estolides described herein may have improved properties which render them useful as base stocks for biodegradable lubricant

applications. Such applications may include, without limitation, crankcase oils, gearbox oils, hydraulic fluids, drilling fluids, two-cycle engine oils, greases, and the like. Other suitable uses may include marine applications, where biodegradability and toxicity are of concern. In certain embodiments, the nontoxic nature of certain estolides described herein may also make them suitable for use as lubricants in the cosmetic and food industries.

[0116] In certain embodiments, the estolide compounds may meet or exceed one or more of the specifications for certain end-use applications, without the need for conventional additives. For example, in certain instances, high-viscosity lubricants, such as those exhibiting a kinematic viscosity of greater than about 120 cSt at 40 °C, or even greater than about 200 cSt at 40 °C, may be desired for particular applications such as gearbox or wind turbine lubricants. Prior-known lubricants with such properties typically also demonstrate an increase in pour point as viscosity increases, such that prior lubricants may not be suitable for such applications in colder environments. However, in certain embodiments, the counterintuitive properties of certain compounds described herein (e.g., increased EN provides estolides with higher viscosities while retaining, or even decreasing, the oil's pour point) may make higher-viscosity estolides particularly suitable for such specialized applications.

[0117] Similarly, the use of prior-known lubricants in colder environments may generally result in an unwanted increase in a lubricant's viscosity. Thus, depending on the application, it may be desirable to use lower-viscosity oils at lower temperatures. In certain circumstances, low-viscosity oils may include those exhibiting a viscosity of lower than about 50 cSt at 40 °C, or even about 40 cSt at 40 °C. Accordingly, in certain embodiments, the low-viscosity estolides described herein may provide end users with a suitable alternative to high-viscosity lubricants for operation at lower temperatures.

[0118] In some embodiments, it may be desirable to prepare lubricant compositions comprising an estolide base stock. For example, in certain embodiments, the estolides described herein may be blended with one or more additives selected from polyalphaolefins, synthetic esters, polyalkylene glycols, mineral oils (Groups I, II, and III), pour point depressants, viscosity modifiers, anti-corrosives, antiwear agents, detergents, dispersants, colorants, antifoaming agents, and demulsifiers. In addition, or in the alternative, in certain embodiments, the estolides described herein may be co-blended with one or more synthetic or petroleum-based oils to achieve desired viscosity and/or pour point profiles. In certain embodiments, certain estolides

described herein also mix well with gasoline, so that they may be useful as fuel components or additives.

[0119] In all of the foregoing examples, the compounds described may be useful alone, as mixtures, or in combination with other compounds, compositions, and/or materials.

[0120] Methods for obtaining the novel compounds described herein will be apparent to those of ordinary skill in the art, suitable procedures being described, for example, in the examples below, and in the references cited herein.

EXAMPLES

Analytics

[0121] **Nuclear Magnetic Resonance:** NMR spectra were collected using a Bruker Avance 500 spectrometer with an absolute frequency of 500.113 MHz at 300 K using $CDCl_3$ as the solvent. Chemical shifts were reported as parts per million from tetramethylsilane. The formation of a secondary ester link between fatty acids, indicating the formation of estolide, was verified with ^1H NMR by a peak at about 4.84 ppm.

[0122] **Estolide Number (EN):** The EN was measured by GC analysis. It should be understood that the EN of a composition specifically refers to EN characteristics of any estolide compounds present in the composition. Accordingly, an estolide composition having a particular EN may also comprise other components, such as natural or synthetic additives, other non-estolide base oils, fatty acid esters, e.g., triglycerides, and/or fatty acids, but the EN as used herein, unless otherwise indicated, refers to the value for the estolide fraction of the estolide composition.

[0123] **Iodine Value (IV):** The iodine value is a measure of the degree of total unsaturation of an oil. IV is expressed in terms of centigrams of iodine absorbed per gram of oil sample. Therefore, the higher the iodine value of an oil the higher the level of unsaturation is of that oil. The IV may be measured and/or estimated by GC analysis. Where a composition includes unsaturated compounds other than estolides as set forth in Formula I, II, and III, the estolides can be separated from other unsaturated compounds present in the composition prior to measuring the iodine value of the constituent estolides. For example, if a composition includes unsaturated fatty

acids or triglycerides comprising unsaturated fatty acids, these can be separated from the estolides present in the composition prior to measuring the iodine value for the one or more estolides.

[0124] **Acid Value:** The acid value is a measure of the total acid present in an oil. Acid value may be determined by any suitable titration method known to those of ordinary skill in the art. For example, acid values may be determined by the amount of KOH that is required to neutralize a given sample of oil, and thus may be expressed in terms of mg KOH/g of oil.

[0125] **Gas Chromatography (GC):** GC analysis was performed to evaluate the estolide number (EN) and iodine value (IV) of the estolides. This analysis was performed using an Agilent 6890N series gas chromatograph equipped with a flame-ionization detector and an autosampler/injector along with an SP-2380 30 m x 0.25 mm i.d. column.

[0126] The parameters of the analysis were as follows: column flow at 1.0 mL/min with a helium head pressure of 14.99 psi; split ratio of 50:1; programmed ramp of 120-135°C at 20°C/min, 135-265°C at 7°C/min, hold for 5 min at 265°C; injector and detector temperatures set at 250°C.

[0127] **Measuring EN and IV by GC:** To perform these analyses, the fatty acid components of an estolide sample were reacted with MeOH to form fatty acid methyl esters by a method that left behind a hydroxy group at sites where estolide links were once present. Standards of fatty acid methyl esters were first analyzed to establish elution times.

[0128] *Sample Preparation:* To prepare the samples, 10 mg of estolide was combined with 0.5 mL of 0.5M KOH/MeOH in a vial and heated at 100°C for 1 hour. This was followed by the addition of 1.5 mL of 1.0 M H_2SO_4/MeOH and heated at 100°C for 15 minutes and then allowed to cool to room temperature. One (1) mL of H_2O and 1mL of hexane were then added to the vial and the resulting liquid phases were mixed thoroughly. The layers were then allowed to phase separate for 1 minute. The bottom H_2O layer was removed and discarded. A small amount of drying agent (Na_2SO_4 anhydrous) was then added to the organic layer after which the organic layer was then transferred to a 2 mL crimp cap vial and analyzed.

[0129] *EN Calculation*: The EN is measured as the percent hydroxy fatty acids divided by the percent non-hydroxy fatty acids. As an example, a dimer estolide would result in half of the fatty acids containing a hydroxy functional group, with the other half lacking a hydroxyl

functional group. Therefore, the EN would be 50% hydroxy fatty acids divided by 50% non-hydroxy fatty acids, resulting in an EN value of 1 that corresponds to the single estolide link between the capping fatty acid and base fatty acid of the dimer.

[0130] *IV Calculation*: The iodine value is estimated by the following equation based on ASTM Method D97 (ASTM International, Conshohocken, PA):

$$IV = \sum 100 \times \frac{A_f \times MW_I \times db}{MW_f}$$

A_f = fraction of fatty compound in the sample

MW_I = 253.81, atomic weight of two iodine atoms added to a double bond

db = number of double bonds on the fatty compound

MW_f = molecular weight of the fatty compound

[0131] The properties of exemplary estolide compounds and compositions described herein are identified in the following examples and tables.

[0132] *Other Measurements:* Except as otherwise described, pour point is measured by ASTM Method D97-96a, cloud point is measured by ASTM Method D2500, viscosity/kinematic viscosity is measured by ASTM Method D445-97, viscosity index is measured by ASTM Method D2270-93 (Reapproved 1998), specific gravity is measured by ASTM Method D4052, flash point is measured by ASTM Method D92, evaporative loss is measured by ASTM Method D5800, vapor pressure is measured by ASTM Method D5191, and acute aqueous toxicity is measured by Organization of Economic Cooperation and Development (OECD) 203.

Example 1

[0133] The acid catalyst reaction was conducted in a 50 gallon Pfaudler RT-Series glass-lined reactor. Oleic acid (65Kg, OL 700, Twin Rivers) was added to the reactor with 70% perchloric acid (992.3 mL, Aldrich Cat# 244252) and heated to 60°C *in vacuo* (10 torr abs) for 24 hrs while continuously being agitated. After 24 hours the vacuum was released. 2-Ethylhexanol (29.97 Kg) was then added to the reactor and the vacuum was restored. The reaction was allowed to continue under the same conditions (60°C, 10 torr abs) for 4 more hours. At which time, KOH

(645.58 g) was dissolved in 90% ethanol/water (5000 mL, 90% EtOH by volume) and added to the reactor to quench the acid. The solution was then allowed to cool for approximately 30 minutes. The contents of the reactor were then pumped through a 1micron (μ) filter into an accumulator to filter out the salts. Water was then added to the accumulator to wash the oil. The two liquid phases were thoroughly mixed together for approximately 1 hour. The solution was then allowed to phase separate for approximately 30 minutes. The water layer was drained and disposed of. The organic layer was again pumped through a 1μ filter back into the reactor. The reactor was heated to 60°C *in vacuo* (10 torr abs) until all ethanol and water ceased to distill from solution. The reactor was then heated to 100°C *in vacuo* (10 torr abs) and that temperature was maintained until the 2-ethylhexanol ceased to distill from solution. The remaining material was then distilled using a Myers 15 Centrifugal Distillation still at 200°C under an absolute pressure of approximately 12 microns (0.012 torr) to remove all monoester material leaving behind estolides (Ex. 1). Certain data are reported below in Tables 1 and 8.

