(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 483 233 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
15.05.2019 Bulletin 2019/20

(51) Int Cl.:
C10M 105/36 *(2006.01)*

(21) Application number: **17200996.1**

(22) Date of filing: **10.11.2017**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA MD

(71) Applicant: **ARKEMA FRANCE**
92700 Colombes (FR)

(72) Inventors:
- **DUBOIS, Jean-Luc**
69390 MILLERY (FR)
- **COUTURIER, Jean-Luc**
69006 LYON (FR)
- **ASADAUSKAS, Svajus**
10314 VILNIUS (LT)
- **LABANAUSKAS, Linas**
10345 VILNIUS (LT)

(74) Representative: **Killis, Andréas**
ARKEMA France
Département Propriété Industrielle
420, rue d'Estienne d'Orves
92705 Colombes Cedex (FR)

(54) LUBRICANT BASE OIL COMPOSITIONS OF MONO-UNSATURATED DIBASIC ACID ESTERS WITH BRANCHED ALCOHOLS

(57) The present invention relates to the use of a composition of dibasic esters of monounsaturated linear α, ω-diacids as a lubricant constituent, said composition comprising from 60 to 100% by weight:
according to option a) of at least one monounsaturated α-ω dibasic ester compound of Formula (I) :

$$R1\text{-}OOC\text{-}(CH_2)_x\text{-}CH{=}CH\text{-}(CH_2)_y\text{-}COO\text{-}R2$$

with
x + y being an integer in the range from 10 to 22,
and with R1 and R2 being identical or different and being selected from the residues of branched alcohols with at least 5 carbon atoms (in C_5) with said branched alcohols being either saturated or mono unsaturated and bearing at least one branch in C_1 to C_6 or according to option b) of a mixture comprising :
b1) at least one monounsaturated α-ω dibasic ester compound of Formula (I) as defined above in option a) and
b2) at least one monounsaturated α-ω dibasic ester compound of Formula (II) :

$$R'1\text{-}OOC\text{-}(CH_2)_x\text{-}CH{=}CH\text{-}(CH2)y\_COO\text{-}R'2 \text{ (II)}$$

with
x + y being as defined in Formula (I) above ;
and with R'1 and R'2 being identical or different and selected from the residues of methanol or ethanol,
said composition having a weight content in estolides of the corresponding mono unsaturated acids of less than 1% w/w.

The invention further relates to a lubricant composition issued from said use and its use in transport, agriculture, food and industrial applications.

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Description

[0001] The present invention relates to the use of a dibasic ester composition comprising specific monounsaturated α-ω dibasic ester compounds, as a main component in a lubricant ("basestock") or an additive in lubricant compositions, the lubricant composition resulting from such a use, its related uses. More particularly, said composition is used in lubricant basestocks which are issued from renewable resources and which are degradable in the environment ("biodegradable" may be used in the present invention with same meaning). These compositions present specific improved performances with respect to prior art known lubricant components, in particular improved fluidity at low temperatures (with respect to cold storage), excellent resistance to viscosity change with temperature ("Viscosity Index") and improved non-volatility.

[0002] More particularly, the said dibasic ester compositions and compounds are issued from linear monounsaturated α-ω dicarboxylic acids ("fatty diacids") and do not contain either branched isomers or estolide compounds derived from fatty diacids. Particularly, detrimental are estolides, representing products of addition of the carboxy group of one fatty diacid on the unsaturation of anotherfatty diacid with a resulting middle-chain esterfunction. Preferably, estolide compounds, if present in the linear monounsaturated fatty diacids used for preparing the dibasic ester compositions of the present invention are in a content of less than 1% w/w more preferably of less than 0.1% or less than 0.05% and even more preferably, the content is 0% of estolides with respect to the weight of said dibasic ester composition. The absence of estolide in the case of the present invention is verified by ^{13}C NMR by the absence of a characteristic peak at 71 ppm corresponding to estolides. Such a content is possible by using metathesis reaction route for preparing the said linear monounsaturated fatty diacids or esters from which are issued the dibasic ester compounds and related compositions of the present invention (see scheme in Fig. 1). In fact, the only prior art where lubricant application of dibasic esters from monounsaturated linear α-ω fatty diacids is mentioned is Yasa, S.R. et al. "Synthesis of 10-undecenoic acid based C22-dimer acid esters and their evaluation as potential lubricant basestocks", published in "Industrial Crops & Products", 2017, 103, 141-151, Elsevier Edition. However, the disclosed products are compositions of various C_{22}-dimer esters, containing dibasic esters from mostly branched monounsaturated α-ω diacids (over 50%), only with some linear monounsaturated α-ω homologues as well as branched estolide compounds and other pyrolysis / esterification products of 10-undecenoic acid. Abundance of branched isomers in reported C_{22}-dimer esters is admitted by authors in this reference and it is also obvious to a person skilled-in-art from low solidification temperatures and Viscosity Index values that branched structures are involved. Significant presence of C_{22} estolides in addition to identified α-ω diacids is evident from much lower acidity than expected theoretically. One of the drawbacks of the presence of significant amounts of estolide compounds is that for a formulated mixture exposed to metal surfaces and to degradation products, a significant estolide fraction will tend to be present in a separate phase from that of linear C_{22}-dimer esters, which fact is harmful for the lubricant, because the functional additives do migrate to the different phases and consequently do perform inefficiently or negatively. This causes wear, corrosion, foaming, haziness and other problems, which jeopardize lubricant performance. The abundance of branched C_{22}-dimer esters also has some negative implications, particularly due to faster viscosity reduction with heating, as expressed by Viscosity Index (VI). Other disadvantages of branched esters, compared with the linear ones, which are well known to a person skilled-in-art, include reduced biodegradability, poorer molecular packing properties and other factors, not-considered in the above report. In conclusion, depending on the origin of the linear mono unsaturated fatty diacids and consequently, depending on the presence or absence of branched fatty diacid isomers and estolides, the lubricants performances will be significantly different between the esterified compounds of the present invention and the compounds as disclosed by the cited prior art (presence of significant amounts of branched α-ω diacids and estolides as a major part or component of said C_{22} diacids composition prepared by dimerization).

[0003] Vegetable oils, fatty derivatives and synthetic esters of petrochemical origin, such as adipate esters or esters of polyhydric alcohols are used as biodegradable basestocks in lubricant formulation for transport, agriculture and industrial applications. The basestock usually comprises around 80-100% w/w of lubricant with remaining 0-20% taken up by additives to impart necessary rheology, low friction, anti-wear properties, low temperature fluidity, corrosion resistance, elastomer compatibility, oxidative stability, water rejection, foam inhibition, air release, microbial resistance, odor, color and many other characteristics. Although many parameters are highly sensitive to the additive use, some key properties, such as low volatility, long term cold storage and biodegradability cannot be improved by using additives. Many other properties are mostly defined by the basestock with only limited capability of the additives to improve them. Viscosimetric properties, low temperature fluidity, volatility, oxidative stability and solvency of the lubricants are primarily determined by the basestock.

[0004] In the recent prior art, a fair amount of attention has been given to metathesis as having potential for producing new types of biobased fluids. Mono-unsaturated α-ω dibasic acids represent one of notable materials, which can be obtained via metathesis, see Ngo, H.L. et al. in "Metathesis of Unsaturated Fatty Acids: Synthesis of Long Chain Unsaturated-α,ω- Dicarboxylic Acids", published in JAOCS, Journal of the American Oil Chemists' Society 2006, 83 (7), 629 - 634, Springer Edition.

[0005] Esterification of the carboxyls (rather than double bonds) in mono-unsaturated α,ω dibasic acids has already been attempted, as described in US 020150259505 and WO 2016/083746A1. US 9,267,013 and US 020150259505 disclose dibasic esters of α-ω C18:0 fatty diacids for the use in plasticizers, while WO 2016/083746A1 discloses unsaturated α-ω dibasic esters for the same use. However, use of pure unsaturated α-ω dibasic esters (or in predominant proportions, from 60 to 100% w/w preferably from 80 to 100%) as lubricant basestocks has not been reported or suggested. The present invention is not readily obvious to those skilled in the art, because dibasic esters are perceived as :

- low viscosity materials, while medium viscosity is essential for lubricants
- materials with excessive volatility, while low volatility is important for lubricants
- in case of unsaturated esters, they are usually associated with poor oxidative stability, while low degradation is important (required) for lubricants
- higher viscosity saturated dibasic esters, especially those from linear fatty diacids, show problems in low temperature fluidity.

[0006] Consequently, these esters so far have targeted the applications as plasticizers, where the issues of volatility, oxidative stability or viscosity are less problematic than in lubricants.

[0007] The global lubricant market comprises nearly 50-60 MMT (millions of metric tons), out of which nearly 40 MMT can be considered the global volume of basestocks for engine oils and hydraulic fluids. Mostly, these basestocks are produced from mineral oils, with synthetic and biobased basestocks comprising less than 10%. Synthetic hydraulic fluids usually fall into ISO VG 46 viscosity grade and to a lesser extent into ISO VG 32. Their kinematic viscosities at 40°C must fall into the intervals of 42-50 mm^2/s and 28.8-35.2 mm^2/s respectively. Most engine oils belong to SAE 30 specifications, such as SAE 5W-30 or SAE 10W-30. Viscosities at 100°C must fall into the interval of 9.3 - 12.5 mm^2/s with good low temperature fluidity at -35°C and -30°C respectively. In engine oils, SAE 40 and SAE 20 are also quite widespread (viscosities at 100°C within 12.5 - 16.3 mm^2/s and 5.6 - 9.3 mm^2/s respectively). Out of all, engine oils 3 MMT or so are made from non-mineral basestocks, the majority of which belongs to poly alpha-olefins (poly α-olefins), produced petrochemically from ethylene (C_2H_4). The basestocks from vegetable or animal sources comprise about 1 MMT globally. However, their proportion can increase at the expense of poly α-olefins, if manufacture costs and technical properties become favorable.

[0008] In addition to viscosity itself, Viscosity Index (VI) is another important parameter. It defines how fast viscosity of a lubricant goes down viscosity with increasing temperature [ASTM D2270 "Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40 °C and 100 °C"]. High VI is usually very desirable for engine oils, hydraulic fluids and other lubricants, since their films are more effective in protecting moving surfaces from wear when heated.

[0009] Performance of lubricants at high temperatures is also dictated by their volatility, because with sizeable losses of any lubricant component the properties of the residual liquid change significantly. This is especially evident in mineral basestocks, which contain significant portion of lower mol. wt. fractions. Volatility losses are less appreciable in synthetic basestocks, constituting a significant performance benefit.

