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(54) LUBRICANT COMPOSITION COMPRISING BRANCHED DIESTERS AND VISCOSITY INDEX IMPROVER

(57) The invention refers to lubricant compositions comprising a specific diester together with a viscosity index improver.

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Description

TECHNICAL FIELD

[0001] This application relates to lubricant compositions comprising branched diester compounds in association with a viscosity index improver. The compositions can be used to reduce the fuel consumption and to improve the cleanliness of an engine, especially a car engine.

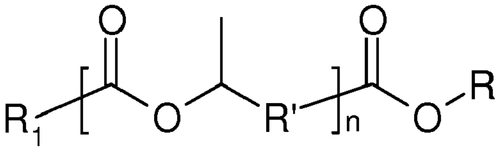
BACKGROUND

[0002] Lubricants are widely used to reduce friction between surfaces of moving parts and thereby reduce wear and prevent damage to such surfaces and parts. Lubricants are composed primarily of a base stock and one or more lubricant additives. The base stock may be a relatively high molecular weight hydrocarbon. In applications where there is a large amount of pressure applied to moving parts, lubricating compositions composed only of hydrocarbon base stock tend to fail and the parts become damaged. The lubricant manufacturer is in constant need to improve their formulations to address increased demands on fuel economy while balancing the need to improve the cleanliness of the engines or to reduce emissions. These demands force manufacturers to address their formulation capabilities and/or look for new base stocks that can meet the performance requirements.

[0003] To make lubricants, such as motor oils, transmission fluids, gear oils, industrial lubricating oils, metal working oils, etc., one starts with a lubricant grade of petroleum oil from a refinery, or a suitable polymerized petrochemical fluid. Into this base stock, small amounts of additive chemicals are blended therein to improve material properties and performance, such as enhancing lubricity, inhibiting wear and corrosion of metals, and retarding damage to the fluid from heat and oxidation. As such, various additives such as oxidation and corrosion inhibitors, dispersing agents, high pressure additives, anti-foaming agents, metal deactivators and other additives suitable for use in lubricant formulations, can be added in conventional effective quantities. It has long been known that synthetic esters can be used both as a base stock and as an additive in lubricants. By comparison with the less expensive, but environmentally less safe mineral oils, synthetic esters were mostly used as base oils in cases where the viscosity/temperature behavior was expected to meet stringent demands. The increasingly important issues of environmental acceptance and biodegradability are the drivers behind the desire for alternatives to mineral oil as a base stock in lubricating applications.

SUMMARY OF THE INVENTION

[0004] The invention provides a lubricant composition comprising at least one compound of formula (I) below and at least one viscosity index improver



(I)

wherein :

n is below 1.1
R1 represents a linear or branched, saturated or unsaturated C3-C20,
R' represents a linear or branched, saturated or unsaturated C2-C16,
R represents a linear or branched, saturated or unsaturated C1-C20.

[0005] According to one embodiment in the formula (I):

n is 1;
the total amount of carbon atoms being more than 15 and less than 40.

[0006] According to one embodiment in the formula (I):

R1 represents a linear or branched, saturated or unsaturated C5-C15 alkyl group;
R' represents a linear or branched, saturated or unsaturated C3-C8 alkyl group;
R represents a linear or branched, saturated or unsaturated C1-C15 alkyl group.

[0007] According to one embodiment in the formula (I),
R1 represents a saturated linear C5-C15 alkyl group, more preferably a saturated linear C5-C12 alkyl group;
R' represents a saturated linear C3-C8 alkyl group, more preferably a saturated linear C5-C8 alkyl group;
R represents a saturated linear or branched C5-C15 alkyl group, more preferably a saturated linear or branched C5-C10 alkyl group.

[0008] According to one embodiment in the formula (I):

R1 represents a saturated linear C5-C10 alkyl group, more preferably a saturated linear C5-C8 alkyl group;
R' represents a saturated linear C5-C8 alkyl group;
R represents a saturated, linear or branched C5-C10 alkyl group, preferably a saturated linear C5-C10 alkyl group.

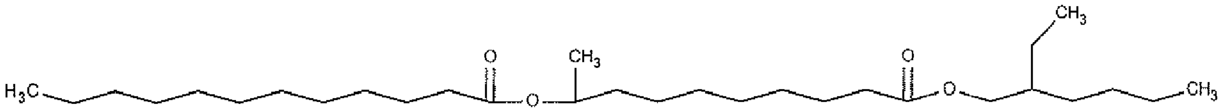
[0009] According to one embodiment, the compound of formula (I) is a compound of formula (Ia)

(Ia)

[0010] According to one embodiment, in the formula (I):

R1 represents a saturated linear or branched C5-C15 alkyl group, more preferably a saturated linear C8-C12 alkyl group;
R' represents a saturated linear C5-C8 alkyl group;
R represents a saturated, linear or branched C5-C10 alkyl group, preferably a saturated branched C5-C10 alkyl group.

[0011] According to one embodiment the compound of formula (I) is a compound of formula (Ib)



(Ib)

[0012] According to one embodiment the viscosity index improver is a polymeric viscosity index improver, preferably chosen among :

polyacrylates and polymethacrylates,
olefin homopolymers or copolymers, preferably ethylene/propylene styrene copolymers, preferably with isoprene or a diene such as butadiene, hydrogenated or not, isoprene polymers, preferably radial hydrogenated polyisoprene, esterified polystyrenes, preferably esterified poly(styrene-co-maleic anhydride) mixtures of two or more of the above.

[0013] According to one embodiment the lubricant composition comprises from 0,1 to 50%, preferably from 1 to 50%, more preferably from 5 to 30% by weight based on the total weight of lubricant composition, of a compound of formula (I).

[0014] According to one embodiment the lubricant composition comprises from 0,01 to 15%, preferably from 1 to 10% by weight based on the total weight of lubricant composition, of at least one viscosity index improver.

[0015] According to one embodiment the lubricant composition further comprises at least one lubricant base oil.

[0016] According to one embodiment lubricant base oil is a group III lubricant base oil.

[0017] According to one embodiment the lubricant composition comprises from 50 to 99%, preferably from 50 to 80% by weight based on the total weight of lubricant composition, of a lubricant base oil.

[0018] According to one embodiment the lubricant composition further comprises further at least one lubricant additive selected from the list consisting of detergent additives, anti-wear additives, friction modifiers additives, extreme pressure additives, antioxidant additives, dispersing agents, pour-point depressant additives, anti-foam agents, thickeners and mixtures of two or more thereof.

[0019] The invention also provides the use of the lubricant composition according to the invention to reduce the fuel consumption of an engine, preferably of a car engine and/or to improve the cleanliness of an engine, preferably of a car engine, more preferably of at least one piston of a car engine.

DETAILED DESCRIPTION

[0020] The present application relates to the compositions and methods for synthesis of diester compounds for use as a base stock for lubricant applications, or a base stock blend component for use in a finished lubricant composition, or for the particular applications of fuel economy and imparting cleanliness to the engines. The present diesters also exhibit improved detergency, as determined based on the Micro Coking Test (MCT).

[0021] Fuel economy is measured as the gain in various driving cycles, especially NEDC (New European Driving Cycle), and compared to trimethylol propane ester (Nycobase 7300 (NB7300)) which is an ester known to provide fuel economy (see e.g. Dodos, G.S., et al., Renewable fuels and lubricants from Lunaria annual. Ind. Crops Prod. (2015), http://dx.doi.org/10.1016/j.indcrop.2015.05.046 and DOI:10.1080/10402004.2015.1025934).

[0022] Cleanliness is measured as a rating of piston merit, especially against PAO which is known to be effective in cleanliness.

[0023] The diesters in accordance with the present embodiments may constitute a lubricant base stock composition, or a base stock blend component for use in a finished lubricant composition, or they may be mixed with one or more additives for further optimization as a finished lubricant or for a particular application. Suitable applications which may be utilized include, but are not limited to, (two-cycle) engine oils, especially car engines. The diesters in accordance with the present embodiments may also have alternative chemical uses and applications, as understood by a person skilled in the art. The content of the diesters of the present embodiments may be found neat. In some aspects, finished lubricant compositions may include between about 1 to about 25% by weight of the diester, from about 50 to about 99% by weight of a lubricating base oil, and from about 1 to about 25% by weight of an additive, especially an additive package.