Example 2

[0134] The acid catalyst reaction was conducted in a 50 gallon Pfaudler RT-Series glass-lined reactor. Oleic acid (50Kg, OL 700, Twin Rivers) and whole cut coconut fatty acid (18.754 Kg, TRC 110, Twin Rivers) were added to the reactor with 70% perchloric acid (1145 mL, Aldrich Cat# 244252) and heated to 60°C *in vacuo* (10 torr abs) for 24 hrs while continuously being agitated. After 24 hours the vacuum was released. 2-Ethylhexanol (34.58 Kg) was then added to the reactor and the vacuum was restored. The reaction was allowed to continue under the same conditions (60°C, 10 torr abs) for 4 more hours. At which time, KOH (744.9 g) was dissolved in 90% ethanol/water (5000 mL, 90% EtOH by volume) and added to the reactor to quench the acid. The solution was then allowed to cool for approximately 30 minutes. The contents of the reactor were then pumped through a 1μ filter into an accumulator to filter out the salts. Water was then added to the accumulator to wash the oil. The two liquid phases were thoroughly mixed together for approximately 1 hour. The solution was then allowed to phase separate for approximately 30 minutes. The water layer was drained and disposed of. The organic layer was again pumped through a 1μ filter back into the reactor. The reactor was heated to 60°C *in vacuo* (10 torr abs) until all ethanol and water ceased to distill from solution. The reactor was then heated to 100°C *in vacuo* (10 torr abs) and that temperature was maintained until the 2-ethylhexanol ceased to distill from solution. The remaining material was then distilled using a Myers 15 Centrifugal

Distillation still at 200°C under an absolute pressure of approximately 12 microns (0.012 torr) to remove all monoester material leaving behind estolides (Ex. 2). Certain data are reported below in Tables 2 and 7.

Example 3

[0135] The estolides produced in Example 1 (Ex. 1) were subjected to distillation conditions in a Myers 15 Centrifugal Distillation still at 300°C under an absolute pressure of approximately 12 microns (0.012 torr). This resulted in a primary distillate having a lower EN average (Ex. 3A), and a distillation residue having a higher EN average (Ex. 3B). Certain data are reported below in Tables 1 and 8.

Table 1

Estolide Base Stock	EN	Pour Point (°C)	Iodine Value (cg/g)
Ex. 3A	1.35	-32	31.5
Ex. 1	2.34	-40	22.4
Ex. 3B	4.43	-40	13.8

Example 4

[0136] Estolides produced in Example 2 (Ex. 2) were subjected to distillation conditions in a Myers 15 Centrifugal Distillation still at 300°C under an absolute pressure of approximately 12 microns (0.012 torr). This resulted in a primary distillate having a lower EN average (Ex. 4A), and a distillation residue having a higher EN average (Ex. 4B). Certain data are reported below in Tables 2 and 7.

Table 2

Estolide Base Stock	EN	Pour Point (°C)	Iodine Value (cg/g)
Ex. 4A	1.31	-30	13.8
Ex. 2	1.82	-33	13.2
Ex. 4B	3.22	-36	9.0

Example 5

[0137] Estolides produced by the method set forth in Example 1 were subjected to distillation conditions (ASTM D-6352) at 1 atm over the temperature range of about 0°C to about 710°C, resulting in 10 different estolide cuts recovered at increasing temperatures The amount of material distilled from the sample in each cut and the temperature at which each cut distilled (and recovered) are reported below in Table 3:

Table 3

Cut (% of total)	Temp. (°C)
1 (1%)	416.4
2 (1%)	418.1
3 (3%)	420.7
4 (20%)	536.4
5 (25%)	553.6
6 (25%)	618.6
7 (20%)	665.7
8 (3%)	687.6
9 (1%)	700.6
10 (1%)	709.1

Example 6

[0138] Estolides made according to the method of Example 2 were subjected to distillation conditions (ASTM D-6352) at 1 atm over the temperature range of about 0°C to about 730°C, which resulted in 10 different estolide cuts. The amount of each cut and the temperature at which each cut was recovered are reported in Table 4.

Table 4

Cut (% of total)	Temp. (°C)
1 (1%)	417.7
2 (1%)	420.2
3 (3%)	472.0
4 (5%)	509.7
5 (15%)	533.7
6 (25%)	583.4
7 (25%)	636.4
8 (5%)	655.4
9 (5%)	727.0
10 (15%)	>727.0

Example 7

[0139] Estolide base oil 4B (from Example 4) was subjected to distillation conditions (ASTM D-6352) at 1 atm over the temperature range of about 0°C to about 730°C, which resulted in 9 different estolide cuts. The amount of each cut and the temperature at which each cut was recovered are reported in Table 5a.

Table 5a

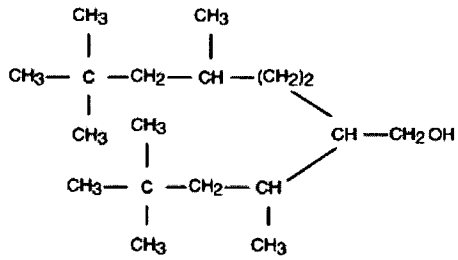
Cut (% of total)	Temp. (°C)
1 (1%)	432.3
2 (1%)	444.0
3 (3%)	469.6
4 (5%)	521.4
5 (15%)	585.4
6 (25%)	617.1
7 (25%)	675.1
8 (5%)	729.9
9 (20%)	>729.9

Example 8

[0140] Estolides were made according to the method set forth in Example 1, except that the 2-ethylhexanol esterifying alcohol used in Example 1 was replaced with various other alcohols.

Alcohols used for esterifictaion include those identified in Table 5b below. The properties of the resulting estolides are set forth in Table 9.

Table 5b

Alcohol	Structure
Jarcol™ I-18CG	iso-octadecanol
Jarcol™ I-12	2-butyloctanol
Jarcol™ I-20	2-octyldodecanol
Jarcol™ I-16	2-hexyldecanol
Jarcol™ 85BJ	cis-9-octadecen-1-ol
Fineoxocol® 180	
Jarcol™ I-18T	2-octyldecanol

Example 9

[0141] Estolides were made according to the method set forth in Example 2, except the 2-ethylhexanol esterifying alcohol was replaced with isobutanol. The properties of the resulting estolides are set forth in Table 9.

Example 10

[0142] Estolides of Formula I, II, and III are prepared according to the method set forth in Examples 1 and 2, except that the 2-ethylhexanol esterifying alcohol is replaced with various other alcohols. Alcohols to be used for esterifictaion include those identified in Table 6 below. Esterifying alcohols to be used, including those listed below, may be saturated or unsaturated, and branched or unbranched, or substituted with one or more alkyl groups selected from methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, neopentyl, hexyl,

isohexyl, and the like, to form a branched or unbranched residue at the R_2 position. Examples of combinations of esterifying alcohols and R_2 Substituents are set forth below in Table 6:

Table 6

Alcohol	R_2 Substituents
C_1 alkanol	methyl
C_2 alkanol	ethyl
C_3 alkanol	n-propyl, isopropyl
C_4 alkanol	n-butyl, isobutyl, sec-butyl
C_5 alkanol	n-pentyl, isopentyl neopentyl
C_6 alkanol	n-hexyl, 2-methyl pentyl, 3-methyl pentyl, 2,2-dimethyl butyl, 2,3-dimethyl butyl
C_7 alkanol	n-heptyl and other structural isomers
C_8 alkanol	n-octyl and other structural isomers
C_9 alkanol	n-nonyl and other structural isomers
C_{10} alkanol	n-decanyl and other structural isomers
C_{11} alkanol	n-undecanyl and other structural isomers
C_{12} alkanol	n-dodecanyl and other structural isomers
C_{13} alkanol	n-tridecanyl and other structural isomers
C_{14} alkanol	n-tetradecanyl and other structural isomers
C_{15} alkanol	n-pentadecanyl and other structural isomers
C_{16} alkanol	n-hexadecanyl and other structural isomers
C_{17} alkanol	n-heptadecanyl and other structural isomers
C_{18} alkanol	n-octadecanyl and other structural isomers
C_{19} alkanol	n-nonadecanyl and other structural isomers
C_{20} alkanol	n-icosanyl and other structural isomers
C_{21} alkanol	n-heneicosanyl and other structural isomers
C_{22} alkanol	n-docosanyl and other structural isomers