[0010] As evident from engine oil nomenclature and many other examples, lubricant basestocks must retain their fluidity at low temperatures in order to assure reliable performance in winter or cold conditions. Final lubricant formulations are tested using several protocols for low temperature fluidity, such as extended storage, cold cranking and similar. Pour point is considered as a very important parameter for describing the low temperature properties of the basestock.

[0011] One more critical property in the two most wide-spread lubricant applications, i.e. engine oils and hydraulic fluids, is oxidative stability, see Cvitkovic, E. et al. in "A Thin Film Test for Measurement of the Oxidation and Evaporation of Ester-Type Lubricants", published in ASLE Trans. (American Society of Lubrication Engineers Transactions), 1979, 22 (4), 395-401, Taylor and Francis Edition. It is important to establish how rapidly the solid phase can start forming, if lubricant basestock is exposed to severe oxidation. In mineral oils, the solid oxidation products often appear as semi-solid residues (hereafter called oxidative polymer), which might dissolve back into liquid with some heating. Increased levels of polar degradation products in fact might even help in keeping the oxidative polymers dissolved. However, precipitation of residues and deposits becomes more likely with further oxidation. In synthetic basestocks and vegetable oils, the oxidative polymerization can often lead to sudden solidification of the whole fluid. Therefore, particular attention must be devoted to oxidative stability and the formation mechanism of insoluble residues or solids.

[0012] It is also important that typical lubricant additives, such as Anti-Wear (AW) agent, antioxidant, corrosion inhibitor, friction modifier, alkalinity carrier, water demulsifier, dispersant, detergent, elastomer conditioner, dye, copper passivator, pour point depressant, tackifier, thickener, viscosity index improver, surfactant, defoamer or similar could dissolve in basestocks. Affinity of esters towards above additives is usually better than that of hydrocarbons.

[0013] The first subject-matter of the present invention relates to the use of a composition of specific dibasic esters of monounsaturated linear α, ω- diacids as a lubricant basestock or constituent.

[0014] A second subject-matter relates to a lubricant composition issued from the said use.

[0015] A third subject-matter relates to the use of said lubricant composition for engine oils and hydraulic fluids in

transport, agriculture, food and industrial applications.

[0016] So, the first subject-matter of the invention relates to the use of a composition of dibasic esters of monounsaturated α, ω-diacids as a lubricant constituent, wherein said composition comprises from 60 to 100% w/w, preferably 80 to 100% by weight: according to option a) of at least one monounsaturated α-ω dibasic ester compound of Formula (I) :

$$R1\text{-}OOC\text{-}(CH_2)_x\text{-}(CH{=}CH\text{-}(CH_2)_y\text{-}COO\text{-}R2 \qquad (I)$$

with

X + y being an integer in the range from 10 to 22, preferably from 10 to 16 ;
and with R1 and R2 being identical or different and being selected from the residues of branched alcohols with at least 5 carbon atoms (in C_5), preferably from 5 to 36 carbon atoms (in C_5 to C_{36}), more preferably from 5 to 26 carbon atoms (in C_5 to C_{26}), even more preferably from 5 to 22 carbon atoms (in C_5 to C_{22}) with said branched alcohols being either saturated or mono unsaturated and bearing at least one branch in C_1 to C_6, preferably in C_2 to C_6 or in C_1 in case of multiple branches (at least two) or
according to option b) of a mixture comprising :

b1) as predominant component at least one monounsaturated α-ω dibasic ester compound of Formula (I) as defined above in option a) and
b2) at least one monounsaturated α-ω dibasic ester compound of Formula (II) :

$$R'1\text{-}OOC\text{-}(CH_2)_x\text{-}CH{=}CH\text{-}(CH_2)_y\text{-}COO\text{-}R'2 \qquad (II)$$

with

x + y being as defined in formula (I) above ;
and with R'1 and R'2 being identical or different and selected from the residues of methanol (residue : methyl) or ethanol (residue : ethyl), preferably being identical and being the residues of methanol (residue : methyl),
and wherein, said composition has a weight content in estolides of the corresponding mono unsaturated acids of less than 1% w/w, preferably less than 0.1% or less than 0.05% w/w and more preferably 0% w/w.

[0017] According to a particular option, the total number of carbon atoms in the diester compound according to formula (I) as defined above can vary from 34 to 42 and preferably from 38 to 42 carbon atoms.

[0018] Predominant component as b1) means in the present case to represent more than 60% of the mixture b1) + b2) and preferably at least 70% and more preferably at least 80% of the mixture b1) + b2).

[0019] More particularly, the said branch of said branched alcohols is in C_2 to C_6 or in C_1 in case of a multiple branches meaning at least 2 branches present. In fact, the presence of a C_1 branch is preferred when at least another additional branch in C_1 or in C_2 to C_6 is present, with a total number of branches (multiple number) of at least 2 branches with at least one in C_1 and another one in C_2 to C_6 or at least two in C_1 or more particularly at least 3 branches with at least one in C_1 and two others in C_2 to C_6 or at least 2 in C_1 and one in C_2 to C_6 or at least 3 in C_1. Said branched alcohols R'1OH and R'2OH may be primary or secondary alcohols and preferably primary alcohols. The chain length (in carbon atoms) of these branched alcohols does not include the number of carbon atoms of the branches. For example, for 2-ethyl hexanol the chain length is in C_6, with one branch in C_2 in position 2 of the hexyl main chain (longer linear chain).

[0020] More particularly, it is preferred to have in said branched alcohol R'1OH and R'2OH a branch or the branch in position 2 (with respect to the -OH functionality), said branch being in C_2 to C_6 and possibly in C_1 under the provision that there are at least 2 branches, at least one being in C_1, preferably at least 3 branches with at least one in C_1.

[0021] Preferably, the number of carbon atoms of R1 or R2 is from 5 to 26 (C_5 to C_{26}) and more preferably from 5 to 22 (C_5 to C_{22}).

[0022] According to a particular option of the present invention, x + y in formula (I) ranges from 10 to 16. In a preferred option, x + y is 14 and more preferably with x = 7 and y = 7.

[0023] According to another particular embodiment, x is from 6 to 9. The ethylenic unsaturation is preferably located in position from 7 to 10.

[0024] More particularly, R1 or R2 are residues of branched alcohols selected from the group consisting of : 2-ethyl-hexyl, 2-butyl octyl, 2-propyl heptyl, phytyl (3,7,11,15-tetramethyl-2-hexadecenyl), 1-methyl heptyl (from 2-octanol), 3,5,5-trimethyl hexyl (isononyl) residue of terpenic alcohols, residue of farnesol, including their partially hydrogenated homologues, isocetyl, isostearyl, isooctyl (2,4,4-trimethylpentyl), cyclohexyl, abietyl and of their mixtures, preferably at least one of : 2-butyl octyl, 2-propyl heptyl, phytyl (3,7,11,15-tetramethyl-2-hexadecenyl), 3,5,5-trimethyl hexyl (isononyl).

[0025] According to a more preferred selection, said dibasic ester of formula (I) corresponds to x = y = 7 with x + y = 14 and with R1 and R2 selected from the group consisting of at least one of: 2-ethylhexyl or 2-butyl octyl, 2-propylheptyl, phytyl (3,7,11,15-tetramethyl-2-hexadecenyl), 1-methylheptyl or 3,5,5-trimethylhexyl and of their mixtures. One specific example of dibasic ester according to the present invention is the 2-ethylhexyl diester of 9-octadecenedioic diacid, having the ethylenic unsaturation in position 9 with 2-ethyl hexanol as branched alcohol. The double bond (ethylenic unsaturation) can be cis or trans or a mixture of both. For example, the proportion may be about 75% mol/mol trans and 25% cis but predominant or near 100% cis is more preferred over trans since the cold flow properties are better. Preferably, according to the present invention, the proportion of cis is at least of 15% mol.mol, preferably of at least 20%.

[0026] The at least one monounsaturated α-ω dibasic ester compound of Formula (I) of said dibasic ester composition can be a blend of at least two different compounds of Formula (I).

[0027] The said at least two different compounds of Formula (I) may be different in :

- x and/or y,
- x + y and/or
- R1 and/or R2 or
- all binary or ternary combinations of the above-cited differences (vs interest of blends).

[0028] More particularly, said at least one dibasic ester compound of Formula (I) may be a blend of a dibasic ester compound of Formula (I) with x = y = 7 and x + y = 14 at a content higher than 60% w/w with respect to said blend, with at least another different dibasic ester compound of Formula (I) with x + y from 16 to 22, preferably with x + y selected to be 16, 18, 20 or 22.

[0029] Another possible option is that R1 and R2 are different and are residues of a blend of different branched alcohols.

[0030] Concerning the composition of dibasic esters of monounsaturated α-ω diacids, it is preferably issued from the transesterification by said branched alcohols as defined above, of an α-ω dialkyl dibasic ester of Formula (II) :

$$R'1\text{-}OOC\text{-}(CH_2)_x\text{-}CH{=}CH\text{-}(CH_2)_y\text{-}COO\text{-}R'2 \qquad (II)$$

with R'1 and R'2 being identical or different and selected from a methyl or an ethyl, preferably being identical and being a methyl,
x, y being as defined above according to the present invention.

[0031] Said dibasic ester of Formula (II) can be issued by the esterification of the corresponding diacid. Said diacid can be obtained either by a metathesis route from the corresponding fatty monoacid or obtained by the hydrolysis of a mixture of other diesters of said diacid or by the fermentation route of a fatty monoacid.

[0032] For example, the dibasic esters can be formed starting from monounsaturated fatty diacids which comprise either 18 carbon atoms by molecule 9-octadecenedioic or 22 carbon atoms by molecule 11-docosenedioic. The preparation of such fatty diacids is disclosed in Ngo, H.L. et al. in "Metathesis of Unsaturated Fatty Acids: Synthesis of Long Chain Unsaturated-α,ω- Dicarboxylic Acids", published in JAOCS J. of Am. Org. Chem. Soc. 2006, 83 (7), 629-634.

[0033] The dibasic esters used within the framework of the invention can be either symmetrical, with the alcohol used for esterification being the same one for the two carboxy acid functions or asymmetrical with two different alcohols. Transesterification of light alcohol esters (such as methyl and/or ethyl esters) of said fatty diacids with heavier alcohols as defined according to the present invention can be used for the preparation of the specific dibasic esters used in the present invention. More particularly, the said fatty diacid can be issued from a self-metathesis reaction of a fatty monounsaturated monoacid or said dibasic ester of Formula (II) is issued from a self-metathesis of a fatty monounsaturated monoacid ester. Diacid can also be obtained from fermentation of monounsaturated fatty acid (especially for the C_{18}).

