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(54) **Dielectric triglyceride fluids**

Dielektrische Triglyceridflüssigkeiten

Fluides de triglycérides diélectriques

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(56) References cited:
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Description**Technical field**

5 [0001] The present invention pertains to triglyceride-based dielectric fluids for electrical and/or power applications, methods for preparing said fluids, electrical and/or power apparatuses comprising said fluids, as well as uses of the dielectric fluids as such.

Technical background

10 [0002] Insulating, dielectric fluids are used in electrical apparatuses like transformers, capacitors, switchgear, bushings, etc., and have a multitude of functions. Dielectric fluids act as electrically insulating medium separating the high voltage and the grounded parts within the apparatus and function as a cooling medium to transfer the heat generated in the current-carrying conductors. Additionally, the fluids provide a medium to monitor the health of a transformer during
15 operation.

[0003] In addition to the basic abovementioned functions, the insulating liquid should also comply with other necessary and desired requirements. The fluid should have a high efficiency, long life, and minimal environmental impact. Further, the fluid has to be compatible with the materials used in the electrical equipment and it should not constitute a hazard for the health and safety of personnel. In practice, insulating fluids should fulfill various physical, electrical, and chemical
20 properties and all these properties are regulated through standards and specifications that stipulate the minimum requirements for each one of the important properties.

[0004] For performing the electrical insulation function, the insulating oil must be designed to withstand the required electrical stresses as per the design specifications of the electrical apparatus. The dielectric breakdown withstand voltage under AC (50/60 Hz) and Lightning Impulse (1.2/50 μ s) is considered as the most important parameter from an electrical
25 insulation perspective. The dielectric breakdown withstand voltage can be defined as the voltage required to obtain a flashover in the oil between two electrodes of specified shape and placed at a certain distance from each other. The standards specify the type of electrodes and the gap distances required for the tests. The breakdown withstand is essentially an indicator of the oil purity from water, conducting particles, organic acids, and other electrolytes. These unwanted impurities in oil can be inherent to the oil or can be generated over a period of time due to aging of the oil
30 itself or from other sources. The other dielectric parameters of importance are the permittivity (which gives a measure of the electric field distribution in the system) and the dissipation factor (gives a measure of the dielectric losses). An understanding of the dielectric losses of insulating oils provides an indication of the impurity content or degradation over time of the oil in question.

[0005] Magnetic and electrical fields in a transformer are associated with losses that translate into heat generation. Solid insulation materials used in conjunction with insulating liquids will degrade over time and it is well known that the
35 degradation rate is a function of temperature. In order to preserve the functionality of the insulation system and also to prolong the apparatus life, it is necessary to regulate the temperature in an electrical apparatus. For example, in a transformer, the cooling system (duct diameter, oil volume and coolers) is designed to guarantee that under normal conditions, the oil flow is adequate to dissipate the heat produced in the system. The oil properties, therefore, affect the
40 heat dissipation and the most relevant parameters are the heat capacity, the viscosity, thermal conductivity and the flow properties.

[0006] Additional important properties of an insulating fluid for applications in power and/or electrical apparatuses are pour point, impregnation capability, blendability and water solubility/max water content. In terms of the chemical prop-
45 erties, the fluid has to be inert with many different materials, be free of sulphur and halogens, possess high flash/fire points and should not release or absorb gasses. A negative gassing tendency is a desirable property for the prevention of partial discharge. Traditionally, petroleum-based oils have been used as the insulating fluid in oil-filled transformers mainly because of advantageous properties relating to low viscosity, low pour point, high dielectric strength, easy avail-
50 ability and low cost. During the last couple of decades, the transformer industry has been undergoing several changes. The market demand for compact and efficient transformers with guaranteed long-term performance coupled with the problems of corrosive sulphur and oil quality issues have warranted the need for enhancement in the properties of transformer oil. Further, strict environmental regulations towards health and safety have been steadily evolving and the huge liability risks in the case of transformer fires or outages have raised a cause for concern. Considering these factors, serious research and development efforts have since the 1990s been directed towards identifying alternatives to mineral
55 oil.