Table 7

PROPERTY	ADDITIVES	ASTM METHOD	Ex. 4A	Ex. 2	Ex. 4B
Color	None	-	Light Gold	Amber	Amber
Specific Gravity (15.5°C), g/ml	None	D 4052	n/a (<1)	0.9046	0.9140
Viscosity - Kinematic at 40°C, cSt	None	D 445	32.5	65.4	137.3
Viscosity - Kinematic at 100°C, cSt	None	D 445	6.8	11.3	19.9
Viscosity Index	None	D 2270	175	167	167
Pour Point, °C	None	D 97	-30	-33	-36
Cloud Point, °C	None	D 2500	-30	-32	-36
Flash Point, °C	None	D 92	n/a (>200)	n/a (>250)	n/a (>286)
Evaporative Loss (NOACK), wt. %	None	D 5800	n/a	1.4	0.32
Vapor Pressure - Reid (RVP), psi	None	D 5191	≈ 0	≈ 0	≈ 0

Table 8

PROPERTY	ADDITIVES	ASTM METHOD	Ex. 3A	Ex. 1	Ex. 3B
Color	None	-	Light Gold	Amber	Amber
Specific Gravity (15.5°C), g/ml	None	D 4052	n/a (<1)	0.906	n/a (<1)
Viscosity - Kinematic at 40°C, cSt	None	D 445	40.9	91.2	211.6
Viscosity - Kinematic at 100°C, cSt	None	D 445	8.0	14.8	27.8
Viscosity Index	None	D 2270	172	170	169
Pour Point, °C	None	D 97	-32	-40	-40
Cloud Point, °C	None	D 2500	-32	-33	-40
Flash Point, °C	None	D 92	n/a (>200)	286	n/a (>286)
Evaporative Loss (NOACK), wt. %	None	D 5800	n/a	0.8	n/a (<0.3)

Vapor Pressure - Reid (RVP), psi	None	D 5191	≈ 0	≈ 0	≈ 0

Table 9

Example #	Alcohol	Estimated EN (approx.)	Pour Pt. °C	Cloud Pt. °C	Visc. @ 40 °C	Visc. @ 100 °C	Visc. Index
8	Jarcol™ I-18CG	2.0 – 2.6	-15	-13	103.4	16.6	174
8	Jarcol™ I-12	2.0 – 2.6	-39	-40	110.9	16.9	166
8	Jarcol™ I-20	2.0 – 2.6	-42	< -42	125.2	18.5	166
8	Jarcol™ I-16	2.0 – 2.6	-51	< -51	79.7	13.2	168
8	Jarcol™ 85BJ	2.0 – 2.6	-15	-6	123.8	19.5	179
8	Fineoxocol® 180	2.0 – 2.6	-39	-41	174.2	21.1	143
8	Jarcol™ I-18T	2.0 – 2.6	-42	< -42	130.8	19.2	167
8	Isobutanol	2.0 – 2.6	-36	-36	74.1	12.6	170
9	Isobutanol	1.5 – 2.2	-36	-36	59.5	10.6	170

Example 11

[0143] Saturated and unsaturated estolides having varying acid values were subjected to several corrosion and deposit tests. These tests included the High Temperature Corrosion Bench Test (HTCBT) for several metals, the ASTM D130 corrosion test, and the MHT-4 TEOST (ASTM D7097) test for correlating piston deposits. The estolides tested having higher acid values (0.67 mg KOH/g) were produced using the method set forth in Examples 1 and 4 for producing Ex. 1 and Ex. 4A (Ex.1* and Ex.4A* below). The estolides tested having lower acid values (0.08 mg KOH/g) were produced using the method set forth in Examples 1 and 4 for producing Ex. 1 and Ex. 4A except the crude free-acid estolide was worked up and purified prior to esterification with $BF_3 \cdot OET_2$ (0.15 equiv.; reacted with estolide and 2-EH in Dean Stark trap at 80°C *in vacuo* (10 torr abs) for 12 hrs while continuously being agitated; crude reaction product washed 4x H_20; excess 2-EH removed by heating washed reaction product to 140°C *in vacuo* (10 torr abs) for 1 hr) (Ex.4A# below). Estolides having an IV of 0 were hydrogenated via

10 wt. % palladium embedded on carbon at 75°C for 3 hours under a pressurized hydrogen atmosphere (200 psig) (Ex.4A*H and Ex.4A#H below) The corrosion and deposit tests were performed with a Dexos™ additive package. Results were compared against a mineral oil standard:

Table 10

	Standard	Ex. 1* Estolide	Ex. 4A* Estolide	Ex. 4A*H Estolide	Ex. 4A# Estolide	Ex. 4A#H Estolide
Acid Value (mg KOH/g)	-	~0.7	0.67	0.67	0.08	0.08
Iodine Value (IV)	-	~45	16	0	16	0
HTCBT Cu	13	739	279	60	9.3	13.6
HTCBT Pd	177	11,639	1,115	804	493	243
HTCBT Sn	0	0	0	0	0	0
ASTM D130	1A	4B	3A	1B	1A	1A
MHT-4	18	61	70	48	12	9.3

Example 12

[0144] "Ready" and "ultimate" biodegradability of the estolide produced in Ex. 1 was tested according to standard OECD procedures. Results of the OECD biodegradability studies are set forth below in Table 11:

Table 11

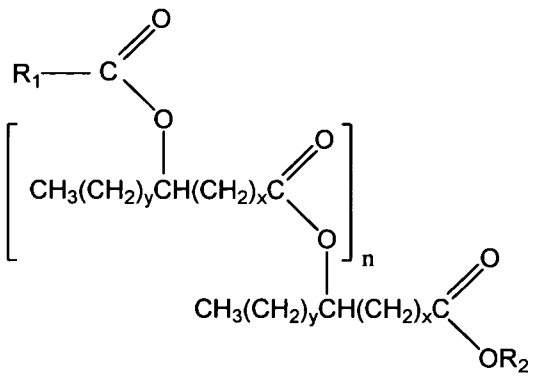
	301D 28-Day (% degraded)	302D Assay (% degraded)
Canola Oil	86.9	78.9
Ex. 1 Base Stock	64.0	70.9

Example 13

[0145] The Ex. 1 estolide base stock from Example 1 was tested under OECD 203 for Acute Aquatic Toxicity. The tests showed that the estolides are nontoxic, as no deaths were reported for concentration ranges of 5,000 mg/L and 50,000 mg/L.

Additional Embodiments

[0146] 1. A composition comprising at least one estolide compound, said composition having an EN selected from an integer or fraction of an integer that is equal to or greater than 4, wherein the EN is the average number of estolide linkages in compounds according to Formula I, a kinematic viscosity equal to or greater than 200 cSt when measured at 40 °C, and a pour point equal to or lower than -40 °C, wherein said at least one estolide compound is a compound of Formula I:



Formula I

wherein

x is, independently for each occurrence, an integer selected from 0 to 20;

y is, independently for each occurrence, an integer selected from 0 to 20;

n is an integer selected from 0 to 12;

R_1 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched; and

R_2 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched,

wherein each fatty acid chain residue of said at least one compound is independently optionally substituted.

[0147] 2. The composition according to claim 1, wherein

x is, independently for each occurrence, an integer selected from 1 to 10;

y is, independently for each occurrence, an integer selected from 1 to 10;

n is an integer selected from 0 to 8;

R_1 is an optionally substituted C_1 to C_{22} alkyl that is saturated or unsaturated, and branched or unbranched; and

R_2 is an optionally substituted C_1 to C_{22} alkyl that is saturated or unsaturated, and branched or unbranched,

wherein each fatty acid chain residue is unsubstituted.

[0148] 3. The composition according to any one of claims 1-2, wherein

x+y is, independently for each chain, an integer selected from 13 to 15; and

n is an integer selected from 0 to 6.

[0149] 4. The composition according to any one of claims 1-3, wherein x+y is 15 for at least one chain.

[0150] 5. The composition according to any one of claims 1-4, wherein R_2 is a branched or unbranched C_1 to C_{20} alkyl that is saturated or unsaturated.

[0151] 6. The composition according to any one of claims 1-5, wherein R_2 is selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decanyl, undecanyl, dodecanyl, tridecanyl, tetradecanyl, pentadecanyl, hexadecanyl, heptadecanyl, octadecanyl, nonadecanyl, and icosanyl, which are saturated or unsaturated and branched or unbranched.

[0152] 7. The composition according to any one of claims 1-6, wherein R_2 is selected from C_6 to C_{12} alkyl.

[0153] 8. The composition according to any one of claims 1-7, wherein R_2 is 2-ethylhexyl.

[0154] 9. The composition according to any one of claims 1-8, wherein R_1 is selected from unsubstituted C_7 to C_{17} alkyl that is unbranched and saturated or unsaturated.

[0155] 10. The composition according to any one of claims 1-9, wherein R_1 is selected from C_{13} to C_{17} alkyl that is unsubstituted, unbranched, and saturated or unsaturated.

[0156] 11. The composition according to any one of claims 1-10, wherein R_1 is selected from saturated C_{13} alkyl, saturated C_{15} alkyl, and saturated or unsaturated C_{17} alkyl, which are unsubstituted and unbranched.

[0157] 12. The composition according to any one of claims 1-4, wherein R_1 and R_2 are independently selected from optionally substituted C_1 to C_{18} alkyl that is saturated or unsaturated, and branched or unbranched.