[0034] The dibasic ester can be formed by self-metathesis reaction from unsaturated monoesters, such a reaction can be either the main reaction or a side reaction during a cross-metathesis reaction. In a reaction A-CH=CH-B + R1-CH=CH-R2, several reactions will take place and lead to the following products A-CH=CH-A, B-CH=CH-B, R1-CH=CH-R1, R2-CH=CH-R2, A-CH=CH-R1, A-CH=CH-R2, B-CH=CH-R1, B-CH=CH-R2. Among those, there are products of self-metathesis reactions characterized by both end groups being identical. This demonstrates that self-metathesis reaction also occurs during the cross metathesis reaction.

[0035] The fatty diacid can also be produced by fermentation of the corresponding fatty mono acid.

[0036] More particularly, in the said use according to the present invention of said composition of dibasic esters, the said composition is a mixture as defined above according to option b). More particularly, said mixture as defined above according to option b) comprises up to 99.9% w/w with respect to said mixture of b1) selected from at least one dibasic ester compound as defined above according to Formula (I) and at least 0.1% w/w of b2) at least one dibasic ester compound as defined according to Formula (II).The second subject of the invention relates to a lubricant composition which results from the use as a lubricant constituent (or additive having same meaning) of at least one dibasic ester composition as defined above according to the present invention. More particularly, the weight ratio of b1)/b2) can vary

from 0.85/0.15 to 0.99/0.01.

[0037] A second subject of the invention relates to a lubricant composition which results from the use as a lubricant constituent, of at least one dibasic ester composition as defined above according to the present invention.

[0038] Said lubricant composition, in addition to said dibasic ester composition at a content of at least 80% w/w, preferably from 90 to 99.7% with respect to the total weight of said lubricant composition, can further comprise up to 20%, preferably from 0.3 to 10% w/w of other additives selected from the group consisting of another lubricant additive, antiwear agent, antioxidant, corrosion inhibitor, friction modifier, alkalinity carrier, biocide, buffering agent, chelating additive, coupler, water demulsifier, dispersant, detergent, elastomer conditioner, dye, mist suppressant, odorant, copper passivator, pour point depressant, tackifier, thickener, viscosity index improver, surfactant or defoamer. Said lubricant composition is preferably a lubricant basestock composition. More particularly, said lubricant basestock composition is issued from renewable resources and it is biodegradable. More particularly, said lubricant composition is a lubricant basestock composition. Said lubricant basestock composition is particularly issued from renewable resources and it is a biodegradable lubricant basestock.

[0039] Finally, the present invention also covers the use of the said lubricant composition as engine oils or as hydraulic fluids in transport, agriculture, food and industrial applications.

[0040] Some experimental examples are presented below for the purpose of illustrating the present invention and its performances and these examples given for such an illustration do not at all limit the covering of the present invention.

[0041] The conditions of synthesis of said mono-unsaturated α-ω dibasic esters is described here-below in the experimental part. Obtained liquids have also been evaluated to compare their viscosimetric properties, low temperature fluidity, volatility, oxidative stability and solvency with as references poly α-olefins and low-erucic rapeseed oil. The former represents the most widespread non-mineral basestock in engine oil formulations, while rapeseed oil is often used as hydraulic fluid basestock.

1. EXAMPLES

[0042] Colloquial lipid terminology (i.e. lipid number) denominations are used to describe the aliphatic portion by listing the number of C atoms and the number of C=C double bonds, separated by colon. For example, instead of writing "hexadecanoate and octadecedienoate", the denominations "C16:0 and C18:2" can be used to indicate palmitate and linoleate moieties respectively. These rules are extended to indicate the positions of carboxyls, such as α-ω C18:0 dibasic ester, position and type of C=C double bonds, such as C18:1 9Z for oleic acid and so on. The list of moiety denominations, compound codes and IUPAC names is provided in Table 1.

Table 1. List of codes and systematic nomenclature for tested structures

In the supplier list "Arkema" and "CPST" mean home-made (synthesis described below).				
Code	Alcohol moiety	Remainder	IUPAC name or trade name	Supplier
Single-alcohol α,ω dibasic esters				
1U18	methyl	α,ω C18:1	1,18-dimethyl octadec-9-enedioate	Arkema
17S18	methyl heptyl (from 2-octanol)	α,ω C18:0	1,18-di(1-methylheptyl) octadecanedioate	CPST
17U18	methyl heptyl	α-ω C18:1	1,18-di(1-methylheptyl) octadec-9-enedioate	CPST
26S9	2-ethylhexyl	α,ω C9:0	1,9-di(2-ethylhexyl) nonanedioate	TCI
26S12	2-ethylhexyl	α,ω C12:0	1,12-di(2-ethylhexyl) dodecanedioate	TCI
26S18	2-ethylhexyl	α,ω C18:0	1,18-di(2-ethylhexyl) octadecanedioate	CPST
26U18	2-ethylhexyl	α,ω C18:1	1,18-di(2-ethylhexyl) octadec-9-enedioate	Arkema
37U18	2-propyl heptyl	α,ω C18:1	1,18-di(2-propylheptyl) octadec-9-enedioate	CPST
48U18	2-butyloctyl	α,ω C18:1	1,18-di(2-butyloctyl) octadec-9-enedioate	CPST
5U18	isoamyl	α,ω C18:1	1,18-di(3-methylbutyl) octadec-9-enedioate	CPST
9U18	isononyl	α-ω C18:1	1,18-di(3,3,5-trimethylhexyl) octadec-9-enedioate	CPST

(continued)

Mixed alcohol α,ω dibasic esters				
2026U18	phytyl:2-ethylhexyl at 1:1 mix	α,ω C18:1	1-(3,7,11,15-tetra methyl-2-hexadecenyl) - 18-(2-ethylhexyl) octadec-9-enedioate	CPST
4826U18	2-butyloctyl: 2-ethylhexyl at 1:1 mix	α,ω C18:1	1-(2-butyloctyl)-18-(2-ethylhexyl)octadec-9-enedioate	CPST
Commercial basestocks for comparison				
350N		paraffinic mineral oil	HVI 350	Shell
LEAR		60% C18:1 9Z	Low erucic rapeseed oil, food grade	Inex OY
PAO8		poly α-olefin	Durasyn 168	Ineos

[0043] The codes of dibasic esters are assigned mostly based on the segment lengths of the alcohol and diacid moieties in the compound molecule. As a prefix, the branches of the alcohol moiety are encoded based on the number of C atoms in the IUPAC name of the alcohol. For example, 2-ethyl hexanol contains two branches of C_2 and C_6, hence a prefix "26" is assigned. Admittedly, isoalkyl, oleyl and mixed esters do not follow this rule strictly. In the middle of the code, a suffix letter is inserted to indicate, whether the fatty diacid moiety is fully saturated ("S") or unsaturated ("U"). The rest of the code denotes the chain length of the fatty diacid moiety. For example, azelaic acid (α,ω C9:0) is denoted "9", while α-ω C18:1 fatty diacid is denoted "18". Most of the latter esters were synthesized in-house by Arkema or CPST by transesterifying 1U18, which was produced in-house by metathesis. However, it must be pointed out that other production pathways for 1U18 are also possible (see Fig. 1 with a scheme of production of 1U18 by self-metathesis).

[0044] Several fluids were acquired from third parties for comparison purposes. Two esters 26S9 and 26S12, manufactured commercially for hydraulic fluid applications, were purchased from TCI Chemicals (Japan). Low-erucic acid rapeseed (LEAR) oil, food grade was purchased in the retail store Prisma with indicated manufacturer Inex Partners OY (Finland) and the origin country of Belgium. Viscosity and acidity measurements were performed at CPST and recorded values were typical of rapeseed oil. Poly α-olefin (code "PAO8") was received from Ineos Oligomers as Durasyn 168 with reported density of 0.832 g/mL at 15°C, average molecular weight (avg mol Wt) of 629 g/mol, viscosities of 47 mm^2/s (cSt) and 0.00078 cm^2/s 7.8 mm^2/s (cSt) at 40°C and 100°C respectively, pour point below -50°C, flash point above 245°C, bromine number below 4 mg Br/g and water contents below 25 ppm.

[0045] Laboratory grade acetone, isopropanol and xylene (Avsista, Lithuania) were used for washing and titrations. KOH and phenolphthalein (Avsista, Lithuania) were used for acidity determinations. The coupons for degradation tests were manufactured in-house from low carbon steel (98.8% w/w. Fe, 0.8% Mn and 0.4% Si) and represented the cylinders of 17 ± 1 mm in diameter. Deionized water for humidity chamber operation and acidity titrations was produced in-house by reverse osmosis system Demiwa 10 Rosa (Watek, Czech), resulting in conductivity below 1 μS/cm. Most used percentages were calculated on weight-to-weight basis, unless indicated otherwise.

2. TEST METHODS

2.1 Thin film testing

[0046] The exact procedure, used here, has been described in detail by Stoncius, A. et al. in "Volatiles from Thin Film Degradation of Bio-based, Synthetic and Mineral Basestocks", published in Industrial Lubrication & Tribology, 2013, 65 (3) 209-215, 2013, Emerald Group Publishing Edition or by Brazinskiene, D. et al. in "Ester Basestock Vaporisation from Thin Oil Films", published in Lubrication Science, DOI: 10.1002/ls.1372, pp 1-17, 2017, Wiley Edition.

[0047] Briefly, an oil film of 500 μm thickness was coated on steel coupon and heated at given temperature for specific duration in a forced-draft oven. Afterwards, the volatile losses and insoluble residues were measured gravimetrically.

2.2 Fluidity measurements

[0048] Kinematic viscosities at 40°C and 100°C were measured using capillary Cannon-Fenske viscometers per ASTM D455. Viscosity Index (the value, describing the rate of thinning with increasing temperature) was calculated per ASTM D2270.

[0049] Pour points and cloud points were determined using the same thermal cooling regime, as instructed by ASTM D97. The sample sizes were 5 to 15 mL during the measurements.

[0050] Cloud points were determined during the same run by visual inspection of the sample appearance at low temperature. The samples were removed from the freezer every 3°C for visual inspection and, if cloudy, meniscus movement with inversion. The pour point resembled the last measurement, at which the meniscus boundary was still moving within 5 seconds of horizontal inversion. All samples were tested in duplicate. If the recorded values did not match at 3°C replicates, more measurements were carried out until a statistically reliable result was obtained.