[0024] Suitable non-limiting examples of additives may include detergents, antiwear agents, antioxidants, metal deactivators, extreme pressure (EP) additives, dispersants, viscosity modifiers, pour point depressants, corrosion protectors, friction coefficient modifiers, colorants, antifoam agents, demulsifiers and the like.

[0025] The diesters of the invention are preferably in combination with a viscosity improver. Viscosity improvers are known in the art and a description thereof can be found in Chemistry and Technology of Lubricants - Editors: Mortier, Roy M., Fox, Malcolm F., Orszulik, Stefan, Ed 2010, which is incorporated herein by reference.

[0026] The viscosity improver is typically:

- polyacrylates or polymethacrylates, typically referred to as PMA,
- olefin homopolymers or copolymers, preferably ethylene/propylene, typically referred to as OCP (Olefin CoPolymers)
- styrene copolymers, preferably with isoprene or a diene such as butadiene, hydrogenated or not, such as HSD (Hydrogenated Styrene Diene), isoprene polymers such as SIP (Styrene Isoprene Polymers), preferably radial hydrogenated polyisoprene (HRI),
- esterified polystyrenes, preferably esterified poly(styrene-co-maleic anhydride), referred to as SPE (Styrene Poly-Ester),
- mixtures of two or more of the above, especially PMA/OCP.

[0027] The amount of viscosity improver can be varied and is generally from 0,01 to 15%, preferably from 1 to 10% by weight based on the total weight of lubricant composition.

[0028] Suitable base oils can be any of the conventionally used lubricating oils, such as a mineral oil, a synthetic oil, or a blend of mineral and synthetic oils, or in some cases, natural oils and natural oil derivatives, all individually or in combinations thereof. Mineral lubricating oil base stocks used in preparing the lubricant compositions can be any conventionally refined base stocks derived from paraffinic, naphthenic and mixed base crudes. The lubricating base oil may include polyolefin base stocks, of both polyalphaolefin (PAO) and polyinternal olefin (PIO) types. Oils of lubricating viscosity derived from coal or shale are also useful.

[0029] Examples of synthetic oils include hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), poly(1-decenes), and mixtures thereof; alkyl-benzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof.

[0030] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, and etherification, constitute another class of known synthetic lubricating oils that can be used. These are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having a number average molecular weight of 1000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C_{3-8} fatty acid esters, the C_{13} Oxo acid diester of tetraethylene glycol, or PAGs, such as PO/BO, e.g. disclosed in WO201270007 and WO2013164457.

[0031] Another suitable class of synthetic lubricating oils that can be used includes the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, and alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, and propylene glycol). Specific examples of these esters include dibutyl adipate, di-(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid. Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols such as neopentyl glycol, trimethylol propane, and pentaerythritol, or polyol ethers such as dipentaerythritol, and tripentaerythritol.

[0032] Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils include another useful class of synthetic lubricants (e.g., tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methylhexyl)silicate, tetra-(p-tert-butylphenyl) silicate, hexyl-(4-methyl-2-pentoxy)disiloxane, poly(methyl)siloxanes, and poly-(methylphenyl)siloxanes). Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), and polymeric tetrahydrofurans.

[0033] Unrefined, refined and re-refined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can be used as the lubricating base oil in the lubricant composition. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from primary distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification acts to improve one or more properties. Many such purification techniques are known to those skilled in the art such as solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, re-refined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such re-refined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0034] Oils of lubricating viscosity can also be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as given in the table that follows. Groups I, II, and III are mineral oil base stocks. In some embodiments, the oil of lubricating viscosity is a Group I, II, III, IV, or V oil or mixtures thereof.

	Saturates	Sulfur	VI
Group I mineral oils	<90%	> 0.03 %	80≤VI<120
Groupe II hydroprocessed oils	≥ 90%	≤ 0.03 %	80≤VI<120
Groupe III hydrocacked or hydroisomerized oils	≥ 90%	≤ 0.03 %	≥ 120
Groupe IV	Polyalphaolefins (PAO)		
Groupe V	All other synthetics		

[0035] In one aspect, the diesters were prepared via a two-act route of transesterification and saturated fatty acid addition. In other aspect, the diesters were prepared via a three-act route of transesterification, formic acid addition, and saturated fatty acid addition.

[0036] Transesterification is well known to those skilled in the art and can be depicted by the following equation: $RCOOR^a+R^bOH \rightarrow RCOOR^b+R^aOH$. The reactant esters are commonly (fatty) acid alkyl esters, including C_1-C_{20} (fatty) acid alkyl esters derived from a natural oil. In certain embodiments, the C_1-C_{20} (fatty) acid alkyl esters may be unsaturated alkyl esters, such as unsaturated fatty acid methyl esters. In further embodiments, such esters may include 9-DAME (9-decenoic acid methyl esters), 9-UDAME (9-undecenoic acid methyl esters), and/or 9-DDAME (9-dodecenoic acid methyl esters). The transesterification reaction is conducted at approximately 60-80°C and approximately 1 atm.

[0037] Such fatty acid alkyl esters are conveniently generated by self-metathesis and/or cross metathesis of a natural oil. Metathesis is a catalytic reaction that involves the interchange of alkylidene units among compounds containing one or more double bonds (i.e., olefinic compounds) via the formation and cleavage of the carbon-carbon double bonds. Cross-metathesis may be represented schematically as shown in Equation I:

(I) $R^a\text{-CH=CH-}R^b + R^c\text{-CH=CH-}R^d \leftrightarrow R^a\text{-CH=CH-}R^c + R^a\text{-CH=CH-}R^d + R^b\text{-CH=CH-}R^c + R^b\text{-CH=CH-}R^d + R^a\text{-CH=CH-}R^a + R^b\text{-CH=CH-}R^b + R^c\text{-CH=CH-}R^c + R^d\text{-CH=CH-}R^d$

wherein R^a, R^b, R^c, and R^d are organic groups.

[0038] Self-metathesis may be represented schematically as shown in Equation II below.

(II) $R^a\text{-CH=CH-}R^b + R^a\text{-CH=CH-}R^b \leftrightarrow R^a\text{-CH=CH-}R^a + R^b\text{-CH=CH-}R^b$

wherein R^a and R^b are organic groups.

[0039] In particular, self-metathesis of natural oils or cross-metathesis of natural oils with olefins. Suitable olefins are internal or α-olefins having one or more carbon-carbon double bonds, and having between about 2 to about 30 carbon atoms. Mixtures of olefins can be used. The olefin may be a monounsaturated C_2-C_{16} α-olefin, such as a monounsaturated C_2-C_{10} α-olefin. The olefin may also include C_4-C_9 internal olefins. Thus, suitable olefins for use include, for example, ethylene, propylene, 1-butene, *cis*- and *trans*-2-butene, 1-pentene, isohexylene, 1-hexene, 3-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, and the like, and mixtures thereof, and in some examples, α-olefins, such as ethylene, propylene, 1-butene, 1-hexene, 1-octene, and the like. Non-limiting examples of procedures for making fatty acid alkyl esters by metathesis are disclosed in WO 2008/048522, the contents of which are incorporated herein by reference. In particular, Examples 8 and 9 of WO 2008/048522 may be employed to produce methyl 9-decenoate and methyl 9-dodecenoate. Suitable procedures also appear in U.S. Pat. Appl. Publ. No. 2011/0113679, the teachings of which are incorporated herein by reference.

[0040] The metathesis catalyst in this reaction may include any catalyst or catalyst system that catalyzes a metathesis reaction. Any known metathesis catalyst may be used, alone or in combination with one or more additional catalysts. Some metathesis catalysts may be heterogeneous or homogenous catalysts. Non-limiting exemplary metathesis catalysts and process conditions are described in PCT/US2008/009635, pp. 18-47, incorporated by reference herein. A number of the metathesis catalysts as shown are manufactured by Materia, Inc. (Pasadena, CA).

[0041] Cross-metathesis is accomplished by reacting the natural oil and the olefin in the presence of a homogeneous or heterogeneous metathesis catalyst. The olefin is omitted when the natural oil is self-metathesized, but the same catalyst types may be used. Suitable homogeneous metathesis catalysts include combinations of a transition metal halide or oxo-halide (e.g., $WOCl_4$ or WCl_6) with an alkylating cocatalyst (e.g., Me_4Sn). Homogeneous catalysts may include well-defined alkylidene (or carbene) complexes of transition metals, particularly Ru, Mo, or W. These include first and second-generation Grubbs catalysts, Grubbs-Hoveyda catalysts, and the like. Suitable alkylidene catalysts may have the following structure:

$$M[X^1X^2L^1L^2(L^3)_n]=C_m=C(R^i)R^{ii}$$

where M is a Group 8 transition metal, L^1, L^2, and L^3 are neutral electron donor ligands, n is 0 (such that L^3 may not be present) or 1, m is 0, 1, or 2, X^1 and X^2 are anionic ligands, and R^i and R^{ii} are independently selected from H, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, and functional groups. Any two or more of X^1, X^2, L^1, L^2, L^3, R^i and R^{ii} can form a cyclic group and any one of those groups can be attached to a support.