[0158] 13. The composition according to any one of claims 1-4, wherein R_1 is selected from optionally substituted C_7 to C_{17} alkyl that is saturated or unsaturated, and branched or unbranched; and R_2 is selected from an optionally substituted C_3 to C_{20} alkyl that is saturated or unsaturated, and branched or unbranched.

[0159] 14. The composition according to any one of claims 1-13, wherein said composition has an EN that is an integer or fraction of an integer selected from 4.0 to 5.0.

[0160] 15. The composition according to any one of claims 1-14, wherein said composition has an EN that is a fraction of an integer selected from 4.2 to 4.8.

[0161] 16. The composition according to any one of claims 1-13, wherein said composition has an EN selected from an integer or fraction of an integer that is equal to or greater than 5.

[0162] 17. The composition according to any one of claims 1-16, wherein said composition has a kinematic viscosity of 200 cSt to 250 cSt at 40 °C.

[0163] 18. The composition according to any one of claims 1-17, wherein said composition has a kinematic viscosity of 210 cSt to 230 cSt at 40 °C.

[0164] 19. The composition according to any one of claims 1-18, wherein said composition has a pour point of -40 °C to -50 °C.

[0165] 20. The composition according to any one of claims 1-19, wherein said composition has a pour point of -42 °C to -48 °C.

[0166] 21. The composition according to any one of claims 1-18, wherein said composition has a pour point of less than -50 °C.

[0167] 22. The composition according to claim 21, wherein said composition has a pour point of -50 °C to -60 °C.

[0168] 23. The composition according to claim 21, wherein said composition has a pour point of -52 °C to -58 °C.

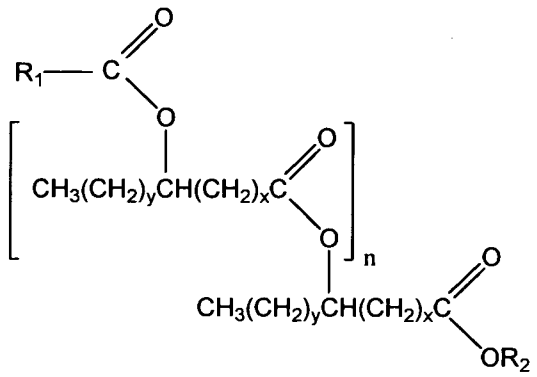
[0169] 24. The composition according to any one of claims 1-23, wherein said composition exhibits an iodine value (IV) of less than 15 cg/g.

[0170] 25. The composition according to any one of claims 1-24, wherein said composition exhibits an iodine value (IV) of less than 10 cg/g.

[0171] 26. The composition according to any one of claims 1-25, wherein said composition comprises two or more estolide compounds of Formula I.

[0172] 27. The composition according to any one of claims 1-26, wherein said composition consists essentially of two or more estolide compounds of Formula I.

[0173] 28. A composition comprising at least one estolide compound, said composition having an EN selected from an integer or fraction of an integer that is equal to or greater than 3, wherein the EN is the average number of estolide linkages in compounds according to Formula I, a kinematic viscosity equal to or greater than 130 cSt when measured at 40 °C, and a pour point equal to or lower than -30 °C, wherein said at least one estolide compound is a compound of Formula I:



Formula I

wherein

x is, independently for each occurrence, an integer selected from 0 to 20;

y is, independently for each occurrence, an integer selected from 0 to 20;

n is an integer selected from 0 to 12;

R_1 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched; and

R_2 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched,

wherein each chain of said composition is independently optionally substituted.

[0174] 29. The composition according to claim 28, wherein

x is, independently for each occurrence, an integer selected from 1 to 10;

y is, independently for each occurrence, an integer selected from 1 to 10;

n is an integer selected from 0 to 8;

R_1 is an optionally substituted C_1 to C_{22} alkyl that is saturated or unsaturated, and branched or unbranched; and

R_2 is an optionally substituted C_1 to C_{22} alkyl that is saturated or unsaturated, and branched or unbranched,

wherein each fatty acid chain residue is unsubstituted.

[0175] 30. The composition according to any one of claims 28 and 29, wherein

x+y is, independently for each chain, an integer selected from 13 to 15; and

n is an integer selected from 0 to 6.

[0176] 31. The composition according to any one of claims 28-30, wherein x+y is 15.

[0177] 32. The composition according to any one of claims 28-31, wherein R_2 is a branched or unbranched C_1 to C_{20} alkyl that is saturated or unsaturated.

[0178] 33. The composition according to any one of claims 28-32, wherein R_2 is selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decanyl, undecanyl, dodecanyl, tridecanyl, tetradecanyl, pentadecanyl, hexadecanyl, heptadecanyl, octadecanyl, nonadecanyl, and icosanyl, which are saturated or unsaturated and branched or unbranched.

[0179] 34. The composition according to any one of claims 28-33, wherein R_2 is selected from branched or unbranched C_6 to C_{12} alkyl that is saturated and unsubstituted.

[0180] 35. The composition according to any one of claims 28-34, wherein R_2 is 2-ethylhexyl.

[0181] 36. The composition according to any one of claims 28-35, wherein R_1 is selected from unsubstituted C_7 to C_{17} alkyl that is unbranched and saturated or unsaturated.

[0182] 37. The composition according to any one of claims 28-36, wherein R_1 is selected from C_{13} to C_{17} alkyl that is unsubstituted, unbranched, and saturated or unsaturated.

[0183] 38. The composition according to claim 36, wherein R_1 is selected from saturated C_7 alkyl, saturated C_9 alkyl, saturated C_{11} alkyl, saturated C_{13} alkyl, saturated C_{15} alkyl, and saturated or unsaturated C_{17} alkyl, which are unsubstituted and unbranched.

[0184] 39. The composition according to any one of claims 28-31, wherein R_1 and R_2 are independently selected from optionally substituted C_1 to C_{18} alkyl that is saturated or unsaturated, and branched or unbranched.

[0185] 40. The composition according to any one of claims 28-31, wherein R_1 is an optionally substituted C_7 to C_{17} alkyl that is saturated or unsaturated, and branched or unbranched; and R_2 is an optionally substituted C_3 to C_{20} alkyl that is saturated or unsaturated, and branched or unbranched.

[0186] 41. The composition according to any one of claims 28-40, wherein said composition has an EN that is an integer or fraction of an integer selected from 3.0 to 4.0.

[0187] 42. The composition according to any one of claims 28-41, wherein said composition has an EN that is an integer or fraction of an integer selected from 3.0 to 3.5.

[0188] 43. The composition according to any one of claims 28-40, wherein said composition has an EN selected from an integer or fraction of an integer that is equal to or greater than 3.5.

[0189] 44. The composition according to any one of claims 28-40, wherein said composition has an EN selected from an integer or fraction of an integer that is equal to or greater than 4.

[0190] 45. The composition according to any one of claims 28-40, wherein said composition has an EN that is an integer or fraction of an integer selected from 4.0 to 5.0.

[0191] 46. The composition according to any one of claims 28-40, wherein said composition has an EN that is a fraction of an integer selected from 4.2 to 4.8.

[0192] 47. The composition according to any one of claims 28-40, wherein said composition has an EN selected from an integer or fraction of an integer that is equal to or greater than 5.

[0193] 48. The composition according to any one of claims 28-47, wherein said composition has a kinematic viscosity of 130 cSt to 160 cSt at 40 °C.

[0194] 49. The composition according to any one of claims 28-48, wherein said composition has a kinematic viscosity of 130 cSt to 145 cSt at 40 °C.

[0195] 50. The composition according to any one of claims 28-49, wherein said composition has a pour point of -30 °C to -40 °C.

[0196] 51. The composition according to any one of claims 28-50, wherein said composition has a pour point of -34 °C to -38 °C.

[0197] 52. The composition according to any one of claims 28-49, wherein said composition has a pour point of less than -35 °C.

[0198] 53. The composition according to any one of claims 28-49, wherein said composition has a pour point of -35 °C to -45 °C.

[0199] 54. The composition according to any one of claims 28-49, wherein said composition has a pour point of -38 °C to -42 °C.

[0200] 55. The composition according to any one of claims 28-49, wherein said composition has a pour point of less than -40 °C.

[0201] 56. The composition according to any one of claims 28-49, wherein said composition has a pour point of -40 °C to -50 °C.

[0202] 57. The composition according to any one of claims 28-49, wherein said composition has a pour point of -42 °C to -48 °C.

[0203] 58. The composition according to any one of claims 28-49, wherein said composition has a pour point of less than -50 °C.

[0204] 59. The composition according to any one of claims 28-49, wherein said composition has a pour point of -50 °C to -60 °C.