3. SYNTHESIS AND STRUCTURES

3.1 Main principles of synthesis

[0051] Most investigated compounds were synthesized by transesterifying a dimethyl ester (code 1U18) of linear α-ω C18:1 fatty diacid. The starting material 1U18 was produced by metathesis as described in WO 2014/106724 A1. In some cases, as a starting material a linear linear α-ω C18:1 fatty diacid was used for direct esterification. After a given dibasic ester was synthesized, its pour point and viscosities were measured, as shown in Fig. 2 (showing a scheme for synthesis and fluidity testing of dibasic esters).

[0052] Transesterification of methyl dibasic ester of α-ω C18:1 dibasic acid (code 1U18) for the most part followed the procedures, as described elsewhere, see Hojabri, L. et al. in "Fatty acid-derived diisocyanate and biobased polyurethane produced from vegetable oil: synthesis, polymerization, and characterization" Published in Biomacromolecules, 2009, 10 (4), 884-891, American Chemical Society Edition. A mixture of cis- and trans- isomers of α-ω C18:1 dibasic acid was used in this synthesis Its methyl ester was analyzed on ^{1}H NMR and GC-MS in order to establish the quantitative ratio between 9E and 9Z (trans- and cis-respectively), see Fig. 3.

[0053] Many properties, important for lubricant basestocks, are strongly dependent on trans- or cis- isomerization, especially low temperature fluidity. Therefore, it would not be correct to assume that any obtained unsaturated ester represented a single organic compound. Saturated esters, synthesized for this report, can be considered as unique organic compounds. However, saturated esters are not the scope of this invention and are used as Comparative Examples.

[0054] The transesterification of 1 U 18 into monounsaturated α-ω C18:1 dibasic esters was performed using excess alcohol in the presence of para-toluene sulfonic acid (PTSA), as shown for the synthesis scheme of Guerbet esters in Fig. 4.

[0055] After the reaction, the mixture was evacuated with mild heating to remove excess alcohol and resultant methanol. In addition to Guerbet, other types of branched alcohols were also utilized for synthesis, such as isononyl or isoamyl. In some cases the esters were synthesized directly from a free α-ω C18:1 dibasic acid by esterifying it with a respective alcohol in the presence of dimethyl aminopyridine (DMAP). Details of both syntheses are described below. Further details for the synthesis can be found in Hojabri, L. et al. in "Fatty acid-derived diisocyanate and biobased polyurethane produced from vegetable oil: synthesis, polymerization, and characterization" published in Biomacromolecules, 2009, 10 (4), 884-891, American Chemical Society Edition.

[0056] Also, synthesis of fully saturated α-ω C18:0 dibasic esters was performed (as comparative reference) by hydrogenating the respective monounsaturated esters over a Palladium catalyst, see Fig. 5 and § 3.4.

3.2 Transesterification procedures

[0057] A mixture of dimethyl octadec-9-enedioate ("1U18", 17.0 g; 50 mmol), corresponding alcohol (105 mmol) and PTSA (ParaToluene Sulfonic Acid) monohydrate (0.67 g; 3.5 mmol) was heated at 100°C under reduced pressure (approximately 20 mmHg) for 2 to 12 h. Reaction progress was monitored by Thin Layer Chromatography (eluent - DCM). Upon reaction completion, Hickman head was attached and reaction was furthermore heated at 100°C under vacuum (0-1 mmHg). Condensed liquid was occasionally removed and the process was continued until no more drops have formed in Hickman head. Then, reaction mixture was cooled to r.t (room temperature) and dissolved in toluene (300 ml). The solution was washed with 10% w/w Na_2CO_3 aqueous solution (200 ml) and with water (200 ml). After desiccation with Na_2SO_4, a solution was eluted (toluene 2 L) through a pad of silica gel (5 cm height). Solvent was evaporated on rotary evaporator and residual volatiles were removed under reduced pressure (0-1 mmHg).

[0058] Di(oct-2-yl) octadec-9-enedioate also noted as Di (methyl heptyl) octadec-9-enedioate (code "**17U18**") :

Yield : 19.55 g (72%). ^{1}H NMR ($CDCl_3$, 400 MHz): 0.85 - 0.93 (m, 6H); 1.18 - 1.40 (m, 38H); 1.44 - 1.53 (m, 2H); 1.53 - 1.71 (m, 6H), 1.94 - 2.04 (m, 4H); 2.28 (t, 4H, *J* = 7.2 Hz); 4.92 (s, 2H, *J* = 6.8 Hz); 5.28 - 5.46 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): 14.0, 20.0, 22.6, 25.1, 29.0, 29.0, 29.1, 29.1, 29.6, 29.7, 31.8, 32.6, 34.8, 36.0, 70.7, 129.8, 130.3, 173.5.

[0059] Di(2-propylheptyl) octadec-9-enedioate (code "**37U18**") :

Yield : 21.1 g (81%). ^{1}H NMR ($CDCl_3$, 400 MHz): 0.84 - 0.95 (m, 12H); 1.10 - 1.40 (m, 40H); 1.55 - 1.70 (m, 6H), 1.92 - 2.08 (m, 4H); 2.31 (t, 4H, *J* = 7.2 Hz); 3.99 (d, 4H, *J* = 6.0 Hz); 5.11 - 5.43 (m, 2H).
^{13}C NMR ($CDCl_3$, 100 MHz): 14.1, 14.4, 19.9, 22.6, 25.1, 26.4, 27.2, 29.0, 29.1, 29.6, 31.2, 32.2, 32.6, 33.6, 34.4, 37.1, 67.0, 129.8, 130.3, 174.1.

[0060] Di(2-butyloctyl) octadec-9-enedioate (code "**48U18**") :

Yield: 23.2 g (71%). ^{1}H NMR ($CDCl_3$, 400 MHz): 0.83-0.93 (m, 12H); 1.08- 1.42 (m, 48H); 1.56 - 1.68 (m, 6H), 1.92 - 2.09 (m, 4H); 2.30 (t, 4H, *J* = 7.2 Hz); 4.01 (d, 4H, *J* = 6.0 Hz); 5.12 - 5.45 (m, 2H).
^{13}C NMR ($CDCl_3$, 100 MHz): 14.0, 14.1, 22.7, 23.0, 25.1, 26.7, 27.2, 28.9, 29.0, 29.2, 29.2, 29.6, 31.0, 31.3, 31.8, 32.6, 34.5, 37.3, 67.0, 129.8, 130.3, 174.1.

[0061] Di(3-methylbutyl) octadec-9-enedioate (code "**5U18**") :

[0062] A mixture of dimethyl octadec-9-enedioate (20.0 g; 58.5 mmol), isoamyl alcohol (25.9 g; 294 mmol) and PTSA monohydrate (0.78 g; 4.1 mmol) was heated at 90°C in open vessel. Occasionally (once in an hour), vacuum was applied to remove methanol vapors. Reaction was continued for 12 hours (progress was monitored by TLC). Then, isoamyl alcohol was removed under reduced pressure. The residue was dissolved in toluene (200 ml) and a solution was eluted (toluene 2 L) through a pad of silica gel (5 cm height). Solvent was evaporated on rotary evaporator and residual volatiles were removed under reduced pressure (0 - 1 mmHg).
Yield : 19.8 g (74%). ^{1}H NMR ($CDCl_3$, 400 MHz): 0.87 - 0.98 (m, 12H); 1.14 - 1.48 (m, 20H); 1.53 (q, 4H, *J* = 7.2 Hz); 1.58 - 1.75 (m, 6H), 1.92 - 2.06 (m, 4H); 2.30 (t, 4H, *J* = 7.2 Hz); 3.85 - 4.01 (m, 1 H); 4.11 (s, 3H, *J* = 7.2 Hz); 5.30 - 5.42 (m, 2H).
^{13}C NMR ($CDCl_3$, 100 MHz): 22.5, 25.0, 25.0, 27.2, 29.0, 29.2, 32.5, 34.4, 37.4, 62.9, 68.9, 129.8, 130.3, 174.0.

3.3 Esterification of free α,ω C18:1 dibasic acid

Octadecenedioic acid : through sodium salt formation form the ester and acidification

[0063] A mixture of dimethyl octadec-9-enedioate - C18:1 dibasic ester - (20 g; 58.5 mmol) and methanol was stirred and heated to 65 - 70°C until clear solution was obtained. Then, NaOH (2.5 M) solution (60 ml) was added. Precipitate have formed soon. The mixture was heated at 65 - 70°C for 30 min. Then, water (600 ml) was added in portions (precipitate dissolves) and the mixture was kept at 70°C for five more hours. Then, HCl solution (approximately 2 M) was added until product have precipitated and pH was acidic. Product was filtered and dried at 60°C.
Yield : 18.3 g (99 %). m.p. 94 - 96°C. ^{1H} NMR ($CDCl_3$, 400 MHz): 1.15 - 1.45 (m, 16H); 1.45 - 1.56 (m, 4H), 1.83 - 2.03 (m, 4H); 2.18 (t, 4H, *J* = 7.2 Hz); 5.25 - 5.45 (m, 2H); 11.7 - 12.3 (br s, 2H).
[0064] To a solution of octadecenedioic acid (14 g; 45 mmol), corresponding alcohol (94 mmol) and 4-N,N-dimethyl amino pyridine ("DMAP", 0.27 g; 2.2 mmol) in dichloro methane ("DCM", 300 ml), dicyclohexyl carbodiimide ("DCC", 18.7 g; 91 mmol) was added. Reaction mixture was stirred for 3 hours at room temperature. Precipitated solid was filtered off, DCM was removed under reduced pressure. Residue was dissolved in hexane (200 ml) and solution was eluted (toluene 2 L) through a pad of silica gel (5 cm height). Solvent was evaporated on rotary evaporator, and residual volatiles were removed under reduced pressure (0 - 1 mmHg).
[0065] Di(3,3,5-trimethylhexyl) octadec-9-enedioate (code "**9U18**") :

Yield : 19.4 g (77%). ^{1}H NMR ($CDCl_3$, 400 MHz): 0.90 (s, 18H); 0.96 (d, 6H, *J* = 7.2 Hz); 1.09 (dd, 2H, ^{2}J = 14, ^{3}J =5.6); 1.21 - 1.38 (m, 18H); 1.41 - 1.52 (m, 2H); 1.56 - 1.69 (m, 8H), 1.91 - 2.05 (m, 4H); 2.29 (t, 4H, *J* = 7.2 Hz); 4.09 (t, 4H, *J* = 7.2 Hz); 5.33 - 5.41 (m, 2H).
^{13}C NMR ($CDCl_3$, 100 MHz): 22.6, 25.0, 26.2, 29.0, 29.1, 29.6, 29.7, 29.9, 31.1, 32.6, 34.4, 37.9, 51.0, 62.8, 129.8, 130.3, 173.9.