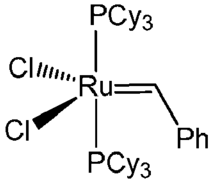
[0042] First-generation Grubbs catalysts fall into this category where m=n=0 and particular selections are made for n, X^1, X^2, L^1, L^2, L^3, R^i and R^{ii} as described in U.S. Pat. Appl. Publ. No. 2010/0145086 ("the ’086 publication"), the teachings of which related to all metathesis catalysts are incorporated herein by reference.

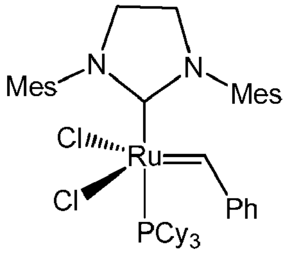
[0043] Second-generation Grubbs catalysts may also have the formula described above, but L^1 is a carbene ligand where the carbene carbon is flanked by N, O, S, or P atoms, such as by two N atoms. The carbene ligand may be part of a cyclic group. Examples of suitable second-generation Grubbs catalysts also appear in the ’086 publication.

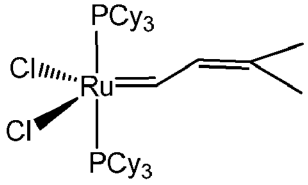
[0044] In another class of suitable alkylidene catalysts, L^1 is a strongly coordinating neutral electron donor as in first- and second-generation Grubbs catalysts, and L^2 and L^3 are weakly coordinating neutral electron donor ligands in the form of optionally substituted heterocyclic groups. Thus, L^2 and L^3 are pyridine, pyrimidine, pyrrole, quinoline, thiophene, or the like.

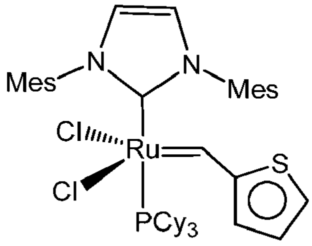
[0045] In yet another class of suitable alkylidene catalysts, a pair of substituents is used to form a bi- or tridentate ligand, such as a biphosphine, dialkoxide, or alkyldiketonate. Grubbs-Hoveyda catalysts are a subset of this type of catalyst in which L^2 and R^2 are linked. A neutral oxygen or nitrogen may coordinate to the metal while also being bonded to a carbon that is α-, β-, or γ- with respect to the carbene carbon to provide the bidentate ligand. Examples of suitable Grubbs-Hoveyda catalysts appear in the ’086 publication.

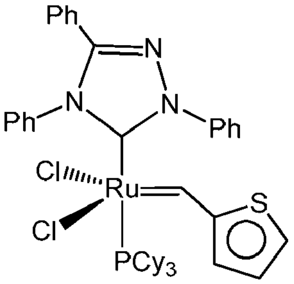
[0046] The structures below provide just a few illustrations of suitable catalysts that may be used:

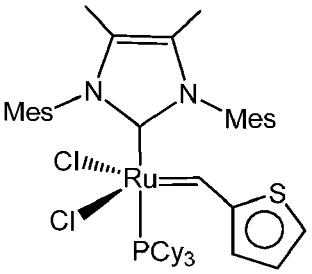












[0047] Heterogeneous catalysts suitable for use in the self- or cross-metathesis reaction include certain rhenium and molybdenum compounds as described, e.g., by J.C. Mol in Green Chem. 4 (2002) 5 at pp. 11-12. Particular examples are catalyst systems that include Re_2O_7 on alumina promoted by an alkylating cocatalyst such as a tetraalkyl tin lead, germanium, or silicon compound. Others include $MoCl_3$ or $MoCl_5$ on silica activated by tetraalkyltins.

[0048] For additional examples of suitable catalysts for self- or cross-metathesis, see U.S. Pat. No. 4,545,941, the teachings of which are incorporated herein by reference, and references cited therein. See also J. Org. Chem. 46 (1981) 1821; J. Catal. 30 (1973) 118; Appl. Catal. 70 (1991) 295; Organometallics, 13 (1994) 635; Olefin Metathesis and Metathesis Polymerization by Ivin and Mol (1997), and Chem. & Eng. News 80(51), Dec. 23, 2002, p. 29, which also disclose useful metathesis catalysts. Illustrative examples of suitable catalysts include ruthenium and osmium carbene catalysts as disclosed in U.S. Pat. Nos. 5,312,940, 5,342,909, 5,710,298, 5,728,785, 5,728,917, 5,750,815, 5,831,108, 5,922,863, 6,306,988, 6,414,097, 6,696,597, 6,794,534, 7,102,047, 7,378,528, and U.S. Pat. Appl. Publ. No. 2009/0264672 A1, and PCT/US2008/009635, pp. 18-47, all of which are incorporated herein by reference. A number of metathesis catalysts that may be advantageously employed in metathesis reactions are manufactured and sold by Materia, Inc. (Pasadena, Calif.).

[0049] Natural oils suitable for use as a feedstock to generate the fatty acid alkyl esters from self-metathesis or cross-metathesis with olefins are well known. Suitable natural oils include vegetable oils, algal oils, animal fats, tall oils, derivatives of the oils, and combinations thereof. Thus, suitable natural oils include, for example, soybean oil, palm oil, rapeseed oil, coconut oil, palm kernel oil, sunflower oil, safflower oil, sesame oil, corn oil, olive oil, peanut oil, cottonseed oil, canola oil, castor oil, linseed oil, tung oil, jatropha oil, mustard oil, pennycress oil, camellina oil, coriander oil, almond oil, wheat germ oil, bone oil, tallow, lard, poultry fat, fish oil, and the like. Soybean oil, palm oil, rapeseed oil, and mixtures thereof are non-limiting examples of natural oils.

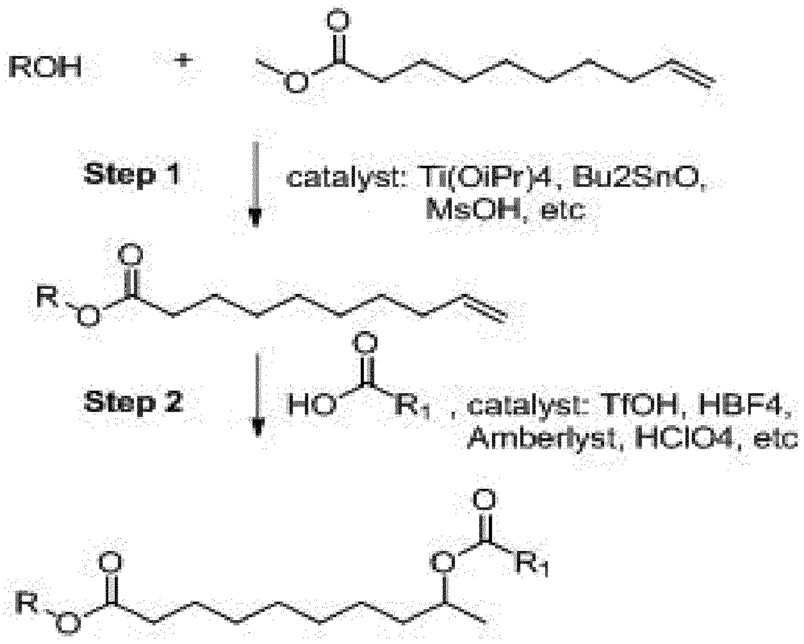
[0050] The fatty acid alkyl esters, including the unsaturated fatty acid alkyl esters, are transesterified under conditions known to a person skilled in the art. Such alcohols can be represented by R-OH, where R is the desired ester group, e.g., a shorter chain hydrocarbon, such as a C_1-C_{20} hydrocarbon, e.g. C_3-C_{15} hydrocarbon. Such hydrocarbon may include alkyl groups, aryl groups, alkenyl groups, alkynyl groups, which may be linear or branched. In some embodiments, the alcohols may include methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, sec.-butanol, tert.-butanol, pentanol, isoamyl, hexanol, cyclohexanol, heptanol, 2-ethyl hexanol, octanol. decanol, undecanol, dodecanol, eicosanol,

[0051] Suitable catalysts for the transesterification reaction include any acidic, non-volatile esterification catalysts, Lewis acids, Bronsted acids, organic acids, substantially non-volatile inorganic acids and their partial esters and heteropolyacids. Particularly suitable esterification catalysts include alkyl, aryl or alkaryl sulfonic acids, such as for example methane sulfonic acid, naphthalene sulfonic acid, p-toluene sulfonic acid, and dodecyl benzene sulfonic acid. Suitable acids may also include aluminum chloride, boron trifluoride, dichloroacetic acid, hydrochloric acid, iodic acid, phosphoric acid, nitric acid, acetic acid, stannic chloride, titanium tetraisopropoxide, dibutyltin oxide, and trichloroacetic acid. These catalysts may be used in quantities of from about 0.1 to 5 percent by weight of the natural oil starting material.