[0007] Amongst the several options which are generally known, e.g., ester-based fluids, silicone fluid, chlorinated benzenes, perchloroethylene, polyalphaolefins etc., ester based fluids (both synthetic and natural) are excellent alter-
natives to mineral oil, primarily due to their high biodegradability (lower environmental risk) and high values of flash
points and fire points (high fire safety factor). Further, natural esters based on vegetable oils, with the main constituent

being triglycerides, are preferred due to their renewability. In spite of their appealing properties in terms of biodegradability and fire safety, vegetable oils are not utilized to any greater extent for power and/or electrical applications, as a result of a number of disadvantageous chemical and/or physical properties.

[0008] US6274067 discloses high oleic acid triglyceride compositions used in electrical insulation fluids.

Summary of the invention

[0009] There are consequently substantial needs in the art for improving the performance of triglyceride-based fluids for power and/or electrical applications, in order to replace the rather disadvantageous insulation fluids currently utilized within the industry.

[0010] Generally, all vegetable oils have a high viscosity as compared to mineral oil. If a transformer has to be operated at higher voltage levels, it may occasionally be necessary to circulate the oil inside the transformer through pumps. The high viscosity of vegetable-based liquids then poses several challenges towards the design of the transformer, especially from a cooling point of view. This leads to the requirement of a lower viscosity value for vegetable-based fluids.

[0011] Biodegradable natural ester-based liquids have high pour point temperatures as compared to mineral oil, which can be considered as a major drawback if the electrical apparatuses comprising the fluid have to be operated in extremely cold environments, a problem that is especially pronounced at higher voltage ratings. Further, a low pour point can cause changes in the dielectric and/or other properties of the fluid and the solid insulation impregnated with this fluid. This in turn can force design changes in the transformer which can lead to an increase in the manufacturing costs. A very low value of pour point is therefore desired for the vegetable fluid.

[0012] Oxidation behavior of the materials is an important parameter when it comes to insulation degradation in a transformer. The aging of pressboard insulation over time releases small amounts of oxygen into the oil, and therefore the oil has to withstand the oxidation-induced degradation. For natural ester fluids, the inherent stability to oxidation is highly dependent on the compositions of fatty acids in the base oil. Ester oils which are composed only of saturates (only C-C bonds in its structure) are stable against oxidation.

[0013] Specific heat in combination with thermal conductivity is also an important property of dielectric fluids. A higher specific heat will cause a lower rise in the temperature of the oil and a higher thermal conductivity will ensure that even if the speed of circulation of the oil is marginally slower than what it is in the case of mineral oil, the amount of heat conducted from the hot-spot regions in the transformer will be higher. A higher thermal conductivity can also result in an enhanced heat transfer at slightly higher temperatures because the viscosity of the ester fluid would be reduced at those temperatures.

[0014] Although several properties of the fluid, for instance viscosity, pour point and oxidation stability, can be modified or improved through the use of additives, there are certain disadvantages associated with the inclusion of any additional material into the fluid system, as this may lead to a reduction in the dielectric properties. This issue generates the need for enhancing the properties of a dielectric, triglyceride fluid without the use of any additives.

[0015] There is consequently a substantial need in the art for providing dielectric fluids, preferably derived from renewable resources, having numerous desirable properties in terms of inter alia reduced viscosity, improved heat transfer properties, reduced pour point, improved oxidation stability, and biodegradability, allowing for improved thermal management and better impregnation of pressboard/paper insulation, increased personnel health and safety, facilitated clean-up and prolonged service life of power and/or electrical apparatuses.

[0016] The present invention fulfils the above-identified needs, as it provides, inter alia, dielectric, triglyceride fluids, comprising various chemical modifications, displaying desirable properties in terms of inter alia reduced viscosity, improved heat transfer properties, reduced pour point, improved oxidation stability, and biodegradability, allowing for improved thermal management and better impregnation of pressboard/paper insulation, increased personnel health and safety, facilitated clean-up and prolonged service life of power and/or electrical apparatuses. Further, the present invention relates to processes and methods for preparing said dielectric, triglyceride fluids, as well as their uses in electrical and/or power apparatuses, in addition to electrical and/or power apparatuses per se comprising said dielectric, triglyceride fluids.