3.4 Hydrogenation of mono-unsaturated esters

[0066] A mixture of octadec-9-enedioic acid ester (20 g) and Pd/C (10% w/w Pd/C, 0.5 g) in ethyl acetate (200 ml) was stirred overnight at room temperature under hydrogen atmosphere. Then, hydrogen was removed, reaction vessel was flushed with Argon and reaction mixture was filtrated through the diatomaceous earth (Celite™, Sigma-Aldrich). Solvent was evaporated on rotary evaporator, and residual volatiles were removed under reduced pressure (0 - 1 mmHg).
[0067] Di(oct-2-yl) octadecanedioate (code "**17S18**") :

Yield : 19.1 g (95%). ^{1}H NMR ($CDCl_3$, 400 MHz): 0.86 (t, 6H, *J* = 7.2 Hz); 1.13 - 1.35 (m, 46H); 1.38 - 1.49 (m, 2H); 1.50 - 1.64 (m, 6H), 2.25 (t, 4H, *J* = 7.2 Hz); 4.88 (s, 2H, *J* = 6.4 Hz).
^{13}C NMR ($CDCl_3$, 100 MHz): 14.0, 20.0, 22.6, 25.1, 25.4, 29.1, 29.1, 29.3, 29.5, 29.6, 29.6, 29.7, 31.7, 34.7, 36.0, 70.7, 173.5.

[0068] Di(2-ethylhexyl) octadecanedioate (code "**26S18**"):

Yield : 19.8 g (98%). ^{1}H NMR ($CDCl_3$, 400 MHz): 0.90 (t, 6H, *J* = 7.2 Hz); 1.22 - 1.41 (m, 40H); 1.53 - 1.67 (m, 6H), 2.31 (t, 4H, *J* = 7.2 Hz); 3.95 - 4.04 (m, 4H).

4. VISCOSIMETRIC CHARACTERISTICS

[0069] Viscosity is the most important property of nearly any lubricant basestock. Viscosities for hydraulic fluids and engine oils are regulated by several specifications, see Table 2.

Table 2. The most widespread viscosity specifications for hydraulic fluids (VG - Viscosity Grade) and engine oils (SAE - Soc. of Automotive Engineers), shown as intervals, along with the predicted kinematic viscosity values at 40°C and 100°C, shown as single numbers, assuming VI = 200

Viscosity Specification	Range at 40°C mm^2/s	Range at 100°C mm^2/s
ISO VG 22	19.8 - 24.2	5.5
ISO VG 32	**28.8 - 35.2**	**7.2**
ISO VG 46	**41.4 - 50.6**	**9.6**
SAE 30	54	9.3 - 12.5
SAE 20	**33**	**5.6 - 9.3**
SAE 16	**31**	**6.1 - 8.2**
SAE 12	25	5 - 7.1
SAE 8	20	4 - 6.1

[0070] Some minor complication can occur when comparing viscosity requirements for engine oils and hydraulic fluids, because their viscosity margins are set at different temperatures, 100°C and 40°C respectively. Since most of tested α-ω dibasic esters have Viscosity Index close to 200, this value was selected to convert the viscosities between the two temperatures. Viscosities of chemically similar organic compounds strongly depend on molecular weight. The correlation of measured values at 40°C for several synthesized compounds is quite evident from Fig. 6.

[0071] Good correlation between measured viscosities and molecular weights indicates that the dibasic esters were synthesized properly and the amounts of partial esters are negligible.

[0072] The most appealing viscosities belong to the dibasic esters, whose molecular weight falls into the interval from 500 to 700 g/mol, such as 2-propylheptyl ester of α-ω C18:1 fatty diacid (code 37U18) of 593 g/mol recording 28.7 mm^2/s at 40°C. It can be expected that 2-ethyl hexyl ester of α-ω C24:1 fatty diacid would demonstrate the viscosity of ISO VG 32 or SAE 0W-20 specification, due to mol. wt. of 621 g/mol.

[0073] In principle, viscosity can be increased by adding polymers and this is often utilized in lubricant formulations. However, with long-term usage polymers are degraded by mechanical shear, which brings down the viscosity. Also, it is better to use the basestock, whose volatility is lower, i.e. flash points are higher. Lower viscosity of basestock usually means more problematic flash points, while polymer additives do not affect volatility significantly.

Table 3. Viscosities of saturated and mono-unsaturated α-ω dibasic esters.

Those, which also serve as comparative examples, are marked with "(comp)"					
Code	Alcohol moiety	Remainder	Viscosity, mm^2/s at 40°C	Viscosity, mm^2/s at 100°C	Viscosity Index
Dibasic esters as Exhibits					
26U18	2-ethylhexyl	α,ω C18:1	22.74	5.53	197
37U18	2-propylheptyl	α,ω C18:1	28.74	6.39	174

(continued)

Those, which also serve as comparative examples, are marked with "(comp)"					
Code	Alcohol moiety	Remainder	Viscosity, mm^2/s at 40°C	Viscosity, mm^2/s at 100°C	Viscosity Index
Dibasic esters as Exhibits					
48U18	2-butyloctyl	α,ω C18:1	36.09	7.09	163
4826U18	2-butyloctyl: 2-ethylhexyl	α,ω C18:1	28.97	6.78	205
9U18	isononyl	α,ω C18:1	28.8	6.7	202
Other pertinent dibasic esters					
1U18 (comp)	methyl	α,ω C18:1	8.68	2.85	204
17U18	methylheptyl	α,ω C18:1	21.2	5.35	205
17S18	methylheptyl	α,ω C18:0	22.7	5.31	180
26S18	2-ethylhexyl	α,ω C18:0	23.9	5.71	194
26S9 (comp)	2-ethylhexyl	α,ω C9:0	10.5	2.8	111
26S12 (comp)	2-ethylhexyl	α,ω C12:0	14.72	3.72	147
5U18	isoamyl	α,ω C18:1	12.93	3.73	196
2026U18	phytyl: 2-ethylhexyl	α,ω C18:1	42.54	8.3	175
Pertinent commercial basestocks					
350N (comp)		paraffinic oil	61.4	8.46	109
LEAR (comp)		60% C18:1	46.76	10.68	222
PAO8 (comp)		poly α-olefin	50.48	8.2	135

[0074] Viscosities in Table 3 show that many dibasic esters of α-ω C18:1 fatty diacid have VI of approximately 200. Such value is considered very beneficial for lubricants. Polymer additives, so called VI Improvers, are often used in final lubricant formulations to increase VI. Consequently, esters of α-ω dibasic acids might need lower proportions of VI Improvers additives. Even more importantly, VI improvers tend to degrade in hydraulic pumps due to mechanical shear, which leads to increased temperature of the hydraulic system. Consequently, more rapid wear and higher energy losses are observed. Therefore, basestocks with inherently high VI, such as dibasic esters of linear monounsaturated fatty diacids, will command a distinct advantage in hydraulic fluid formulations.

5. LOW TEMPERATURE FLUIDITY

[0075] In engine oils and hydraulic fluids, low temperature fluidity is primarily determined by pour points [ASTM D97]. Generally, pour points below -30°C are considered sufficient. Some polymer additives, e.g. "Pour Point Depressants" (PPD), are able to improve low temperature fluidity. It must be noted that esters without PPD additives, which demonstrate pour points below -30°C, usually meet the requirements of cold storage, pumpability and cold cranking tests. Therefore, initially pour points and cloud points [ASTM D2500 "Standard Test Method for Cloud Point of Petroleum Products and Liquid Fuels"] of α-ω dibasic esters were evaluated and shown in Table 4.

[0076] Testing shows that pour points or cloud points do not correlate to molecular weight. For α-ω dibasic esters, ethyl or larger branches and the presence of C=C double bond assure pour points significantly below -30°C. Linear α-

ω dibasic esters, such as 1U18 or esters with few methyl branches only, such as 17U18, show much poorer low temperature fluidity. The influence of molecular weight (mol. wt.) is significant, but by no means direct. Lower molecular weight esters tend to show better low temperature fluidity, but the presence of C=C double bonds and ethyl branches is not less important. This makes it very likely that 2-ethylhexyl esters of α-ω C24:1 dibasic acid would demonstrate pour points below -30°C.

Table 4. Low temperature fluidity of α-ω dibasic esters and commercial basestocks

Code	Alcohol moiety	Remainder	Pour point, °C	Cloud point, °C	Mol. wt. g/mol
Dibasic esters as Exhibits					
26U18	2-ethylhexyl	α-ω C18:1	-57	-36	536.9
37U18	2-propylheptyl	α-ω C18:1	-51	-51	593
48U18	2-butyloctyl	α-ω C18:1	-54	-48	649.1
4826U18	2-butyloctyl: 2-ethylhexyl	α-ω C18:1	-51	-51	593
9U18	isononyl	α-ω C18:1	-33	-33	565
Other pertinent dibasic esters					
1U18	methyl	α-ω C18:1	> +15	> +15	340.4
17S18	methylheptyl	α-ω C18:0	+9	+9	536.9
17U18	methylheptyl	α-ω C18:1	-21	-18	536.9
26S18	2-ethylhexyl	α-ω C18:0	-9	-9	536.9
26S9	2-ethylhexyl	α-ω C9:0	-57	-38	413
26S12	2-ethylhexyl	α-ω C12:0	-48	-30	454.5
5U18	isoamyl	α-ω C18:1	-24	-24	451.4
2026U18	phytyl: 2-ethylhexyl	α-ω C18:1	-66	-63	704
Pertinent commercial basestocks					
350N		paraffinic oil	-15	-15	
LEAR		60% C18:1	-24	-18	890
PAO8		poly α-olefin	< -66	< -66	629

[0077] In case of multiple methyl branches, sufficiently low pour points can be achieved. Isononyl dibasic ester 9U18, which contains 3 methyl branches on each alcohol moiety, shows an acceptable pour point of -33°C. Even better pour point of -66°C is demonstrated by the mixed dibasic ester 2026U18, whose monounsaturated phytyl moiety contains 4 methyl branches. Despite the abundance of trans- isomers, monounsaturation in fatty diacids of C_{18} or longer chain lengths is essential for good low temperature performance. Hydrogenated dibasic esters 17S18 and 26S18 showed very problematic low temperature fluidity. Since the moieties trans-double bonds might often engage into the same molecular packing structures as saturated moieties, it is important that monounsaturated dibasic esters contain some cis-isomers, preferably in excess of 15% mol/mol.