[0052] In some embodiments, the second act is a fatty acid addition that is performed across the double bond(s) of the unsaturated fatty acid alkyl ester. In another embodiment, the third act is a fatty acid addition is performed across the double bond(s) of the unsaturated fatty acid alkyl ester. The fatty acid is a saturated fatty acid, and may be a straight chain or branched acid, and in some examples, a straight chain saturated fatty acid. Some non-limiting examples of saturated fatty acids include propionic, butyric, valeric, caproic, enanthic, caprylic, pelargonic, capric, undecylic, lauric, tridecylic, myristic, pentadecanoic, palmitic, margaric, stearic, nonadecyclic, arachidic, heneicosylic, behenic, tricosylic, lignoceric, pentacoyslic, cerotic, heptacosylic, carboceric, montanic, nonacosylic, melissic, lacceroic, psyllic, geddic, ceroplastic acids.

[0053] The reaction of the saturated fatty acid and the unsaturated fatty acid alkyl ester is catalyzed by a strong acid. The strong acid may be a Lewis Acid, a Bronsted acid, or a solid acid catalyst. Examples of such acids include transition metal triflates and lanthanide triflates, hydrochloric acid, nitric acid, perchloric acid, tetrafluoroboric acids, or triflic acid. Acids may include alkyl, aryl or alkaryl sulfonic acids, such as methane sulfonic acid, naphthalene sulfonic acid, trifluoromethane sulfonic acid, p-toluene sulfonic acid, and dodecyl benzene sulfonic acid. Solid acid catalysts may include include cation exchange resins, such as Amberlyst® 15, Amberlyst® 35, Amberlite® 120, Dowex® Monosphere M-31, Dowex® Monosphere DR-2030, and acidic and acid- activated mesoporous materials and natural clays such a kaolinites, bentonites, attapulgites, montmorillonites, and zeolites. These catalysts may be used in quantities of from about 0.1 to 5 percent by weight of the natural oil starting material.

[0054] The reaction of the saturated fatty acid and the unsaturated fatty acid alkyl ester yields a diester product and isomer mixtures thereof. One non-limiting reaction scheme for the aforementioned synthesis, using 9-DAME as the unsaturated alkyl ester, is shown below:

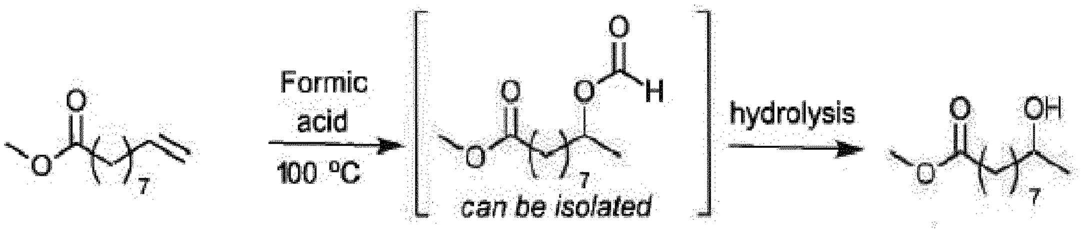


[0055] In the above reaction scheme, R and R1 may be one or more of the following: C_1-C_{20} alkyl, e.g. C_3-C_{20} alkyl, which may be linear or branched, saturated or unsaturated. Other non-limiting diesters are to be shown in the Examples below.

[0056] In some embodiments, the diesters were prepared via a three-act route of transesterification, formic acid addition, and saturated fatty acid addition.

[0057] The transesterification conditions were similar to those described above. The second act is the addition of formic acid across the double bond(s) of the unsaturated fatty acid alkyl ester. Formic acid is distinct in the category of linear monocarboxylic acids in that it is approximately ten times more reactive that its higher carbon number analogues. Specifically, formic acid has a pKa value of 3.75, whereas acetic acid and propionic acid have pKa values of 4.75 and 4.87. The significance of the relatively high acidity of formic acid was the addition of formic acid to the unsaturated fatty acid alkyl ester did not require the addition of strong acid catalysts. The omission of strong acid catalysts can lead to improved product quality, and the production of specific structural isomer products. The use of formic acid has other benefits, as in where free hydroxy species are the target compounds, the preparation of formyloxy esters is advantageous. For example, where acetic acid addition adducts are prepared, saponification of the acetyloxy ester would generate a stoichiometric amount of acetate salt waste. Conversely, the saponification of formyloxy esters would yield aqueous alkaline formate salts.

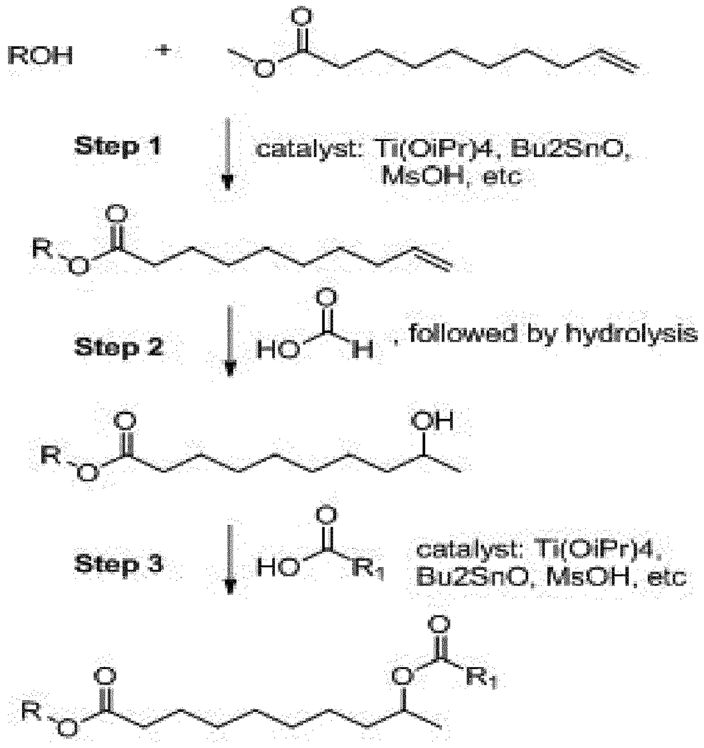
[0058] Using 9-decenoic acid methyl ester as a non-limiting example for the unsaturated fatty acid alkyl ester, formic acid was added to yield a formyloxy derivative (9-OCHO-DAME). This derivative then underwent hydrolysis to yield 9-hydroxy decanoic acid methyl ester. A reaction scheme for this process is shown below:



9-DAMe **9-OCHO-DAMe** **9-OH-DAMe**

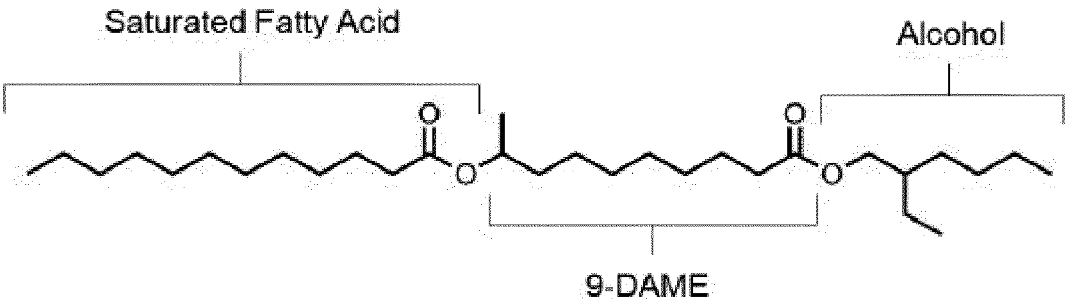
[0059] The hydroxyl group of the 9-hydroxy decanoic acid methyl ester is then esterified with a saturated fatty acid and an esterification catalyst. Some non-limiting examples of saturated fatty acids include propionic, butyric, valeric, caproic, enanthic, caprylic, pelargonic, capric, undecylic, lauric, tridecylic, myristic, pentadecanoic, palmitic, margaric, stearic, nonadecyclic, arachidic, heneicosylic, behenic, tricosylic, lignoceric, pentacoyslic, cerotic, heptacosylic, carboceric, montanic, nonacosylic, melissic, lacceroic, psyllic, geddic, ceroplastic acids. The esterification catalysts may be acidic, non-volatile catalysts, Lewis acids, Bronsted acids, organic acids, substantially non-volatile inorganic acids and their partial esters and heteropolyacids. Particularly suitable esterification catalysts include alkyl, aryl or alkaryl sulfonic acids, such as for example methane sulfonic acid, naphthalene sulfonic acid, p-toluene sulfonic acid, and dodecyl benzene sulfonic acid. Suitable acids may also include aluminum chloride, boron trifluoride, dichloroacetic acid, hydrochloric acid, iodic acid, phosphoric acid, nitric acid, acetic acid, stannic chloride, titanium tetraisopropoxide, dibutyltin oxide, and trichloroacetic acid.

[0060] Another non-limiting reaction scheme for the aforementioned synthesis, using 9-DAME as the unsaturated alkyl ester, is shown below:



[0061] In the above reaction scheme, R and R1 may be one or more of the following: C_1-C_{20} alkyl, e.g. C_3-C_{20} alkyl, which may be linear or branched, saturated or unsaturated.

[0062] Other non-limiting examples of the synthesized diesters may include the following structure:



[0063] The labels indicate the origin of each component. A shorthand nomenclature can be used to describe these compositions. For the above diester, the composition can be labeled C12/9-DA-2EH, to reference the C12 fatty acid, 9-DAME, and 2-ethyl hexanol.

[0064] Other non-limiting diesters are to be shown in the Examples below, which may include isomers thereof, including cis- and trans- isomers.

EXAMPLES

[0065] 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.

[0066] NOACK Volatility (TGA) is a measure of evaporative loss of a lubricating base oil over a period of time. The values reported were measured by ASTM Method ASTM D6375 - 09.

[0067] Pour point was measured by ASTM Method D97-96a. Viscosity/kinematic viscosity was measured by ASTM Method D445-97. Viscosity index was measured by ASTM Method D2270-93 (Reapproved 1998).

Preparation of Diester Starting Material - Procedure for Transesterification of 9-DAME Used to Prepare Various Unsaturated Alkyl Esters

[0068] A 3-neck round bottom flask was fitted with a Dean-Stark trap under a condenser. The reaction vessel was charged with 1.0 molar equivalent of the desired unsaturated fatty acid methyl ester (FAME, e.g. methyl-9-decenoate, methyl-9-dodecenoate), 1.2 molar equivalents of the desired alcohol (e.g. 2- ethylhexanol, 1-octanol, isobutanol), and 10 wt% octanol. The mixture was treated with 0.025 molar equivalents of p-toluenesulfonic acid and the temperature was elevated to 130 °C. To aid removal of methanol, the headspace was continuously purged with nitrogen, and the temperature of the reaction mixture was increased 5 °C every 30 minutes until GC-FID indicated that all FAME had been consumed (e.g., ≤4 hour reaction time). The catalyst was quenched with an equal equivalent of KOH in water (0.1 N concentration). The mixture was then phase separated, and the organic phase was washed with water three times (20 g water / 100 g reaction mixture), dried with $MgSO_4$, and filtered. The unsaturated esters were purified by distillation; isolated yields may be in the range of 75-90% of the theoretical yield.

Procedure for Preparation of Diesters

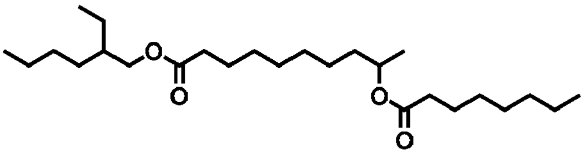
[0069] In a 2-neck RBF fitted with a heating mantel and stir bar, 1.0 mol equivalents of unsaturated alkyl ester with 1.25 mol equivalents of the saturated fatty acid and 5.0 wt% triflic acid were combined. Reagents were stirred for 18 hours at 60° C, to provide that reaction is absent of water, especially on humid days (hydrolysis of ester can cause many side products). The triflic acid was quenched with an equal molar equivalent of 5 M KOH in water (e.g., If reaction uses 7 mmol TfOH, quench with 7 mmol of KOH in water). Water washing occurred three times, with an effort not to use any brine. A pH strip was used to provide the pH is greater than ~6.5 before distillation (as decomposition may occur). Distillation occurred at <2 Torr (head temperature may be >230°C, pot temp >245°C). Add a plug of dry basic alumina (0.5" - 1" of alumina) to a fritted funnel and filter with a very weak vacuum (~650 Torr). If acid value was > ~0.5 mg KOH/g, repeat filtration over the same plug of alumina. Before disposal of the alumina, stirring with 5% EtOAc in Hexanes to release residual diester occurred. This portion can be thoroughly evaporated and then combined with the bulk product. If lower acid numbers are desired, it might be useful to take up the product in hexanes prior to filtration through alumina. There are also a number of products other than basic alumina which are commonly used to reduce acid number by filtration, e.g. Florisil - a magnesium silicate. The isolated yield may be 35 - 45%.

Example 1 - caprylic (octanoic) acid

C8:0 / 2-EH-9-DA

[0070] A mixture of 2-ethylhexyl-9-decenoate (≥98%, 200 g, 0.708 mol) and octanoic acid (Sigma Aldrich, ≥98%, 306 g, 2.12 mol) was treated with trifluoromethanesulfonic acid (Sigma Aldrich, 98%, 10 g, 0.067 mol). The mixture was stirred at 60 °C for 18 h. The mixture was cooled to 25 °C and washed with 3 x 100 mL of saturated aqueous sodium bicarbonate and 100 mL brine. The organic phase was dried over magnesium sulfate and filtered. The product was recovered by vacuum distillation at 210 °C - 220 °C, 2 Torr; light fractions and bottoms were discarded. The precipitate was removed by vacuum filtration through a fritted funnel to provide 103 g of colorless oil. Physical properties were reported as follows: Kinematic Viscosity (KV) at 100°C was 3.24 cSt, KV at 40°C was 12.02 cSt, Viscosity Index (VI) 143, pour point <-45 °C, NOACK volatility 15 wt%.

[0071] In one particular aspect, the diester is represented by the structure



which also may be referred to herein as 2-ethylhexyl 9-(octanoyloxy)decanoate.

C8:0 / octyl-9-DA

[0072] Octyl-9-decenoate (>98%, 200 g, 0.708 mol) and octanoic acid (Aldrich, ≥98%, 306 g, 2.12 mol) were treated with trifluoromethanesulfonic acid (Sigma Aldrich 98%, 10 g, 0.067 mol). The mixture was stirred at 60 °C for 20 h. At room-temperature, a saturated solution of NaHCO3 (250 mL) was added to the reaction vessel and stirred for 30 minutes. The mixture was transferred to a separatory funnel and phase separated. The organic phase was washed with brine (200 mL x 3), dried over MgSO4, and distilled at 234°C, 2 torr. The distillate was washed again with water and dried by rotary evaporation to yield 77 g of clear colorless oil. Physical properties were reported as follows: KV at 100°C was 3.16 cSt, KV at 40°C was 11.3 cSt, VI 151, NOACK volatility 10 wt%. The diester may be referred to herein as octyl-9-(octanoyloxy)decanoate. This is ester of formula I(a)

Example 2 - capric (decanoic) acid

C10:0 / 2-EH-9-DA

[0073] A mixture of 2-ethylhexyl-9-decenoate (≥98%, 400 g, 1.42 mol) and decanoic acid (Aldrich, ≥98%, 489 g, 2.83 mol) was treated with trifluoromethanesulfonic acid (20 g, 0.133 mol). The mixture was stirred at 60 °C for 20 h. The mixture was cooled to 25 °C and quenched with 150 mL of 1 M KOH which resulted in formation of a precipitate. Water was added to the mixture and stirred rigorously. The resulting emulsion was transferred to a separation vessel and phase separated. The mixture was washed continuously with 5 x 150 mL H2O. The product was recovered by vacuum distillation at 225°C, 2 Torr; light fractions and bottoms were discarded. Distillation yielded 223.1 g of product as a mixture of isomers, 99% pure by GC-FID. Physical properties were reported as follows: KV at 100 °C was 3.6 cSt, KV at 40 °C was 14.1 cSt, VI 145, pour point <-45°C, NOACK volatility 10 wt%.