[0017] In a first aspect, the present invention relates to the dielectric triglyceride fluid obtained by reacting the at least one carbon-carbon double bond of a dielectric, triglyceride fluid having a fatty acid composition of between 10% and 100% fatty acids having at least one carbon-carbon double bond with at least one conjugated diene, resulting in the formation of a modified triglyceride having increased triglyceride fluidity.

[0018] In a second aspect, the present invention pertains to a method for preparing a dielectric, triglyceride fluids. The method comprises the steps of providing a triglyceride composition having a fatty acid composition of between approximately 10% and approximately 100% fatty acids having at least one carbon-carbon double bond. The at least one carbon-carbon double bond is subsequently reacted with at least one conjugated diene, normally in the presence of a catalyst, resulting in the formation of said dielectric, triglyceride fluids in accordance with the present invention.

[0019] A third aspect of the present invention relates to an electrical and/or power apparatus comprising the dielectric triglyceride fluid of the present invention. In one embodiment, the dielectric fluid functions as an insulating medium, as

a result of its superior properties in terms of oxidation stability, fluidity, insulation, permittivity, reduced pour point, reduced viscosity, etc.

[0020] In a fourth aspect, the present invention pertains to various uses of the dielectric triglyceride fluid in electrical apparatuses, and/or in apparatuses for power applications, and/or in components utilized in said apparatuses. Apparatuses of interest as per the present invention may for instance be transformers, capacitors, switchgear, bushings, etc., as well components and/or parts utilized in power or electrical applications.

[0021] In a fifth aspect, the present invention relates to the use of a chemically modified triglyceride in dielectric fluids, wherein said chemically modified triglyceride is obtainable by reacting at least one carbon-carbon double bond of a triglyceride fatty acid moiety with at least one conjugated diene

Detailed Description of the Invention

[0022] The present invention pertains to dielectric, triglyceride fluids for various power and/or electrical applications, methods for preparing said fluids, electrical and/or power apparatuses and components comprising said fluids, as well as various uses of said fluids.

[0023] Where features, embodiments, or aspects of the present invention are described in terms of Markush groups, a person skilled in the art will recognize that the invention may also thereby be described in terms of any individual member or subgroup of members of the Markush group. The person skilled in the art will further recognize that the invention may also thereby be described in terms of any combination of individual members or subgroups of members of Markush groups. Additionally, it should be noted that embodiments and features described in the context of one of the aspects and/or embodiments of the present invention may also apply mutatis mutandis to all the other aspects and/or embodiments of the invention. For instance, the fatty acid compositions described in connection with one aspect/embodiment may naturally also apply mutatis mutandis in the context of other aspects/embodiments of the invention, all in accordance with the present invention as such.

[0024] All words and abbreviations used in the present application shall be construed as having the meaning usually given to them in the relevant art, unless otherwise indicated. For clarity, some terms are however specifically defined below.

[0025] As will be apparent from the description and the examples, the term "fatty acids" shall be understood to relate to any one of the three acyl moieties of a triglyceride, meaning that, for instance, in a triglyceride fluid having a fatty acid composition of approximately 40% fatty acids having one carbon-carbon double bond, approximately 40% of all the acyl moieties in the triglyceride fluid as a whole comprises one carbon-carbon double bond.

[0026] Further, the term "triglyceride fluidity" generally relates to the reciprocal of the triglyceride viscosity, i.e. in the context of the present invention it shall be understood to pertain to the dynamics and/or mobility of the triglyceride fatty acid chains.

[0027] The term "naturally derived" shall be understood to pertain to natural fluids and/or oils derived from renewable resources, for instance natural and/or genetically modified (GMO) plant vegetable seeds and/or fat from various animal sources. Said fluids and/or oils are generally comprised of triglycerides, i.e. three fatty acids linked to a glycerol moiety. The fatty acids may be saturated or un-saturated, with the unsaturations being either conjugated and/or unconjugated. Conjugation may be introduced synthetically, enzymatically, or by using any other types of physical and/or chemical means, or it may be naturally occurring.