6. OTHER PROPERTIES OF LUBRICANT BASESTOCKS

[0078] Fully formulated engine oils and hydraulic fluids must address a long series of performance criteria and therefore must be tested for many properties. In case of lubricant basestock, it is not reasonable to screen any candidate for the full set of final product properties. As discussed in prior art review, the most important parameters for lubricant basestocks are viscosity, low temperature fluidity, high temperature volatility, resistance to oxidative degradation and additive compatibility. These properties are discussed below in the same order.

6.1 Volatility

[0079] As discussed in the prior-art review, volatility can be successfully evaluated in a thin film test as described by

Stoncius, A. et al. in "Volatiles from Thin Film Degradation of Bio-based, Synthetic and Mineral Basestocks" published in Industrial Lubrication & Tribology, 2013, 65 (3) 209-215, Emerald Group Publishing Edition or by Brazinskiene, D. et al. in "Ester Basestock Vaporisation from Thin Oil Films" published in Lubrication Science, DOI: 10.1002/ls.1372, pp 1-17, 2017, Wiley Edition. This thin-film method is much better suited for hydraulic fluid applications than NOACK or other tests, which employ 250°C or similar temperatures, related to engine oil applications. Also, the above method accounts for longer term decomposition reactions due to exposure to metal surfaces and oxidation, which is prevalent in hydraulic applications. Therefore, using the thin-film method short-term vapor losses were measured after 16 hrs and decomposition trends were compared after 36 hrs of testing. Heating temperature of 120°C was selected to compare thin films of α,ω dibasic esters with commercial basestocks.

Table 5. Volatile emissions, % w/w from 500 μm thick films of α-ω dibasic esters and commercial basestocks at 120°C

Code	Alcohol moiety	Remainder	16 hrs	36 hrs
			% w/w	% w/w
Dibasic esters as Exhibits				
26U18	2-ethylhexyl	α-ω C18:1	5.5	10.7
37U18	2-propylheptyl	α-ω C18:1	3.5	10.6
48U18	2-butyloctyl	α-ω C18:1	1.7	9.8
9U18	isononyl	α-ω C18:1	5	13.9
4826U18	2-butyloctyl: 2-ethylhexyl	α-ω C18:1	3.8	10.1
Other pertinent dibasic esters				
1U18	methyl	α-ω C18:1	9.4	25.6
17U18	methylheptyl	α-ω C18:1	0.87	7
26S9	2-ethylhexyl	α-ω C9:0	2.65	4.7
26S12	2-ethylhexyl	α-ω C12:0	0.8	1.75
5U18	isoamyl	α-ω C18:1	12.6	23.7
2026U18	phytyl: 2-ethylhexyl	α-ω C18:1	6.7	13.4
Pertinent commercial basestocks				
350N		paraffinic oil	3.1	4.6
LEAR		60% C18:1	1.2	4 (solid)
PAO8		poly α-olefin	2	7.7

[0080] Table 5 shows that despite lower viscosity, monounsaturated α-ω dibasic esters have similar volatility to that of conventional synthetic basestock PAO8. It must be noted that all monounsaturated α-ω dibasic esters were prepared in the laboratory, which made it difficult to avoid contaminants and byproducts of volatile nature. Their absence was one reason, why commercially produced α-ω dibasic ester 26S12 showed much lower volatility. Reaction on the double bond site is another reason of decomposition processes in monounsaturated α-ω dibasic esters, which increases the rates of long-term vaporization. Volatility of LEAR appears similar to 48U18 initially, but later its film solidifies and the volatile emissions cannot be reliably measured. When compared to α-ω C18:1 dibasic esters, the vaporization of PAO8 is not dramatically different. Therefore, it can be concluded that volatility of α-ω dibasic esters with C_{18} or longer chain lengths of fatty diacids is comparable to that of conventional vegetable oils and synthetic basestocks, while low temperature fluidity and viscosimetric properties are superior with some other specific performances good enough or improved, as shown below.

6.2 Oxidative Stability

[0081] Lubricants often degrade during field use because of oxidation and exposure to high temperatures. Although oxidative degradation can be controlled to some extent by using free radical scavengers, peroxide decomposers, metal passivators and other types of antioxidants, lubricant basestock plays a key role on the oxidation rate. The presence of double bonds accelerates oxidation significantly. Consequently, monounsaturated α,ω dibasic esters might oxidize faster

than poly α-olefin ("PAO8") or other commercial basestocks.

[0082] Oxidation can be monitored by using a number of techniques, which usually address degradation reactions, primarily viscosity increase due to oxidative polymerization. Formation of oxypolymers might not only increase the viscosity, but may also result in formation of insoluble residues or even solidification of the whole lubricant.

[0083] Therefore, thin films of commercial basestocks and α-ω dibasic esters were compared by exposing their thin films to 120°C as described by Stoncius, A. et al. in "Volatiles from Thin Film Degradation of Bio-based, Synthetic and Mineral Basestocks" published in Industrial Lubrication & Tribology, 2013, 65 (3), 209-215, Emerald Group Publishing Edition or by Brazinskiene, D. et al. in "Ester Basestock Vaporisation from Thin Oil Films" published in Lubrication Science, DOI: 10.1002/ls.1372, pp 1-17, 2017, Wiley Edition.

[0084] The thin-film method determines how resistant oil is against formation of insoluble residues during oxidation. Degradation durations until initial formation of solid residues and complete solidification directly relate to oxidative stability. Test results are listed in Table 6.

Table 6. Durations until initial formation of insoluble residues were observed in 500 μm thick films of α-ω dibasic esters at 120°C

Vapor losses at test duration when full film solidification was observed are also listed					
Code	Alcohol moiety	Remainder	Initial residues observed	Full solidification observed	Vapor loss at solidification
			hrs	hrs	% w/w
Dibasic esters as Exhibits					
26U18	2-ethylhexyl	α,ω C18:1	248	320	57%
37U18	2-propylheptyl	α,ω C18:1	248	324	54%
48U18	2-butyloctyl	α,ω C18:1	248	320	47%
4826U18	2-butyloctyl: 2-ethylhexyl	α,ω C18:1	248	325	57%
9U18	isononyl	α,ω C18:1	344	367	71%
Other pertinent dibasic esters					
1U18	methyl	α,ω C18:1	248	344	
17U18	methylheptyl	α,ω C18:1	343	463	63%
26S9	2-ethylhexyl	α,ω C9:0	367	553	92%
26S12	2-ethylhexyl	α,ω C12:0	583	655	86%
5U18	isoamyl	α,ω C18:1	152	225	66%
2026U18	phytyl: 2-ethylhexyl	α-ω C18:1	152	176	39%
Pertinent commercial basestocks					
350N		paraffinic oil	> 722	> 722	
LEAR		60% C18:1	20	26	3%
PAO8		poly α-olefin	722	> 722	55%

[0085] The degradation results show that rapeseed oil ("LEAR") produces insolubles in just 26 hrs, which is much faster than any other sample. Despite somewhat shorter durations of full solidification, oxidative stability of monounsaturated α-ω dibasic esters is more similar to that of PAO8 than to LEAR. The intermediate character of resistance to oxidation is fully sufficient for monounsaturated α-ω dibasic esters to function as hydraulic fluids.

6.3 Compatibility with lubricant additives

[0086] Several typical lubricant additives have been tested for solubility in α-ω dibasic esters of 2-ethyl hexanol 26U18 and 26S12 as well as commercial basestock 350N. The additives were mixed in at temperatures of 50°C or lower and

held for longer than a week at room temperature. Additive descriptions are listed in Table 7.

Table 7. Solubility of lubricant additives, dissolved in α-ω dibasic esters and commercial basestocks

Additive concentration & tradename	1% w/w Cobratec TT-100	1% w/w Irgalube ML605A	1% w/w Vanlube 7611 M	1% w/w Vanlube 7723	2% w/w Vanlube RI- A	5% w/w Viscoplex 10-310
Chemical category	Tolyl triazole	Amine and phosphate derivatives	Phos-phoro dithioate	Alkyl dithiocarbamate	Soap and ester derivatives	Poly alkyl methacrylate
Additive function	Corrosion inhibitor, copper passivator	Additive package for ashless hydraulic fluids	Antioxidant, lubricity additive	Anti-Wear additive	Lubricity additive for hydraulic fluids	Pour point depressant
Additive appearance	Light brown solid flakes	Yellow liquid	Yellow liquid	Yellow liquid	Yellow liquid	Yellow liquid
Recommended concentration in hydraulic fluids	0.05% - 0.2%	0.2%-1.0%	0.1% - 0.5%	0.1% - 0.5%	0.1% - 0.5%	0.5% - 2%
26S12	soluble	soluble	soluble	soluble	soluble	soluble
26U18	soluble	soluble	soluble	soluble	soluble	soluble
LEAR	soluble	soluble	soluble	soluble	soluble	soluble
350N	cloudy	soluble	soluble	soluble	soluble	soluble

[0087] The additives were selected to represent different chemical categories: soaps, heterocycles, phosphorous derivatives, polymers, etc. Most of these additives are designed to be dissolved in paraffinic mineral oils and synthetic lubricants with some heating. It is often thought that esters are better solvents than mineral oils or synthetic hydrocarbons like poly α-olefins. Therefore, the tested concentrations were much higher than additive proportions for hydraulic fluids, as recommended by the additive manufacturers.

[0088] Additives did not show any problems when blending in with α-ω dibasic esters 26U18 and 26S12. Initial solution appearance was bright and clear. The appearance of stored solutions after 1 week at room temperature remained unchanged. Presence of monounsaturation did not affect additive solubility negatively. Since tested concentrations were so much higher than recommended additive proportions, additive solubility does not present any problem. All tested additives stayed dissolved in mineral oil 350N as well, except tolyl triazole, which is widely used in hydraulic fluids as corrosion inhibitor. Initially, it fully dissolved at 1% w/w concentration in 350N with heating. However, after some storage at room temperature significant portion precipitated out and made the formulation cloudy, see Fig. 7. This demonstrates that solubilizing power of dibasic esters is better compared to mineral oils and paraffinic hydrocarbons.