C10:0 / 2-EH-9-DA

[0074] A mixture of 2-ethylhexyl-9-decenoate (≥98%, 800 g, 2.83 mol) and decanoic acid (Aldrich, ≥98%, 490.2 g, 2.84 mol) was treated with trifluoromethanesulfonic acid (Aldrich, ≥98%, 40 g). The mixture was stirred at 60 °C for 20 h. The reaction mixture was then cooled to room temperature and 67 g of $NaHCO_3$ was added. The suspension was stirred continuously for >24 hours, until pH strip indicated pH ≥ 6 (neutralization is also indicated by bleaching of the dark reaction mixture to yellow). The mixture was gravity filtered, and the product was recovered by vacuum distillation at 224°C, 2 Torr; starting materials were recovered as light fractions and the bottoms were discarded. The major fraction was gravity filtered to yield the product as a colorless oil (397 g, 0.87 mol). Light fractions during distillation were combined to provide a 512 g mixture containing 2-ethylhexyl-9-decenoate (69 w% by GC-FID) and decanoic acid (26 w% by GC-

FID). The entire quantity was treated with trifluoromethanesulfonic acid (Aldrich, ≥98%, 10 g) and stirred for 18 h at 60°C. At room temperature, the mixture was stirred with $NaHCO_3$ (17g, 0.2 mol) until pH ≥ 6. Purified by vacuum distillation at 224°C, 2 Torr to give the product as a colorless oil (170 g, 0.37 mol). The product fractions obtained over two reactions were combined and purity was verified by GC-FID. Physical properties were reported as follows: KV at 100° C was 3.6 cSt, KV at 40°C was 14.0 cSt, VI 146, pour point <-45 °C, NOACK volatility 10%.

Example 3 - Lauric Acid

C12:0/2-ethylhexyl-9-decenoate

[0075] A mixture of 2-ethylhexyl-9-decenoate (≥98%, 200g, 0.708 mol) and dodecanoic acid (Sigma Aldrich, ≥98%, 425 g, 2.12 mol) was heated to 60°C then treated with trifluoromethanesulfonic acid (Sigma Aldrich, ≥98%, 10 g, 0.067 mol). The reaction was stirred at 60°C for 22 h. The reaction mixture was then cooled to 45°C and 100 mL of hexanes was added. The contents of the reaction vessel was transferred to a drop funnel and dodecanoic acid was recrystallized out of solution by dropwise addition of the mixture into isopropanol at -20°C. The resulting suspension was vacuum filtered through Whatman 6 filter paper. The filtrate was concentrated in vacuo and the oil was washed with a 0.1 M aqueous solution of K_2CO_3 until pH was 7, then washed with water. The organic phase was dried over Na_2SO_4 then purified by vacuum distillation at 218°C, 0.1 Torr to give 69 g of oil. The distillate was passed through a bed of Al_2O_3 to give a clear colorless oil. KV at 100°C was 3.97 cSt, KV at 40°C was 15.62 cSt, VI 160.6, pour point -40°C, NOACK volatility 5.5 wt%. The synthesized diester may be referred to as 10-[(2-ethylhexyl)oxy]-10-oxodecan-2-yl dodecanoate. This is ester of formula I(b).

C12:0/iBu-9-decenoate

[0076] Isobutyl-9-decenoate (≥98%, 399.2 g) and dodecanoic acid (Sigma Aldrich, ≥98%, 1056g, 5.3 mol) were combined. The mixture was heated to 60 °C then treated with trifluoromethanesulfonic acid (Sigma Aldrich, ≥98%, 20g, 0.13 mol). The reaction was stirred at 60 °C for 22 h. Lauric acid was precipitated by dropwise addition of the reaction mixture into a dry ice bath of isopropanol. The suspension was cold-filtered. The filtrate was concentrated in vacuo then transferred into a separatory funnel and washed with water (150 mL x 7). The organic phase was dried with Na_2SO_4, and purified by distillation. The major fraction was obtained as 292 g of oil at 215 °C, 0.1 Torr. The distillate was filtered through basic alumina. KV at 100°C was 3.35 cSt, KV at 40 °C was 12.24 cSt, VI 154, pour point <-18°C, NOACK volatility 12 wt%.

C10:0/2-ethylhexyl-9-dodecenoate

[0077] 2-ethylhexyl-9-dodecenoate (≥98%, 416 g, 1.47 mol) and dodecanoic acid (Sigma Aldrich, ≥98%, 357 g, 2.07 mol) were treated with trifluoromethanesulfonic acid (Sigma Aldrich, 98%, 20 g, 0.13 mol) and stirred at 60°C for 18 h. The reaction was cooled to 25°C while stirring and the catalyst was quenched within the reaction vessel by dropwise addition of KOH solution (7.5 g KOH in 75 mL H2O). The mixture was transferred to a separatory funnel and phase separated. The organic phase was washed with of DI water (200 mL x 2), dried over $MgSO_4$, and filtered. The product was purified by distillation at 224°C, <1 Torr and vacuum filtration through Al_2O_3 on a fritted funnel at 650 Torr to yield 230 g of clear yellowish oil. KV at 100°C 3.9 cSt, KV at 40°C 15.7 cSt, VI 149, pour point <-45°C, NOACK volatility 6.0 wt%.

C12:0/2-ethylhexyl-9-decenoate

[0078] 9-OH-2-Ethylhexyldecanoate (50 g, 0.17 mol), dodecanoic acid (40g), methanesulfonic acid (0.8 g) and toluene (200 mL) were added to a 500 mL 3-necked round-bottom flask at 23 °C under an atmosphere of air. The flask was then fitted with a thermocouple temperature regulator with heating mantle, Dean-Stark distillation trap with water condenser. The top of the condenser was fitted with a rubber stopper with nitrogen needle inlet. Through the headspace of the apparatus was passed N_2 (flow rate = 2.5 ft^3/hr) for 10 minutes, and subsequently, the temperature was increased to 125 °C. After approximately 8 hours approximately 3 mL of water was collected in the trap and the Dean-Stark trap was replaced with a distillation head and receiving flask and the toluene was removed via distillation. Vacuum (2 Torr) and the temperature was increased to 150 °C to remove the excess dodecanoic acid. After 1 hour no more distillate was observed and the crude product was filtered through basic alumina oxide. The product was isolated as a slight yellow oil, 45 g (55%). KV at 100° C 3.9 cSt, KV at 40°C 15.78 cSt, VI 157, pour point <-45°C.

[0079] Each of the three components of the diester compositions (methyl ester, alcohol, and saturated fatty acid) impart predictable performance qualities on the final structure. Thus, the properties of a diester may be tuned to fit within specific performance specifications by carefully selecting the combination of starting materials.

Example 4 - Formic Acid

Methyl- 9-decenoate/formic acid

[0080] Methyl -9-decenoate (50 g, 0.27 mol) and formic acid (100 mL) were added to a 250 mL 2-necked round bottom flask at 23 °C under an atmosphere of air. The flask was then fitted with a thermocouple temperature regulator with heating mantle and water condenser. The top of the condenser was fitted with a rubber stopper with nitrogen needle inlet. Through the headspace of the apparatus N_2 (flow rate = 2.5 ft^3/hr) for 10 minutes, and subsequently, the temperature was increased to 105 °C. After approximately 15 hours, the heating source was removed and the reaction was allowed to cool to ambient temperature. An aliquot was taken for GCMS (method GCMS1) to evaluate conversion. The reaction mixture was transferred to a single-neck round bottom flask and the excess formic acid was removed by rotorary evaporator (50 Torr, 35 °C). 9-OCHO-DAMe was obtained as a slight yellow/brown oil, 60.15 g (97%) and used without further purification.