[0028] Further, vegetable fluids and/or oils may for instance be selected from the group comprising, but that is not limited to, peanut, rapeseed, castor, olive, corn, cotton, canola, soybean, sesame, linseed, safflower, grapeseed, palm, avocado, pumpkin kernel, macadamia nut, sunflower, and any combinations and/or mixtures thereof. Additionally, fluids and/or oils may be obtained from essentially any organisms being a suitable fluid and/or oil source. Fluids and/or oils derived from animal sources may be selected from the group comprising beef tallow, fish oils, lard, and any combinations and/or mixtures thereof. Naturally, various combinations of the above fluids and/or oils may be utilized, irrespective of the source.

[0029] The fatty acids comprised in the triglycerides may be of essentially any length, having essentially any number of unsaturations, either conjugated and/or unconjugated. Fatty acids may be for instance be selected from the group comprising, but that is not limited to, oleic acid, linoleic acid, α -linolenic acid, myristoleic acid, arachidonic acid, icosapentaenoic acid, palmitoleic acid, erucic acid, and docosahexaenoic acid, butyric acid, caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, vaccenic acid, gamma-linolenic acid, behenic acid, erucic acid, lignoceric acid, or any other fatty acids, suitably modified, if needed, in accordance with the requirements of the present invention.

[0030] The term "alkyl" or "alkylene", as used herein, is a (C₁-C₅₀)alkyl or (C₁-C₅₀)alkylene moiety, e.g. a (C₂-C₃₀)alkyl or (C₁₀-C₄₀)alkylene moiety and is intended to encompass also the alkyl or alkylene portion of any functional group, e.g. an alkoxy, alkylamino, or carboxypolyoxyalkylene group. Also, any alkyl or alkylene group in accordance with the present invention may be branched or unbranched, and/or cyclic. The term "alkyl" includes the monoradical derived from

a branched or unbranched and/or cyclic alkane.

[0031] In a first aspect, the present invention relates to the dielectric triglyceride fluid obtained by reacting the at least one carbon-carbon double bond of a dielectric, triglyceride fluid having a fatty acid composition of between 10% and 100% fatty acids having at least one carbon-carbon double bond with at least one conjugated diene, resulting in the

formation of a modified triglyceride having increased triglyceride fluidity.

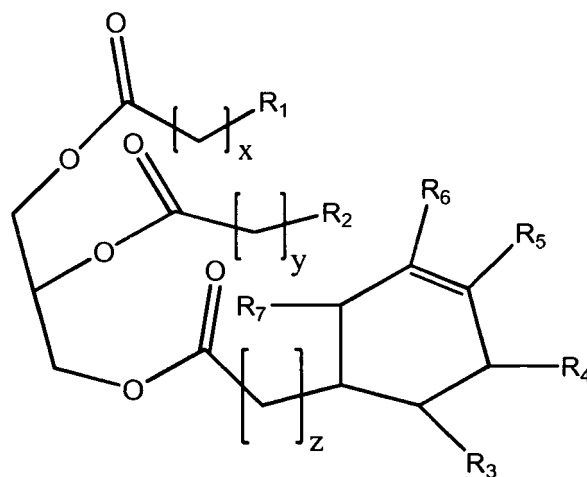
[0032] The reaction between fatty acids having at least one carbon-carbon double bond and the at least one conjugated diene may take place through a Diels-Alder reaction mechanism, or a radical mechanism, or through any other reaction mechanism, known and/or unknown. In case the reaction occurs through a Diels-Alder mechanism, the at least one conjugated diene acts as the diene whereas the at least one carbon-carbon double bond acts as the dienophile.

[0033] The reaction between fatty acids having at least one carbon-carbon double bond and the at least one conjugated diene, which essentially results in the introduction of steric hindrance between the fatty acyl chains, leads to increased triglyceride fluidity, i.e. increased dynamics and facilitated motion of the triglyceride fatty acyl chains.