[0089] Most other lubricant properties can be successfully controlled by additives, as long as the basestock shows acceptable viscosity, low temperature fluidity, volatility, oxidative stability and additive compatibility. A number of synthesized monounsaturated α-ω dibasic esters, presented as Exhibits, demonstrate all the key properties, necessary for the basestock to function successfully in most lubricant applications as claimed below.

Claims

1. Use of a composition of dibasic esters of monounsaturated α, ω-diacids as a lubricant constituent, wherein said composition comprises from 60 to 100%, preferably 80 to 100% by weight:

   according to option a) of at least one monounsaturated α-ω dibasic ester compound of Formula (I) :

   $$R1\text{-}OOC\text{-}(CH_2)_xCH{=}CH\text{-}(CH_2)_y\text{-}COO\text{-}R2$$

   with

X + y being an integer in the range from 10 to 22, preferably from 10 to 16 ;
and with R1 and R2 being identical or different and being selected from the residues of branched alcohols with at least 5 carbon atoms (in C_5), preferably from 5 to 36 carbon atoms (in C_5 to C_{36}), more preferably from 5 to 26 carbon atoms (in C_5 to C_{26}), even more preferably from 5 to 22 carbon atoms (in C_5 to C_{22}) with said branched alcohols being either saturated or mono unsaturated and bearing at least one branch in C_1 to C_6, preferably in C_2 to C_6 or in C_1 in case of multiple branches (at least two) or
according to option b) of a mixture comprising :

b1) as predominant component at least one monounsaturated α-ω dibasic ester compound of Formula (I) as defined above in option a) and
b2) at least one monounsaturated α-ω dibasic ester compound of Formula (II) :

$$R'1\text{-}OOC\text{-}(CH_2)_x\text{-}CH{=}CH\text{-}(CH_2)_y\text{-}COO\text{-}R'2 \qquad (II)$$

with

x + y being as defined in Formula (I) above ;
and with R'1 and R'2 being identical or different and selected from the residues of methanol or ethanol, preferably being identical and being the residues of methanol,
and wherein, said composition has a weight content in estolides of the corresponding mono unsaturated acids of less than 1% w/w, preferably less than 0.1% w/w or less than 0.05% w/w and more preferably 0% w/w.

2. The use according to claim 1, wherein said branch is in C_2 to C_6 or in C_1 in case of a multiple branches (at least 2 branches present).

3. The use according to claim 1 or 2, wherein R1 and R2 have a number of carbon atoms varying from 5 to 22 (in C_5 to C_{22}).

4. The use according to any one of claims 1 to 3, wherein x + y ranges from 10 to 16.

5. The use according to any one of claims 1 to 4, wherein x + y is 14, preferably with x = 7 and y = 7.

6. The use according to any one of claims 1 to 5, wherein x is from 6 to 9.

7. The use according to any one of claims 1 to 6, wherein R1 or R2 are residues of branched alcohols selected from the group consisting of : 2-ethylhexyl, 2-butyl octyl, 2-propyl heptyl, phytyl (3,7,11,15-tetramethyl-2-hexadecenyl), 1-methyl heptyl, 3,5,5-trimethyl hexyl, residues of terpenic alcohols, residue of farnesol, including their partially hydrogenated homologues, isocetyl, isostearyl, isooctyl (2,4,4-trimethylpentyl), cyclohexyl, abietyl and of their mixtures, preferably at least one of: 2-butyl octyl, 2-propyl heptyl, phytyl (3,7,11,15-tetramethyl-2-hexadecenyl), 3,5,5-trimethyl hexyl (isononyl) and of their mixtures.

8. The use according to any one of claims 1 to 7, wherein the said at least one monounsaturated α-ω dibasic ester compound of Formula (I) is selected from diesters with x + y = 14 with x = y = 7 and with R1 and R2 selected from the group consisting of at least one of : 2-ethylhexyl or 2-butyl octyl, 2-propylheptyl, phytyl (3,7,11,15-tetramethyl-2-hexadecenyl), 1-methylheptyl or 3,5,5-trimethylhexyl and of their mixtures.

9. The use according to any one of claims 1 to 8, wherein said at least one monounsaturated α-ω dibasic ester compound of Formula (I) is a blend (mixture) of at least two different dibasic ester compounds of Formula (I).

10. The use according to claim 9, wherein the at least two different compounds of Formula (I) are different in :

- x and/or y,
- x + y and/or
- R1 and/or R2 or
- in all possible binary or ternary combinations of the above-cited differences.

11. The use according to claims 9 or 10, wherein said blend is a blend of : a dibasic ester compound of Formula (I)

having x = y = 7 and x + y = 14 at a content higher than 60% w/w with respect to the said blend, with at least another different dibasic ester compound of Formula (I) with x + y from 16 to 22, preferably with x + y of 16, 18, 20 or 22.

12. The use according to any one of claims 1 to 11, wherein R1 and R2 are different and are residues of a blend of different branched alcohols.

13. The use according to any one of claims 1 to 12, wherein said composition of dibasic esters of monounsaturated α-ω diacids is issued from the transesterification by said branched alcohols as defined in any one of claims 1 to 3, 7 or 8, of an α-ω dialkyl dibasic ester of Formula (II) :

$$R'1\text{-}OOC\text{-}(CH_2)_x\text{-}CH{=}CH\text{-}(CH_2)_y\text{-}COO\text{-}R'2 \qquad (II)$$

with R'1 and R'2 being identical or different and selected from a methyl or an ethyl, preferably being identical and being a methyl and
x, y being as defined in any one of claims 1, 4, 5, 10 or 11.

14. The use according to claim 13, wherein said diacid is issued from a self-methathesis reaction of a fatty mono unsaturated monoacid or said dibasic ester of Formula (II) is issued from a self-metathesis of a fatty mono unsaturated monoacid ester.

15. The use according to anyone of claims 1 to 14, wherein said composition comprises a mixture according to option b).

16. The use according to claim 15, wherein said mixture according to option b) comprises up to 99.9% by weight of b1) selected from at least one dibasic ester compound according to Formula (I) and at least 0.1% w/w of at least one dibasic ester compound according to Formula (II) which is a diester of methanol or of ethanol or of a mixture of methanol and ethanol, preferably of methanol.

17. The use according to claim 15 or 16, wherein the ratio in weight of b1)/b2) varies from 0.85/0.15 to 0.99/0.01.

18. The use according to any one of claims 1 to 17, wherein the total number of carbon atoms in said diester compound as defined according to Formula (I) varies from 34 to 42 and preferably from 38 to 42.

19. The use according to any one of claims 1 to 18, wherein the said branch of said branched alcohol is in position 2 of said alcohol.

20. A lubricant composition, wherein it results from the use as a lubricant constituent, of at least one dibasic ester composition as defined according to any one of claims 1 to 19.

21. The lubricant composition according to claim 20, wherein in addition to said dibasic ester composition comprised at a content of at least 80%, preferably from 90 to 99.7% w/w with respect to the total weight of said lubricant composition, it further comprises up to 20%, preferably from 0.3 to 10% w/w of other additives selected from the group consisting of other lubricant additive, antiwear agent, antioxidant, corrosion inhibitor, friction modifier, alkalinity carrier, biocide, buffering agent, chelating additive, coupler, water demulsifier, dispersant, detergent, elastomer conditioner, dye, mist suppressant, odorant, copper passivator, pour point depressant, tackifier, thickener, viscosity index improver, surfactant or defoamer.

22. The lubricant composition according to claim 20 or 21, wherein it is a lubricant basestock composition.

23. The lubricant composition according claim 22, wherein said lubricant basestock composition is issued from renewable resources and it is a biodegradable lubricant composition.

24. Use of the lubricant composition according to any one of claims 20 to 23, wherein it is as engine oils or as hydraulic fluids in transport, agriculture, food and industrial applications.

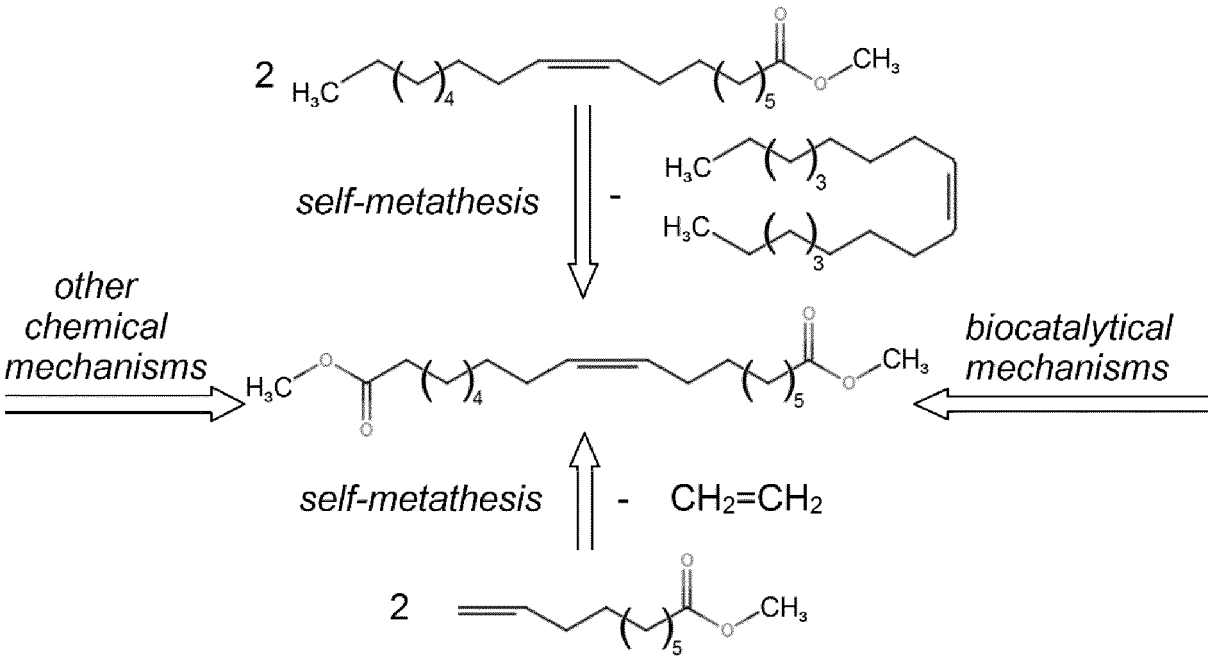

Fig. 1 Scheme of 1U18 production by self-metathesis from oleic or from 9-decenoic acids, with other pathways possible (includes the self-metathesis reaction occurring as a side reaction during cross metathesis reactions)