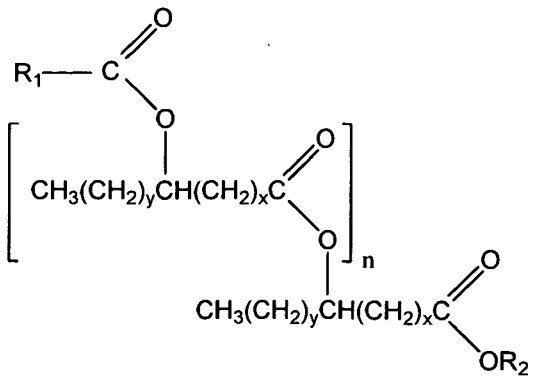
[0205] 60. The composition according to any one of claims 28-49, wherein said composition has a pour point of -52 °C to -58 °C.

[0206] 61. The composition according to any one of claims 28-60, wherein said composition exhibits an iodine value (IV) of less than 10 cg/g.

[0207] 62. The composition according to any one of claims 28-61, wherein said composition comprises two or more estolide compounds of Formula I.

[0208] 63. The composition according to any one of claims 28-62, wherein said composition consists essentially of two or more estolide compounds of Formula I.

[0209] 64. A composition comprising at least one estolide compound, said composition having an EN selected from an integer or fraction of an integer that is equal to or less than 2, wherein the EN is the average number of estolide linkages in compounds according to Formula I, a kinematic viscosity equal to or less than 55 cSt when measured at 40 °C, and a pour point equal to or lower than -25 °C, wherein said at least one estolide compound is a compound of Formula I:



Formula I

wherein

x is, independently for each occurrence, an integer selected from 0 to 20;

y is, independently for each occurrence, an integer selected from 0 to 20;

n is an integer selected from 0 to 12;

R_1 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched; and

R_2 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched,

wherein each fatty acid chain residue of said composition is independently optionally substituted.

[0210] 65. The composition according to claim 64, wherein

x is, independently for each occurrence, an integer selected from 1 to 10;

y is, independently for each occurrence, an integer selected from 1 to 10;

n is an integer selected from 0 to 8;

R_1 is an optionally substituted C_1 to C_{22} alkyl that is saturated or unsaturated, and branched or unbranched; and

R_2 is an optionally substituted C_1 to C_{22} alkyl that is saturated or unsaturated, and

branched or unbranched,

wherein each chain is unsubstituted.

[0211] 66. The composition according to any one of claims 64 and 65, wherein

x+y is, independently for each chain, an integer selected from 13 to 15; and

n is an integer selected from 0 to 6.

[0212] 67. The composition according to any one of claims 64-66, wherein x+y is 15.

[0213] 68. The composition according to any one of claims 64-67, wherein R_2 is a branched or unbranched C_1 to C_{20} alkyl that is saturated or unsaturated.

[0214] 69. The composition according to any one of claims 64-68, wherein R_2 is selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decanyl, undecanyl, dodecanyl, tridecanyl, tetradecanyl, pentadecanyl, hexadecanyl, heptadecanyl, octadecanyl, nonadecanyl, and icosanyl, which are saturated or unsaturated and branched or unbranched.

[0215] 70. The composition according to any one of claims 64-69, wherein R_2 is selected from C_6 to C_{12} alkyl.

[0216] 71. The composition according to any one of claims 64-70, wherein R_2 is 2-ethylhexyl.

[0217] 72. The composition according to any one of claims 64-71, wherein R_1 is selected from unsubstituted C_7 to C_{17} alkyl that is unbranched and saturated or unsaturated.

[0218] 73. The composition according to any one of claims 64-72, wherein R_1 is selected from C_{13} to C_{17} alkyl that is unsubstituted, unbranched, and saturated or unsaturated.

[0219] 74. The composition according to any one of claims 64-73, wherein R_1 is selected from saturated C_{13} alkyl, saturated C_{15} alkyl, and saturated or unsaturated C_{17} alkyl, which are unsubstituted and unbranched.

[0220] 75. The composition according to any one of claims 64-67, wherein R_1 and R_2 are independently selected from optionally substituted C_1 to C_{18} alkyl that is saturated or unsaturated, and branched or unbranched.

[0221] 76. The composition according to any one of claims 64-67, wherein R_1 is selected from optionally substituted C_7 to C_{17} alkyl that is saturated or unsaturated, and branched or unbranched; and R_2 is selected from an optionally substituted C_3 to C_{20} alkyl that is saturated or unsaturated, and branched or unbranched.

[0222] 77. The composition according to any one of claims 64-76, wherein said composition has an EN that is an integer or fraction of an integer selected from 1.0 to 2.0.

[0223] 78. The composition according to any one of claims 64-77, wherein said composition has an EN that is a fraction of an integer selected from 1.0 to 1.6.

[0224] 79. The composition according to any one of claims 64-78, wherein said composition has a kinematic viscosity of 25 cSt to 55 cSt at 40 °C.

[0225] 80. The composition according to any one of claims 64-79, wherein said composition has a kinematic viscosity of 35 cSt to 45 cSt at 40 °C.

[0226] 81. The composition according to any one of claims 64-80, wherein said composition has a pour point of -27 °C to -37 °C.

[0227] 82. The composition according to any one of claims 64-81, wherein said composition has a pour point of -30 °C to -34 °C.

[0228] 83. The composition according to any one of claims 64-80, wherein said composition has a pour point of less than -50 °C.

[0229] 84. The composition according to any one of claims 64-80, wherein said composition has a pour point of -50 °C to -60 °C.

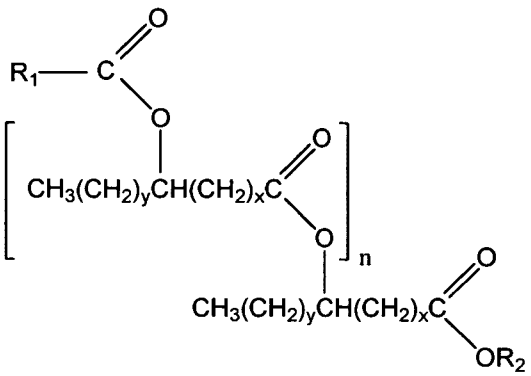
[0230] 85. The composition according to any one of claims 64-80, wherein said composition has a pour point of -52 °C to -58 °C.

[0231] 86. The composition according to any one of claims 64-85, wherein said composition exhibits an iodine value (IV) of less than 35 cg/g.

[0232] 87. The composition according to any one of claims 64-86, wherein said composition comprises two or more estolide compounds of Formula I.

[0233] 88. The composition according to any one of claims 64-87, wherein said composition consists essentially of two or more estolide compounds of Formula I.

[0234] 89. A composition comprising at least one estolide compound, said composition having an EN selected from an integer or fraction of an integer that is equal to or less than 2, wherein the EN is the average number of estolide linkages in compounds according to Formula I, a kinematic viscosity equal to or less than 45 cSt when measured at 40 °C, and a pour point equal to or lower than -25 °C, wherein said at least one estolide compound is a compound of Formula I:



Formula I

wherein

x is, independently for each occurrence, an integer selected from 0 to 20;

y is, independently for each occurrence, an integer selected from 0 to 20;

n is an integer selected from 0 to 12;

R_1 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched; and

R_2 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched,

wherein each fatty acid chain residue of said composition is independently optionally substituted.

[0235] 90. The composition according to claim 89, wherein

x is, independently for each occurrence, an integer selected from 1 to 10;

y is, independently for each occurrence, an integer selected from 1 to 10;

n is an integer selected from 0 to 8;

R_1 is an optionally substituted C_1 to C_{22} alkyl that is saturated or unsaturated, and branched or unbranched; and

R_2 is an optionally substituted C_1 to C_{22} alkyl that is saturated or unsaturated, and branched or unbranched,

wherein each chain is unsubstituted.

[0236] 91. The composition according to any one of claims 89 and 90, wherein

x+y is, independently for each chain, an integer selected from 13 to 15; and

n is an integer selected from 0 to 6.

[0237] 92. The composition according to any one of claims 89-91, wherein x+y is 15.

[0238] 93. The composition according to any one of claims 89-92, wherein R_2 is a branched or unbranched C_1 to C_{20} alkyl that is saturated or unsaturated.

[0239] 94. The composition according to any one of claims 89-93, wherein R_2 is selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decanyl, undecanyl, dodecanyl, tridecanyl, tetradecanyl, pentadecanyl, hexadecanyl, heptadecanyl, octadecanyl, nonadecanyl, and icosanyl, which are saturated or unsaturated and branched or unbranched.

[0240] 95. The composition according to any one of claims 89-94, wherein R_2 is selected from branched or unbranched C_6 to C_{12} alkyl that is saturated and unsubstituted.

[0241] 96. The composition according to any one of claims 89-95, wherein R_2 is 2-ethylhexyl.

[0242] 97. The composition according to any one of claims 89-96, wherein R_1 is selected from unsubstituted C_7 to C_{17} alkyl that is unbranched and saturated or unsaturated.

[0243] 98. The composition according to any one of claims 89-97, wherein R_1 is selected from C_{13} to C_{17} alkyl that is unsubstituted, unbranched, and saturated or unsaturated.

[0244] 99. The composition according to claim 97, wherein R_1 is selected from saturated C_7 alkyl, saturated C_9 alkyl, saturated C_{11} alkyl, saturated C_{13} alkyl, saturated C_{15} alkyl, and saturated or unsaturated C_{17} alkyl, which are unsubstituted and unbranched.