[0034] In one embodiment, the at least one conjugated diene further comprises at least one second moiety that further increases triglyceride fluidity. In another embodiment, the at least one second moiety may be a saturated or unsaturated, branched, linear and/or cyclic hydrocarbon, optionally substituted with at least one heteroatom. The at least one second moiety may be attached to any part of the conjugated diene and, in yet another embodiment, the at least one second moiety may for instance be selected from the group comprising inter alia branched or linear, and/or cyclic, (C₁-C₅₀)alkyl, (C₁-C₅₀)alkenyl, and (C₁-C₅₀)alkynyl, any hydrocarbonyl, aromatic hydrocarbons comprising at least one aromatic ring structure, any combination of the above and all of the above optionally substituted with at least one heteroatom, selected from the group comprising inter alia nitrogen, oxygen, phosphorous, boron, silicone, etc, and optionally further comprising various functional groups and/or moieties such as carboxylic acids, carboxylates, amines, primary amines, secondary amines, tertiary amines, quaternary amines, amides, imines, imides, azides, azo, cyanates, isocyanides, isocyanates, nitro, nitriles, nitrosooxy, nitrate, nitroso, pyridyl, esters, ethers, alcohols, acyl, ketones, carbonates, peroxy, carboxamide, thio, phosphine, phosphodiester, phosphono, phosphate, phenyl, benzyl, aryl, etc., or any combinations thereof.

[0035] In a further embodiment, the conjugated diene may for instance be selected from the group comprising, alkyl-, alkenyl-, and/or alkynyl-substituted cyclopentadiene.

[0036] In one embodiment, the dielectric triglyceride fluid may comprise inter alia a triglyceride exemplified in a non-limiting manner by the following structural formula (I), shown merely in a schematic, inexact manner for simplicity, as will be immediately recognized by a person skilled in the art:



(I)

wherein, x, y, and z may be independently selected from integers of 0-50, each R₁ and R₂ may independently be selected from the group comprising saturated or unsaturated, branched, linear, and/or cyclic (C₀-C₅₀)alkyl, each R₃, R₄, R₅, R₆ and R₇ may be independently selected from hydroxy, hydroxyalkyl, hydroxyalkoxy, hydroxyalkoxyalkyl, hydroxypolyoxyalkylene, alkoxy, alkoxyalkyl, polyoxyalkylene, carboxy, carboxyalkyl, carboxyalkoxy, carboxyalkoxyalkyl, carboxypolyoxyalkylene, alkoxy carbonyl, alkoxy carbonylalkyl, alkoxy carbonylalkoxy, alkoxy carbonylalkoxyalkyl, alkoxy carbonylpolyoxyalkylene, amino, alkylamino, dialkylamino, aminoalkyl, alkylaminoalkyl, dialkylaminoalkyl, aminoalkoxy, alkylaminoalkoxy, dialkylaminoalkoxy, aminopolyoxyalkylene, alkylaminopolyoxyalkylene, dialkylaminopolyoxyalkylene, aminoalkoxyalkyl, alkylaminoalkoxyalkyl, dialkylaminoalkoxy alkyl, (amino) (carboxy)alkyl, (alkylamino) (carboxy)alkyl, (dialkylamino) (carboxy) alkyl, (amino) (carboxy) alkoxy, (alkylamino) (carboxy)alkoxy, (dialkylamino) (carboxy) alkoxy,