2-Ethylhexyl 9-decenoate/formic acid

[0081] 2-Ethylhexyl 9-decenoate (282 g, 1 mol) and formic acid (460g) were added to a 2 L 3-necked round-bottom flask at 23 °C under an atmosphere of air. The flask was then fitted with a thermocouple temperature regulator with heating mantle and water condenser. The top of the condenser was fitted with a rubber stopper with nitrogen needle inlet. Through the headspace of the apparatus was passed N_2 (flow rate = 2.5 ft^3/hr) for 10 minutes, and subsequently, the temperature was increased to 105 °C. After approximately 15 hours, additional formic acid (200g) was added and the reaction was continued. Following an additional 24 hours the heating source was removed and the reaction was allowed to cool to ambient temperature. An aliquot was taken for GCMS (method GCMS1) to evaluate conversion. The reaction mixture was transferred to a single-neck round bottom flask and the excess formic acid was removed by rotorary evaporator (50 Torr, 35 °C), followed by vacuum distillation (2 Torr, 125 °C). 9-OCHO-2-ethylhexyldecanoate was obtained as a slight yellow/brown oil, 320 g (97%). In a single neck, 1 Liter round-bottom flask was added 9-OCHO-DAEH and 6 M aqueous potassium hydroxide solution. The reaction flask was fitted with a reflux condenser and heated to reflux for 24 hours. The reaction was allowed to cool, the layers were separated and the organic product was dried by vacuum stripping (5 Torr, 100 °C) for 1 hour to obtain the desired 9-OH-2-ethylhexyldecanoate as a slight brown oil, 275 g (91%).

[0082] The table below shows the physicochemical characteristics of esters of formulas I(a) and I(b). These esters were compared with various base oils. These esters are thus compared to a group III base oil (YUBASE4) and to a trimethylol propane ester known for good performance (NYCOBASE 7300 or NB7300).

Table 1: Physicochemical characteristics of esters of formulas I(a) and I(b) in comparison with other base oils.

Characteristic	Method	Units	YUBASE4	NB7300	ESTER I(a)	ESTER I(b)
KV 40°C	ASTM D445-97	mm^2/s	19.4	14	11.3	15.62
KV 100°C	ASTM D445-97	mm^2/s	4.24	3.4	3.16	3.97
VI	ASTM D2270-93	No unit	126	118	151	160
VI: Viscosity index KV: Kinematic viscosity						

[0083] The two esters were evaluated in 0W-20 engine formula, together with a known additive package, namely Pack Infineum P6660. SV261 is a known VI improver of Infineum, which is a Poly Isobutene Styrene Hydrogenated (PISH). Infineum V385 is a known Pour Point Depressant.

[0084] The formulas prepared are grade 0W-20 formulas. They were carried out at iso-HTHS (2.6 mPa.s). HTHS is the value at High Temperature High Shear. The compositions and characteristics of the formulas tested are given in the table below

Composition			
	Comp	Ester I(a)	Ester I(b)
P6660	13.30	13.30	13.30
SV261	3.60	3.60	3.60
INFINEUM V385	0.20	0.20	0.20
YUBASE 4	82.90	72.90	72.90
ESTER I(a)		10.00	
ESTER I(b)			10.00

Physicochemical characteristics				
Ex		Comp	Ester I(a)	Ester I(b)
KV at 40°C	mm^2/s	44.26	40.70	42.63
KV at 100°C	mm^2/s	8.311	7.828	8.179
VI	No Unit	166	166	170
HTHS	mPa.s	2.59	2.6	2.60
Density (15°C)	kg/m^3	849.7	861.1	856.6
CCS (-35°C) ASTM D5293	mPa.s	6520	5340	5750
MRV (ASTM D4684)	mPa.s	54600	30600	34300

[0085] The compositions according to the invention (Ester I(a) and Ester I(b)) have an improved « cold » behaviour.

Detergency

[0086] A Micro Coking Test (MCT) is performed to assess the detergency of the esters of the invention. The standard applied is GFC-Lu-027-T-07.

[0087] The results are in the below table.

MCT test			
Ex	Comp	Ester I(a)	Ester I(b)
Cotation meth	7.1	7.8	8.4
Temp at initial point	252	254	249

Engine tests.

Engine cleanliness.

[0088] The following compositions are prepared.

Composition			
	Comp.	Ester I(a)	Ester I(b)
Additive package	10.9	10.9	10.9
SV261	6.5	6.5	6.5
MoDTC	0.1	0.1	0.1

(continued)

<table>
<tr><th colspan="5">Composition</th></tr>
<tr><td></td><td>Comp.</td><td colspan="2">Ester I(a)</td><td>Ester I(b)</td></tr>
<tr><td>YUBASE 4+</td><td>62.5</td><td colspan="2">62.5</td><td>62.5</td></tr>
<tr><td>YUBASE 6</td><td>10.0</td><td colspan="2">10.0</td><td>10.0</td></tr>
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<tr><td>ESTER I(a)</td><td></td><td colspan="2">10.0</td><td></td></tr>
<tr><td>ESTER I(b)</td><td></td><td colspan="2"></td><td>10.0</td></tr>
<tr><td colspan="5"></td></tr>
<tr><td colspan="5">Physicochemical characteristics</td></tr>
<tr><td>Ex</td><td></td><td>Comp</td><td>I(a)</td><td>I(b)</td></tr>
<tr><td>KV at 40°C</td><td>mm^2/s</td><td>53.16</td><td>50.34</td><td>50.87</td></tr>
<tr><td>KV at 100°C</td><td>mm^2/s</td><td>9.93</td><td>9.74</td><td>9.76</td></tr>
<tr><td>VI</td><td>No Unit</td><td>176</td><td>183</td><td>181</td></tr>
<tr><td>HTHS</td><td>mPa.s</td><td>2.9</td><td>2.88</td><td>2.9</td></tr>
</table>

[0089] The test that is used to determine cleanliness is based on the piston merit. Each lubricant composition (10 kg) was evaluated in a test of cleanliness diesel common rail (common rail) for automobile. The engine is a 1.4L 4 cylinders engine. Its power is 80 kW. The cycle time of the test is 96 hours, alternating idle and 4000rpm regime. The temperature of the lubricating composition is 145°C and the temperature of the cooling water system is 100°C. No drain nor any extra to lubricating composition is made during the test. Fuel EN590 is used. The test is performed in two phases for a total of 106 hours and in a first rinsing step and lapping for 10 hours and then in a second step with the composition to be evaluated(4 kg), and finally according to an endurance step with a duration of 96 hours with the composition to be evaluated (4 kg). During the test, one evaluates the physicochemical parameters of the lubricant. Then the lubricant consumption during lapping and during the test.

[0090] The results are summarized in the below table.

Ex.	Co-base	Piston
Comp.	PAO	65.75
Ester I(a)	Ester I(a)	70.76
Ester I(b)	Ester I(b)	72.27

[0091] The choice of the reference (PAO) is correct with a score of 65 which is already high as is expected for PAOs. The present esters are thus compared to a good formula for a cleanliness standpoint, and it can be seen that the esters I(a) and I(b) improve both this scoring value by 5 and 7 points, respectively.

Fuel economy

[0092] The following compositions are prepared. OLOA 249SX is an over-based sulphonate detergent from Oronite.