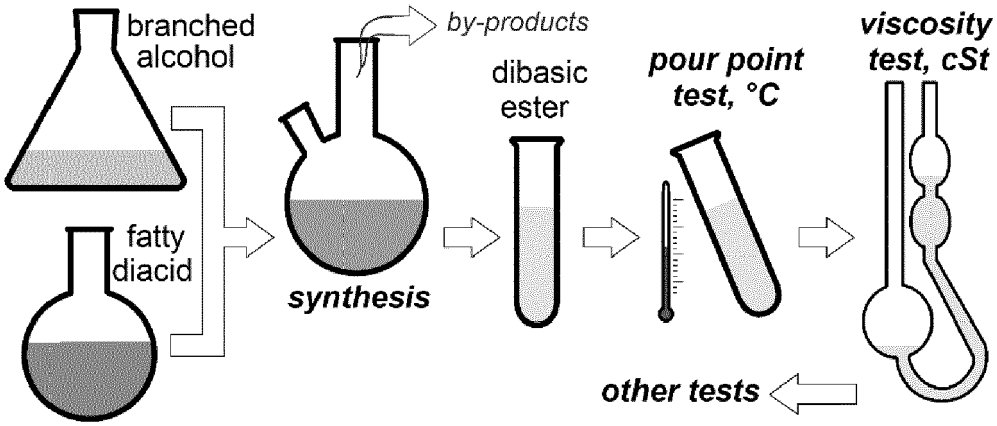

Fig. 2 Scheme of synthesis and fluidity measurements by recording kinematic viscosities at 40°C and 100°C with cloud and pour points

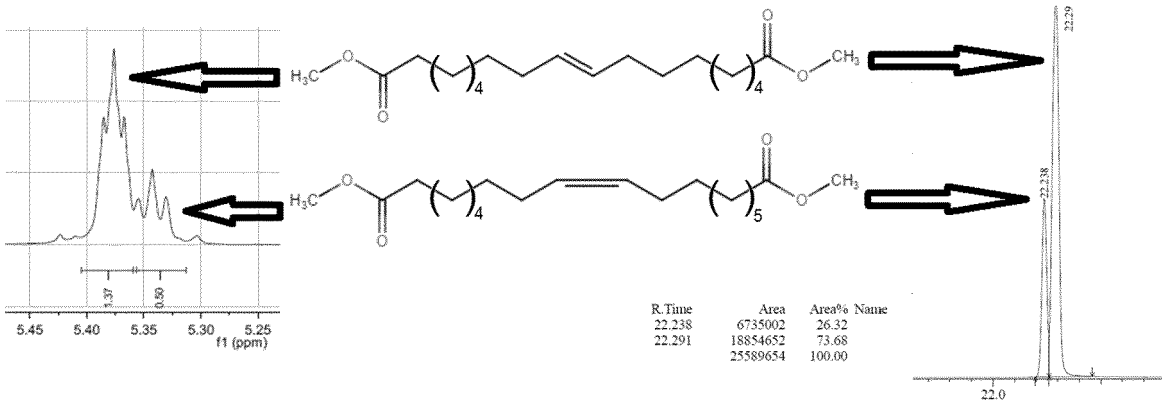

Fig. 3 Isomeric ratio of α-ω C18:1 dibasic methyl ester (code 1U18) between trans- and cis-, i.e. 9E (upper) : 9Z (lower), showing 2.74:1 proportion on ^{1}H NMR (left) and 2.80:1 on GC-MS (right)

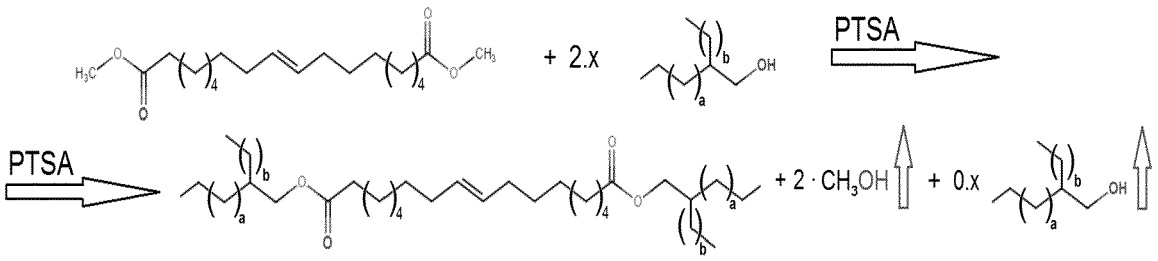

Fig. 4 Synthesis scheme of α-ω C18:1 dibasic Guerbet esters. Incoming reagent 1U18 and reaction products (a = 3 b = 2 for compound code 37U18 ; a = 4 b = 3 for 48U18) also contain cis- isomers

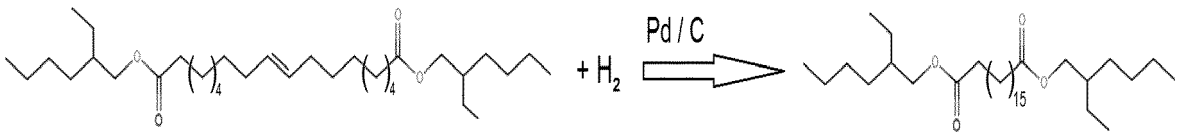

Fig. 5 Hydrogenation of monounsaturated α-ω dibasic ester into fully saturated dibasic ester

Synthesis details are provided in the description § 3.4

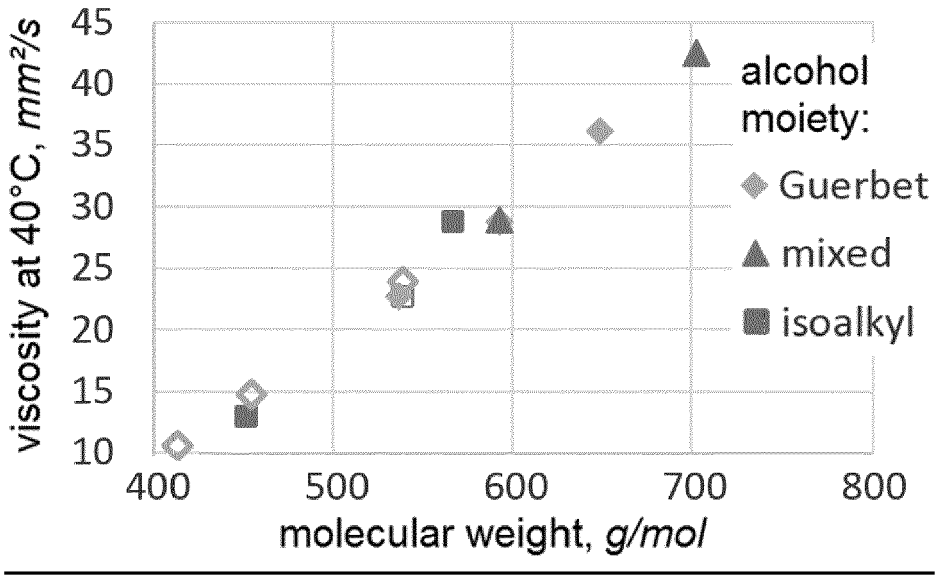

Fig. 6 Dependence of kinematic viscosities of synthesized dibasic esters with α-ω fatty diacids on the molecular weights of the compounds. Diamonds – Guerbet alcohols esters of fatty diacids. Squares – esters of isoalkyl alcohols with fatty diacids. Triangles – mixed esters 4826U18 and 2026U18. Hollow symbols – fully saturated dibasic esters

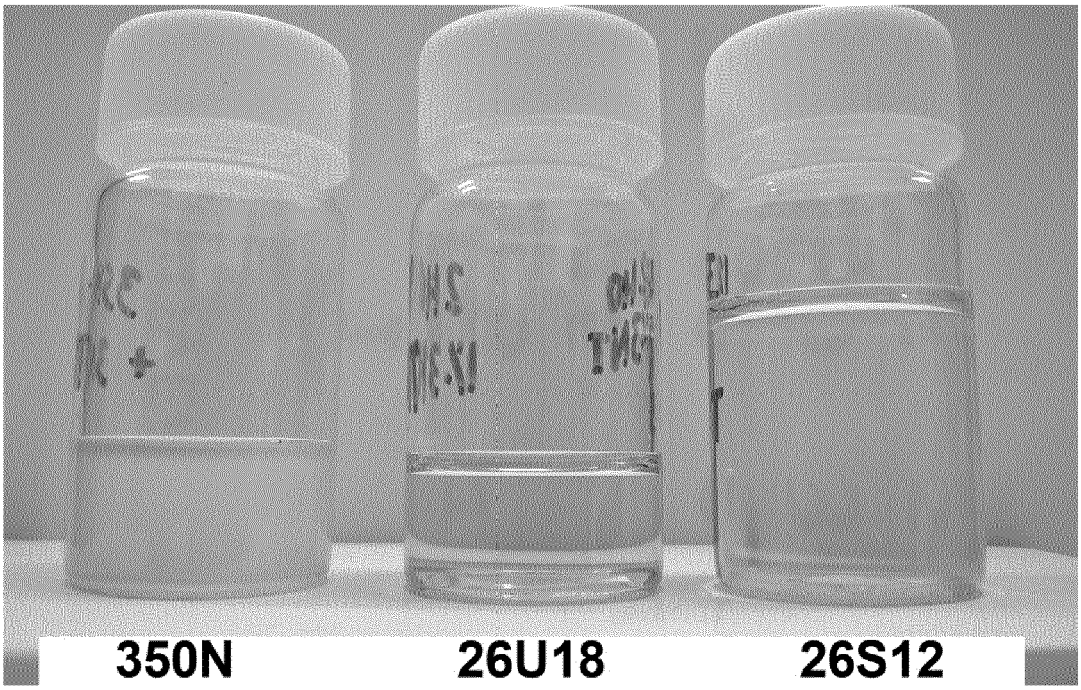

Fig. 7 Appearance of 1% w/w mixtures of tolyl triazole in mineral oil 350N, monounsaturated dibasic ester 26U18 and saturated dibasic ester 26S12 after storage at room temperature. Initially, clear solutions were produced with heating to 50°C.
From left to right : 350N cloudy yellow solution, 26U18 clear yellow solution, 26S12 water clear solution.

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EUROPEAN SEARCH REPORT

Application Number
EP 17 20 0996

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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	16 April 2018	Bork, Ana-Maria

CATEGORY OF CITED DOCUMENTS

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