[0245] 100. The composition according to any one of claims 89-92, wherein R_1 and R_2 are independently selected from optionally substituted C_1 to C_{18} alkyl that is saturated or unsaturated, and branched or unbranched.

[0246] 101. The composition according to any one of claims 89-92, wherein R_1 is an optionally substituted C_7 to C_{17} alkyl that is saturated or unsaturated, and branched or unbranched; and R_2 is an optionally substituted C_3 to C_{20} alkyl that is saturated or unsaturated, and branched or unbranched.

[0247] 102. The composition according to any one of claims 89-101, wherein said composition has an EN that is an integer or fraction of an integer selected from 1.0 to 2.0.

[0248] 103. The composition according to any one of claims 89-102, wherein said composition has an EN that is a fraction of an integer selected from 1.1 to 1.7.

[0249] 104. The composition according to any one of claims 89-103, wherein said composition has a kinematic viscosity of 20 cSt to 45 cSt at 40 °C.

[0250] 105. The composition according to any one of claims 89-104, wherein said composition has a kinematic viscosity of 28 cSt to 38 cSt at 40 °C.

[0251] 106. The composition according to any one of claims 89-105, wherein said composition has a pour point of -25 °C to -35 °C.

[0252] 107. The composition according to any one of claims 89-106, wherein said composition has a pour point of -28 °C to -32 °C.

[0253] 108. The composition according to any one of claims 89-105, wherein said composition has a pour point of less than -50 °C.

[0254] 109. The composition according to any one of claims 89-105, wherein said composition has a pour point of -50 °C to -60 °C.

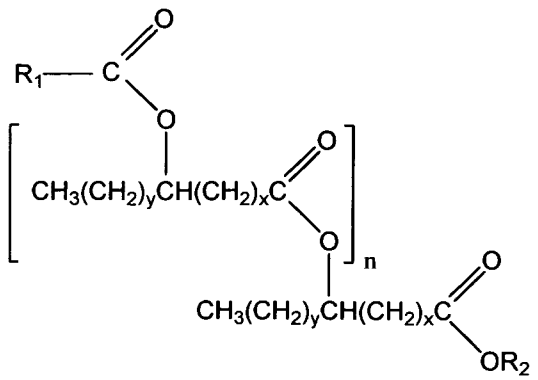
[0255] 110. The composition according to any one of claims 89-105, wherein said composition has a pour point of -52 °C to -58 °C.

[0256] 111. The composition according to any one of claims 89-110, wherein said composition exhibits an iodine value (IV) of less than 20 cg/g.

[0257] 112. The composition according to any one of claims 89-111, wherein said composition comprises two or more estolide compounds of Formula I.

[0258] 113. The composition according to any one of claims 89-112, wherein said composition consists essentially of two or more estolide compounds of Formula I.

[0259] 114. At least one compound of Formula III:



Formula III

wherein

x is, independently for each occurrence, an integer selected from 0 to 20;

y is, independently for each occurrence, an integer selected from 0 to 20;

n is an integer greater than or equal to 0;

R_1 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched; and

R_2 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched,

wherein each fatty acid chain residue of said at least one compound is independently optionally substituted.

[0260] 115. The at least one compound according to claim 114, wherein x is, independently for each occurrence, an integer selected from 1 to 10.

[0261] 116. The at least one compound according to any one of claims 114 and 115, wherein y is, independently for each occurrence, an integer selected from 1 to 10.

[0262] 117. The at least one compound according to any one of claims 114-116, wherein n is an integer selected from 0 to 12.

[0263] 118. The at least one compound according to any one of claims 114-117, wherein n is an integer selected from 0 to 8.

[0264] 119. The at least one compound according to any one of claims 114-118, wherein n is an integer selected from 0 to 4.

[0265] 120. The at least one compound according to any one of claims 114-119, wherein R_1 is an optionally substituted C_1 to C_{22} alkyl that is saturated or unsaturated, and branched or unbranched.

[0266] 121. The at least one compound according to any one of claims 114-120, wherein R_2 is an optionally substituted C_1 to C_{22} alkyl that is saturated or unsaturated, and branched or unbranched.

[0267] 122. The at least one compound according to any one of claims 114-121, wherein each chain is saturated, unsubstituted, and unbranched.

[0268] 123. The at least one compound according to any one of claims 114-122, wherein x+y is, independently for each chain, an integer selected from 13 to 15.

[0269] 124. The at least one compound according to any one of claims 114-123, wherein x+y is 15.

[0270] 125. The at least one compound according to any one of claims 114-124, wherein R_2 is selected from a branched or unbranched C_1 to C_{20} alkyl that is saturated or unsaturated.

[0271] 126. The at least one compound according to any one of claims 114-125, wherein R_2 is selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl,

decanyl, undecanyl, dodecanyl, tridecanyl, tetradecanyl, pentadecanyl, hexadecanyl, heptadecanyl, octadecanyl, nonadecanyl, and icosanyl, which are saturated or unsaturated and branched or unbranched.

[0272] 127. The at least one compound according to any one of claims 114-126, wherein R_2 is selected from C_6 to C_{12} alkyl.

[0273] 128. The at least one compound according to any one of claims 114-127, wherein R_2 is 2-ethylhexyl.

[0274] 129. The at least one compound according to any one of claims 114-128, wherein R_1 is selected from unsubstituted C_7 to C_{17} alkyl that is unbranched and saturated or unsaturated.

[0275] 130. The at least one compound according to claim 129, wherein R_1 is selected from saturated C_7 alkyl, saturated C_9 alkyl, saturated C_{11} alkyl, saturated C_{13} alkyl, saturated C_{15} alkyl, and saturated or unsaturated C_{17} alkyl, which are unsubstituted and unbranched.

[0276] 131. The at least one compound according to any one of claims 114-129, wherein R_1 is selected from C_{13} to C_{17} alkyl that is unsubstituted, unbranched, and saturated or unsaturated.

[0277] 132. The at least one compound according to claim 130, wherein R_1 is selected from saturated C_{13} alkyl, saturated C_{15} alkyl, and saturated or unsaturated C_{17} alkyl, which are unsubstituted and unbranched.

[0278] 133. The at least one compound according to any one of claims 114-125, wherein R_1 is an optionally substituted C_1 to C_{18} alkyl that is saturated or unsaturated, and branched or unbranched.

[0279] 134. The at least one compound according to any one of claims 114-125, wherein R_2 is an optionally substituted C_1 to C_{18} alkyl that is saturated or unsaturated, and branched or unbranched.

[0280] 135. The at least one compound according to any one of claims 114-125, wherein R_1 is an optionally substituted C_7 to C_{17} alkyl that is saturated or unsaturated, and branched or unbranched.

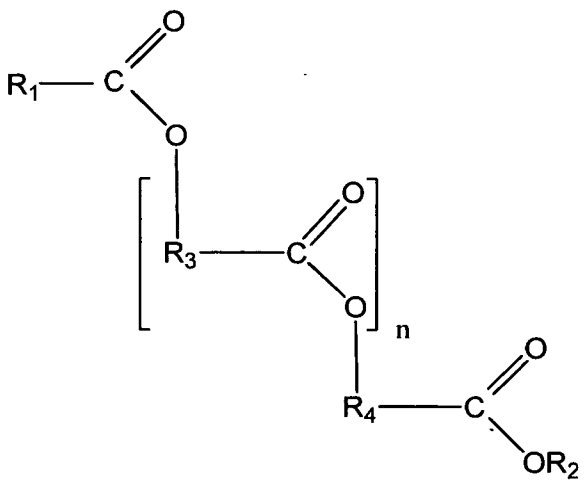
[0281] 136. The at least one compound according to any one of claims 114-125, wherein R_2 is an optionally substituted C_3 to C_{20} alkyl that is saturated or unsaturated, and branched or unbranched.

[0282] 137. A composition comprising the at least one estolide compound according to any one of claims 114-136.

[0283] 138. The composition according claim 137, wherein said composition comprises two or more estolide compounds.

[0284] 139. The composition according to claim 137, wherein said composition consists essentially of the two or more estolide compounds.

[0285] 140. A composition comprising at least one estolide compound of Formula II:



Formula II

wherein

n is an integer greater than or equal to 0;

R_1 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched;

R_2 is selected from hydrogen and optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched; and

R_3 and R_4, independently for each occurrence, are selected from optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched;

wherein said composition has:

an EN selected from an integer that is equal to or greater than 4, a kinematic viscosity equal to or greater than 200 cSt when measured at 40 °C, and a pour point equal to or lower than -40 °C;

an EN selected from an integer or fraction of an integer that is equal to or greater than 3, a kinematic viscosity equal to or greater than 130 cSt when measured at 40 °C, and a pour point equal to or lower than -30 °C;

an EN selected from an integer or fraction of an integer that is equal to or less than 2, a kinematic viscosity equal to or less than 55 cSt when measured at 40 °C, and a pour point equal to or lower than -25 °C; or

an EN selected from an integer or fraction of an integer that is equal to or less than 2, a kinematic viscosity equal to or less than 45 cSt when measured at 40 °C, and a pour point equal to or lower than -25 °C

wherein the EN is the average number of estolide linkages in compounds according to Formula II.