Composition			
	Comp.	Ester I(a)	Ester I(b)
Additive package	10.6	10.6	10.6
SV261	6.2	6.2	6.2
MoDTC	0.5	0.5	0.5
OLOA 249SX	0.7	0.7	0.7

(continued)

<table>
<tr><th colspan="5">Composition</th></tr>
<tr><td></td><td>Comp.</td><td colspan="2">Ester I(a)</td><td>Ester I(b)</td></tr>
<tr><td>YUBASE 4+</td><td>72.0</td><td colspan="2">72.97</td><td>72.7</td></tr>
<tr><td>NICOBASE 7300</td><td>10.0</td><td colspan="2"></td><td></td></tr>
<tr><td>ESTER I(a)</td><td></td><td colspan="2">9.03</td><td></td></tr>
<tr><td>ESTER I(b)</td><td></td><td colspan="2"></td><td>9.3</td></tr>
<tr><td colspan="5"></td></tr>
<tr><td colspan="5">Physicochemical characteristics</td></tr>
<tr><td>Ex</td><td></td><td>Comp</td><td>I(a)</td><td>I(b)</td></tr>
<tr><td>KV at 40°C</td><td>mm^2/s</td><td>41.25</td><td>42.04</td><td>43.28</td></tr>
<tr><td>KV at 100°C</td><td>mm^2/s</td><td>8.43</td><td>8.51</td><td>8.64</td></tr>
<tr><td>VI</td><td>No Unit</td><td>187</td><td>185</td><td>183</td></tr>
<tr><td>HTHS</td><td>mPa.s</td><td>2.62</td><td>2.59</td><td>2.63</td></tr>
</table>

[0093] The test is run on an engine of 2.0L displacement and maximum power 180kW, driven by an electric motor generator. The various lubricant compositions are compared with a reference lubricating composition (SAE 0W-30). Each friction measurement is performed for about 12 hours and enables a detailed mapping of the friction torque induced by each lubricant composition. The tests are performed in the following sequence:

- rinsing of the engine with a rinsing oil with detergents as additive followed by rinsing with the lubricant reference composition,
- friction measurement of torque at four temperatures with the reference composition,
- rinsing of the engine with a rinsing oil with detergents as additive followed by rinsing with the lubricating composition to be evaluated,
- friction measurement of torque at four temperatures with the lubricating composition to be evaluated,
- rinsing of the engine with a rinsing oil with detergents as additive followed by rinsing with the reference composition,
- friction measurement of torque at four temperatures with the lubricant reference composition,

[0094] The ranges of variation of the regime and the temperature levels were chosen to cover the most representative operating points of the NEDC certification cycle. 4 selected temperature levels are consistent with the cycles considered.

[0095] The instructions implemented are:

- water temperature in engine output: 40°C/60°C/90°C/110°C ± 2°C,
- oil temperature ramp: 40°C/60°C/90°C/110°C ± 2°C,
- air temperature at the inlet: 21 °C ± 2°C
- backpressure at exhaust: 40 mbar at 4000 rpm

[0096] Friction gain is evaluated for each lubricant composition according to the temperature and the engine speed measured and compared to friction for the lubricant reference composition.

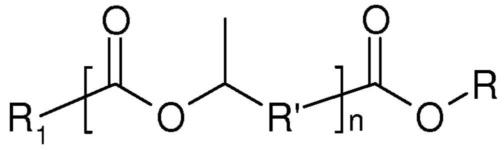
[0097] From these friction gains and after processing by a transfer function, it is estimated friction gains and loss on the NEDC standardized approval cycle resulting from the use of lubricating compositions

Ex.	Gain / Loss
Ester I(a)	-0.03%
Ester I(b)	-0.05%

[0098] The choice of the reference (NB7300) is driven by the fact that NB7300 is known for providing elevated fuel economy. The results indicate that the three formulas are at least equivalent, if not better, from a fuel economy standpoint with gains of 0.05% and 0.03%.

Claims

1. Lubricant composition comprising at least one compound of formula (I) below and at least one viscosity index improver



(I)

wherein :

n is below 1.1
R1 represents a linear or branched, saturated or unsaturated C3-C20,
R' represents a linear or branched, saturated or unsaturated C2-C16,
R represents a linear or branched, saturated or unsaturated C1-C20.

2. Lubricant composition of claim 1, wherein in the formula (I):

n is 1;
the total amount of carbon atoms being more than 15 and less than 40.

3. Lubricant composition of claim 1 or 2, wherein in the formula (I):

R1 represents a linear or branched, saturated or unsaturated C5-C15 alkyl group;
R' represents a linear or branched, saturated or unsaturated C3-C8 alkyl group;
R represents a linear or branched, saturated or unsaturated C1-C15 alkyl group.

4. Lubricant composition according to any one of claims 1 to 3, wherein in the compound of formula (I), R1 represents a saturated linear C5-C15 alkyl group, more preferably a saturated linear C5-C12 alkyl group; R' represents a saturated linear C3-C8 alkyl group, more preferably a saturated linear C5-C8 alkyl group; R represents a saturated linear or branched C5-C15 alkyl group, more preferably a saturated linear or branched C5-C10 alkyl group.

5. Lubricant composition according to any one of claims 1 to 4, wherein in the formula (I):

R1 represents a saturated linear C5-C10 alkyl group, more preferably a saturated linear C5-C8 alkyl group;
R' represents a saturated linear C5-C8 alkyl group;
R represents a saturated, linear or branched C5-C10 alkyl group, preferably a saturated linear C5-C10 alkyl group.

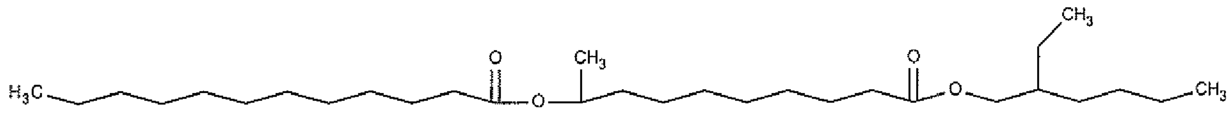
6. Lubricant composition according to claim 5, wherein the compound of formula (I) is a compound of formula (Ia)

(Ia)

7. Lubricant composition according to any one of claims 1 to 4, wherein in the formula (I):

   R1 represents a saturated linear or branched C5-C15 alkyl group, more preferably a saturated linear C8-C12 alkyl group;
   R' represents a saturated linear C5-C8 alkyl group;
   R represents a saturated, linear or branched C5-C10 alkyl group, preferably a saturated branched C5-C10 alkyl group.

8. Lubricant composition according to claim 7, wherein the compound of formula (I) is a compound of formula (Ib)



(Ib)

9. Lubricant composition according to any one of claims 1 to 8, wherein the viscosity index improver is a polymeric viscosity index improver, preferably chosen among :

   polyacrylates and polymethacrylates,
   olefin homopolymers or copolymers, preferably ethylene/propylene styrene copolymers, preferably with isoprene or a diene such as butadiene,
   hydrogenated or not, isoprene polymers, preferably radial hydrogenated polyisoprene,
   esterified polystyrenes, preferably esterified poly(styrene-co-maleic anhydride) mixtures of two or more of the above.

10. Lubricant composition according to any of the previous claims comprising from 0,1 to 50%, preferably from 1 to 50%, more preferably from 5 to 30% by weight based on the total weight of lubricant composition, of a compound of formula (I).

11. Lubricant composition according to any of the previous claims comprising from 0,01 to 15%, preferably from 1 to 10% by weight based on the total weight of lubricant composition, of at least one viscosity index improver.

12. Lubricant composition according to any of the previous claims further comprising at least one lubricant base oil.

13. Lubricant composition according to any of the previous claims, wherein the lubricant base oil is a group III lubricant base oil.

14. Lubricant composition according to any of the previous claims, comprising from 50 to 99%, preferably from 50 to 80% by weight based on the total weight of lubricant composition, of a lubricant base oil.

15. Lubricant composition according to any of the previous claims further comprises further at least one lubricant additive selected from the list consisting of detergent additives, anti-wear additives, friction modifiers additives, extreme pressure additives, antioxidant additives, dispersing agents, pour-point depressant additives, anti-foam agents, thickeners and mixtures of two or more thereof.

16. Use of a lubricant composition according to any of the previous claims to reduce the fuel consumption of an engine, preferably of a car engine and/or to improve the cleanliness of an engine, preferably of a car engine, more preferably of at least one piston of a car engine.

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EUROPEAN SEARCH REPORT

Application Number
EP 15 17 9371

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2015/094246 A1 (BREDSGUARD JAKOB [US]) 2 April 2015 (2015-04-02) * paragraph [0005] - paragraphs [0011], [0082], [0086], [0087] * * paragraph [0145] * * paragraph [0133] * * paragraphs [0125], [0126] * * paragraphs [0160], [0172] * -----	1-16	INV. C10M101/02 C10M105/34 C10M105/42 C10M129/70 C10M129/78
A	US 2013/158277 A1 (THOMPSON TRAVIS [US] ET AL) 20 June 2013 (2013-06-20) * the whole document * -----	1-15	
A	WO 98/10041 A1 (EXXON CHEMICAL PATENTS INC [US]) 12 March 1998 (1998-03-12) * page 1, line 4 - line 14 * -----	1-16	
A	WO 2011/037778 A1 (DOW GLOBAL TECHNOLOGIES INC) 31 March 2011 (2011-03-31) * page 1, paragraph 0001 * * page 4, paragraph 0013 - page 5 * -----	1-15	TECHNICAL FIELDS SEARCHED (IPC)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	18 December 2015	Kaluza, Nora

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 15 17 9371

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