[0286] 141. A method of retaining or decreasing the pour point of an estolide base oil by increasing the EN of a base oil, said method comprising:

selecting an estolide base oil having an initial EN and an initial pour point; and

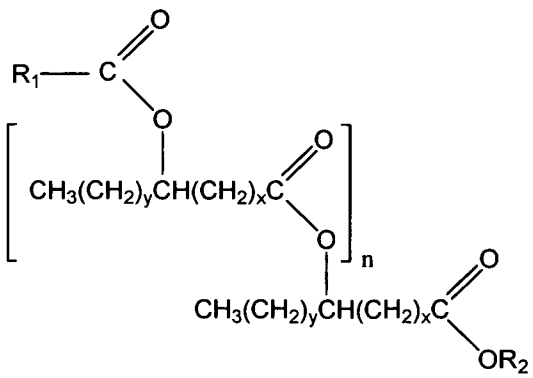
removing at least a portion of abase oil, said portion exhibiting an EN that is less than the initial EN of the base oil,

wherein the resulting estolide base oil exhibits an EN that is greater than the initial EN of the base oil, and a pour point that is equal to or lower than the initial pour point of the base oil, and wherein EN is the average number of estolide linkages in estolides of the estolide base oil.

[0287] 142. The method according to claim 141, wherein removing at least a portion of the base oil is accomplished by distillation, chromatography, membrane separation, phase separation, affinity separation, or combinations thereof.

[0288] 143. The method according to claim 142, wherein the distillation takes place at a temperature of at least 250°C and a pressure of no greater than 25 microns absolute.

[0289] 144. The method according to any one of claims 141-143, wherein the estolide base oil has an initial EN of equal to or less than 2.5 and an initial pour point of equal to or greater than -40 °C, said estolide base oil comprising at least one compound of Formula I:



Formula I

wherein

x is, independently for each occurrence, an integer selected from 0 to 20;

y is, independently for each occurrence, an integer selected from 0 to 20;

n is an integer selected from 0 to 12;

R_1 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched; and

R_2 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched,

wherein each fatty acid chain residue of said compounds is independently optionally substituted.

[0290] 145. The method according to claim 144, wherein

x is, independently for each occurrence, an integer selected from 1 to 10;

y is, independently for each occurrence, an integer selected from 1 to 10;

n is an integer selected from 0 to 8;

R_1 is an optionally substituted C_1 to C_{22} alkyl that is saturated or unsaturated, and branched or unbranched; and

R_2 is an optionally substituted C_1 to C_{22} alkyl that is saturated or unsaturated, and branched or unbranched,

wherein each chain is unsubstituted.

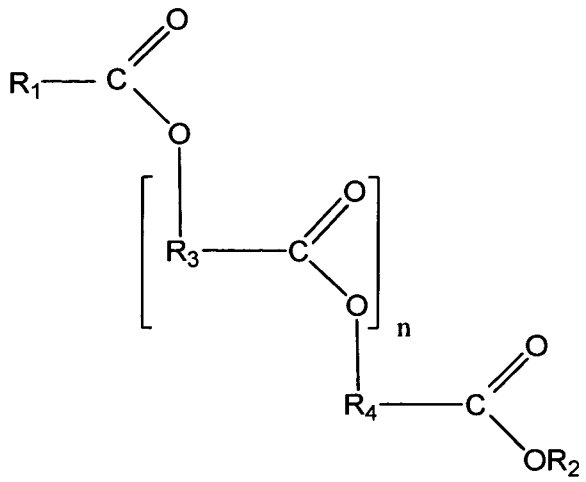
[0291] 146. The method according to any one of claims 144 and 145, wherein

x+y is, independently for each chain, an integer selected from 13 to 15; and

n is an integer selected from 0 to 6.

[0292] 147. The method according to any one of claims 144-146, wherein x+y is 15.

[0293] 148. The method according to any one of claims 141-143, wherein the estolide base oil has an initial EN of equal to or less than 2.5, wherein the EN is the average number of estolide linkages in compounds according to Formula II, and an initial pour point of equal to or greater than -40 °C, said estolide base oil comprising at least one compound of Formula II:



Formula II

wherein

n is an integer greater than or equal to 0;

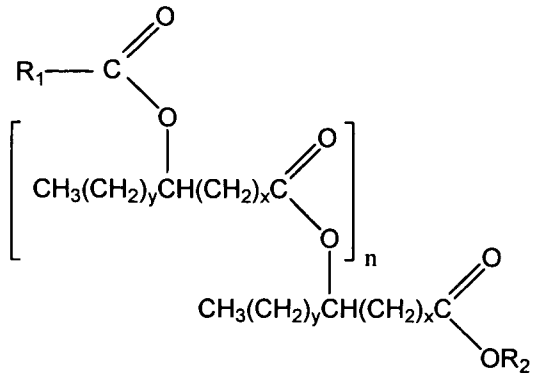
R_1 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched;

R_2 is selected from hydrogen and optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched; and

R_3 and R_4, independently for each occurrence, are selected from optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched.

[0294] 149. The method according to any one of claims 141-143, wherein the estolid base oil has an initial EN of equal to or less than 2.5, wherein the EN is the average number of estolide linkages in compounds according to Formula III, and an initial pour point

of equal to or greater than -40 °C, said estolide base oil comprising at least one compound of Formula III:



Formula III

wherein

x is, independently for each occurrence, an integer selected from 0 to 20;

y is, independently for each occurrence, an integer selected from 0 to 20;

n is an integer greater than or equal to 0;

R_1 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched; and

R_2 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched,

wherein each fatty acid chain residue of said at least one compound is independently optionally substituted.

[0295] 150. The method according to any one of claims 144-149, wherein R_2 is a branched or unbranched C_1 to C_{20} alkyl that is saturated or unsaturated.

[0296] 151. The composition according to any one of claims 144-150, wherein R_2 is selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decanyl, undecanyl, dodecanyl, tridecanyl, tetradecanyl, pentadecanyl, hexadecanyl,

heptadecanyl, octadecanyl, nonadecanyl, and icosanyl, which are saturated or unsaturated and branched or unbranched.

[0297] 152. The method according to any one of claims 144-151, wherein R_2 is selected from branched or unbranched C_6 to C_{12} alkyl that is saturated and unsubstituted.

[0298] 153. The method according to any one of claims 143-152, wherein R_2 is 2-ethylhexyl.

[0299] 154. The method according to any one of claims 144-153, wherein R_1 is selected from unsubstituted C_7 to C_{17} alkyl that is unbranched and saturated or unsaturated.

[0300] 155. The method according to any one of claims 144-154, wherein R_1 is selected from saturated C_7 alkyl, saturated C_9 alkyl, saturated C_{11} alkyl, saturated C_{13} alkyl, saturated C_{15} alkyl, and saturated or unsaturated C_{17} alkyl, which are unsubstituted and unbranched.

[0301] 156. The method according to any one of claims 144-155, wherein R_1 is selected from C_{13} to C_{17} alkyl that is unsubstituted, unbranched, and saturated or unsaturated.

[0302] 157. The method according to claim 144-156, wherein R_1 is selected from saturated C_{13} alkyl, saturated C_{15} alkyl, and saturated or unsaturated C_{17} alkyl, which are unsubstituted and unbranched.

[0303] 158. The method according to any one of claims 144-149, wherein R_1 and R_2 are independently selected from optionally substituted C_1 to C_{18} alkyl that is saturated or unsaturated, and branched or unbranched.

[0304] 159. The method according to any one of claims 144-149, wherein R_1 is an optionally substituted C_7 to C_{17} alkyl that is saturated or unsaturated, and branched or unbranched; and R_2 is an optionally substituted C_3 to C_{20} alkyl that is saturated or unsaturated, and branched or unbranched.

[0305] 160. The method according to any one of claims 144-159, wherein the portion of the base oil exhibits an EN that is less than 2.5.

[0306] 161. The method according to any one of claims 144-160, wherein the portion of the base oil exhibits an EN that is less than 2.0.

[0307] 162. The method according to any one of claims 144-161, wherein the portion of the base oil exhibits an EN that is less than 1.5.

[0308] 163. The method according to any one of claims 144-162, wherein the EN of the resulting base oil is greater than 2.5.

[0309] 164. The method according to any one of claims 144-163, wherein the EN of the resulting base oil is greater than 3.0.

[0310] 165. The method according to any one of claims 144-164, wherein the EN of the resulting base oil is greater than 4.0.

[0311] 166. The method according to any one of claims 144-165, wherein the pour point of the resulting base oil is equal to or less than -40 °C.

[0312] 167. The method according to claim 144, 148, or 149, wherein the estolide base oil has an initial EN of equal to or less than 2.0 and an initial pour point of equal to or greater than -35 °C.

[0313] 168. The method according to claim 144, 148, or 149, wherein the portion of the base oil exhibits an EN that is less than 2.0.

[0314] 169. The method according to claim 144, 148, or 149, wherein the portion of the base oil exhibits an EN that is less than 1.5.

[0315] 170. The method according to any one of claims 166-169, wherein the EN of the resulting base oil is greater than 2.5.

[0316] 171. The method according to any one of claims 166-169, wherein the EN of the resulting base oil is greater than 3.0.

[0317] 172. The method according to any one of claims 166-169, wherein the pour point of the resulting base oil is equal to or less than -35 °C.

[0318] 173. The method according to any one of claims 144-172, wherein said base oil comprises two or more estolide compounds of Formula I, II, or III.

[0319] 174. The method according to any one of claims 144-172, wherein said base oil consists essentially of two or more estolide compounds of Formula I, II or III.

[0320] 175. The composition according to any one of claims 1-113 where x+y for one or more fatty acid chain residues differs from x+y for one or more other fatty acid chain residues in a compound of formula I.

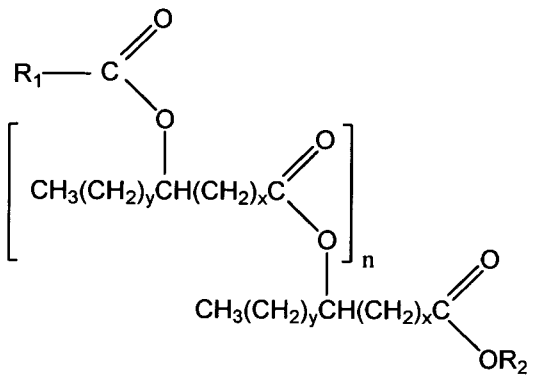
[0321] 176. The composition according to any one of claims 114-139 where x+y for one or more fatty acid chain residues differs from x+y for one or more other fatty acid chain residues in a compound of formula III.

[0322] 177. The composition according to any one of claims 176-177 where the one or more fatty acid chain residues with differing x+y are fatty acid chain residues of the same estolide molecule.

[0323] 178. The composition according to claim 148 where the length of one or more R_3 or R_4 differ from one or more R_3 or R_4 of the same estolide molecule.

CLAIMS:

1. A composition comprising at least one estolide compound, said composition having an EN selected from an integer or fraction of an integer that is equal to or greater than 4, wherein the EN is the average number of estolide linkages in compounds according to Formula I, a kinematic viscosity equal to or greater than 200 cSt when measured at 40 °C, and a pour point equal to or lower than -40 °C, wherein said at least one estolide compound is a compound of Formula I:



Formula I

wherein

x is, independently for each occurrence, an integer selected from 0 to 20;

y is, independently for each occurrence, an integer selected from 0 to 20;

n is an integer selected from 0 to 12;

R_1 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched; and

R_2 is an optionally substituted alkyl that is saturated or unsaturated, and branched or unbranched,

wherein each fatty acid chain residue of said at least one compound is independently optionally substituted.

2. The composition according to claim 1, wherein

x is, independently for each occurrence, an integer selected from 1 to 10;

y is, independently for each occurrence, an integer selected from 1 to 10;

n is an integer selected from 0 to 8;

R_1 is an optionally substituted C_1 to C_{22} alkyl that is saturated or unsaturated, and branched or unbranched; and

R_2 is an optionally substituted C_1 to C_{22} alkyl that is saturated or unsaturated, and branched or unbranched,

wherein each fatty acid chain residue is unsubstituted.

3. The composition according to any one of claims 1-2, wherein

x+y is, independently for each chain, an integer selected from 13 to 15; and

n is an integer selected from 0 to 6.

4. The composition according to any one of claims 1-3, wherein x+y is 15 for at least one chain.

5. The composition according to any one of claims 1-4, wherein R_2 is a branched or unbranched C_1 to C_{20} alkyl that is saturated or unsaturated.

6. The composition according to any one of claims 1-5, wherein R_2 is selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decanyl, undecanyl, dodecanyl, tridecanyl, tetradecanyl, pentadecanyl, hexadecanyl, heptadecanyl, octadecanyl, nonadecanyl, and icosanyl, which are saturated or unsaturated and branched or unbranched.

7. The composition according to any one of claims 1-6, wherein R_2 is selected from C_6 to C_{12} alkyl.

8. The composition according to any one of claims 1-7, wherein R_2 is 2-ethylhexyl.

9. The composition according to any one of claims 1-8, wherein R_1 is selected from unsubstituted C_7 to C_{17} alkyl that is unbranched and saturated or unsaturated.

10. The composition according to any one of claims 1-9, wherein R_1 is selected from C_{13} to C_{17} alkyl that is unsubstituted, unbranched, and saturated or unsaturated.

11. The composition according to any one of claims 1-10, wherein R_1 is selected from saturated C_{13} alkyl, saturated C_{15} alkyl, and saturated or unsaturated C_{17} alkyl, which are unsubstituted and unbranched.

12. The composition according to any one of claims 1-4, wherein R_1 and R_2 are independently selected from optionally substituted C_1 to C_{18} alkyl that is saturated or unsaturated, and branched or unbranched.

13. The composition according to any one of claims 1-4, wherein R_1 is selected from optionally substituted C_7 to C_{17} alkyl that is saturated or unsaturated, and branched or unbranched; and R_2 is selected from an optionally substituted C_3 to C_{20} alkyl that is saturated or unsaturated, and branched or unbranched.

14. The composition according to any one of claims 1-13, wherein said composition has an EN that is an integer or fraction of an integer selected from 4.0 to 5.0.

15. The composition according to any one of claims 1-14, wherein said composition has an EN that is a fraction of an integer selected from 4.2 to 4.8.

16. The composition according to any one of claims 1-13, wherein said composition has an EN selected from an integer or fraction of an integer that is equal to or greater than 5.

17. The composition according to any one of claims 1-16, wherein said composition has a kinematic viscosity of 200 cSt to 250 cSt at 40 °C.

18. The composition according to any one of claims 1-17, wherein said composition has a kinematic viscosity of 210 cSt to 230 cSt at 40 °C.

19. The composition according to any one of claims 1-18, wherein said composition has a pour point of -40 °C to -50 °C.

20. The composition according to any one of claims 1-19, wherein said composition has a pour point of -42 °C to -48 °C.

21. The composition according to any one of claims 1-18, wherein said composition has a pour point of less than -50 °C.

22. The composition according to claim 21, wherein said composition has a pour point of -50 °C

to -60 °C.

23. The composition according to claim 21, wherein said composition has a pour point of -52 °C to -58 °C.

24. The composition according to any one of claims 1-23, wherein said composition exhibits an iodine value (IV) of less than 15 cg/g.

25. The composition according to any one of claims 1-24, wherein said composition exhibits an iodine value (IV) of less than 10 cg/g.

26. The composition according to any one of claims 1-25, wherein said composition comprises two or more estolide compounds of Formula I.

27. The composition according to any one of claims 1-26, wherein said composition consists essentially of two or more estolide compounds of Formula I.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/001537

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M105/42 C07C69/675 C11C3/00
ADD. C10N20/02 C10N30/02

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 C07C C11C

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 practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 011 629 A (BILBO RAYMOND E [US]) 30 April 1991 (1991-04-30) claim 1; examples; table col.8	1-27
A	WO 01/53247 A1 (US AGRICULTURE [US]) 26 July 2001 (2001-07-26) claim 1; tables 1-3	1-27

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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 document 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

"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.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 October 2011	30/11/2011

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Bertrand, Samuel

1

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	TOMODA HIDEYUKI ET AL: "CHARACTERISTIC PROPERTIES OF CUTTING FLUID ADDITIVES DERIVED FROM THE REACTION PRODUCTS OF HYDROXYL FATTY ACIDS WITH SOME ACID ANHYDRIDES", JOURNAL OF SURFACTANTS AND DETERGENTS, SPRINGER, BERLIN, DE, vol. 1, no. 4, 1 January 1998 (1998-01-01) , pages 533-537, XP008079792, ISSN: 1097-3958 tables 2-3	1-27
A	Steven C. Cermak: "Physical properties of saturated estolides and their 2-ethylhexyl esters", Industrial Crops and Products, 1 January 2002 (2002-01-01), pages 119-127, XP55010400, Retrieved from the Internet: URL:http://ddr.nal.usda.gov/bitstream/10113/14500/1/IND23333726.pdf [retrieved on 2011-10-25] table 3	1-27
A	WILLIAM J SIMONSICK ET AL: "Detailed structural elucidation of polyesters and acrylates using Fourier transform mass spectrometry", ANALYTICAL AND BIOANALYTICAL CHEMISTRY, SPRINGER, BERLIN, DE, vol. 392, no. 4, 22 August 2008 (2008-08-22), pages 575-583, XP019652878, ISSN: 1618-2650, DOI: 10.1007/S00216-008-2322-3 Scheme 1figure 1c	1-27

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2011/001537

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5011629 A	30-04-1991	NONE	
WO 0153247 A1	26-07-2001	AU 3292901 A	31-07-2001