(amino)(carboxy)alkoxyalkyl, (alkylamino)(carboxy)alkoxyalkyl, (dialkylamino) (carboxy)alkoxy alkyl, (amino)(carboxy) polyoxyalkylene, (alkylamino)(carboxy)polyoxyalkylene, (dialkylamino)(carboxy)polyoxyalkylene, (alkoxycarbonyl)(amino)alkyl, (alkoxycarbonyl)(alkylamino)alkyl, (alkoxycarbonyl)(dialkylamino)alkyl, (alkoxycarbonyl) (amino) alkoxy, (alkoxycarbonyl)(alkylamino)alkoxy, (alkoxycarbonyl) (dialkylamino) alkoxy, (alkoxycarbonyl) (amino) alkoxyalkyl, (alkoxycarbonyl) (alkylamino)alkoxyalkyl, (alkoxycarbonyl)(dialkylamino)alkoxyalkyl, (alkoxycarbonyl)(amino)polyoxyalkylene, (alkoxycarbonyl)(alkylamino)polyoxyalkylene, (alkoxycarbonyl)(dialkylamino)polyoxyalkylene, acylamino, acylaminoalkyl, acylaminoalkoxy, acylaminoalkoxyalkyl, acylaminopolyoxyalkylene, acylalkylamino, acylalkylaminoalkyl, acylalkylaminoalkoxy, acylalkylaminoalkoxyalkyl, acylalkylaminopolyoxyalkylene, hydrazinocarbonyl, hydrazinocarbonylalkyl, hydrazinocarbonylalkoxy, hydrazinocarbonylalkoxyalkyl, hydrazinocarbonylpolyoxyalkylene, nitro, nitroalkyl, nitroalkoxy, nitroalkoxyalkyl, nitropolyoxyalkylene, cyano, cyanoalkyl, cyanoalkoxy, cyanoalkoxyalkyl, and cyanopolyoxyalkylene. The person skilled in the art immediately recognizes that the above structural formula may be varied, for instance in terms of inter alia the number and location of substituted cyclohexenes (e.g. on which fatty acid chain(s) the substituted cyclohexene(s) are located, the position along the fatty acid chain(s)), the number and locations of unsaturations of the fatty acid chains (e.g. the presence of conjugated or unconjugated unsaturation(s), whether the unsaturations are located on the ester side or on the alkyl side of the substituted cyclohexene(s)), and the length and the branching of the fatty acid chains (e.g. the presence of branches either on the ester side and/or on the alkyl side of the substituted cyclohexene(s)), the length of the alkyl chains on the ester side and on the alkyl side of the substituted cyclohexene(s)), without departing from the spirit of the present invention. The person skilled in the art moreover recognizes that additional groups and moieties not specifically mentioned above are within the scope of the present invention. The introduction of the at least one substituted cyclohexene increases the fluidity of the triglyceride, rendering the fluid inter alia less viscous as well as more oxidation stable, as well as endowing the fluid with properties such as improved permittivity, reduced pour point, and improved insulation properties. In one embodiment, the at least one second moiety that further increases the triglyceride fluidity may correspond to R₃, R₄, R₅, R₆ and/or R₇, in accordance with structural formula (I) above. In additional embodiment, any pair of R₃, R₄, R₅, R₆ and R₇ may form a second ring system on the cyclohexene ring, for instance may a norbornene moiety be generated from a reaction between cyclopentadiene and the fatty acid having at least one carbon-carbon double bond.

[0037] The above-outlined structural formula merely depicts exemplary embodiments according to the present invention. A person skilled in the art would hence immediately realize that the above structural formula is primarily meant for illustrative purposes, and that other structures and moieties not specifically mentioned and/or illustrated above are encompassed by the present invention. Further, a person skilled in the art would immediately recognize the schematic nature of the above formula, and that additional suitable moieties may be incorporated in the formula without departing from the scope of the present invention.

[0038] As per a further embodiment of the present invention, the dielectric triglyceride fluid may further comprise less than approximately 20% saturated fatty acids, less than approximately 40% di-unsaturated fatty acids, less than approximately 20% tri-unsaturated fatty acids, and more than approximately 0% of other fatty acids, in order to endow the fluid with desirable properties in terms of oxidation stability, fluidity, insulation, permittivity, reduced pour point, reduced viscosity, etc. In a further embodiment, the dielectric triglyceride fluid may further comprise less than approximately 15% saturated fatty acids, or less than approximately 10% saturated fatty acids, or less than approximately 5% saturated fatty acids. As per another embodiment, the dielectric triglyceride fluid may further comprise less than approximately 30% di-unsaturated fatty acids, or less than approximately 20% di-unsaturated fatty acids, or less than approximately 10% di-unsaturated fatty acids. In accordance with yet another embodiment in line with the present invention, the dielectric triglyceride fluid may further comprise less than approximately 15% tri-unsaturated fatty acids, or less than approximately 10% tri-unsaturated fatty acids, less than approximately 5% tri-unsaturated fatty acids. In accordance with a further another embodiment of the present invention, the dielectric triglyceride fluid may further comprise more than approximately 5% of other fatty acids, or more than approximately 10% of other fatty acids, or more than approximately 15% of other fatty acids, or more than approximately 20% of other fatty acids.

[0039] The triglycerides utilized for the aspects and/or embodiment of the present invention may be naturally derived, optionally comprising synthetic modifications. Employing naturally derived triglycerides enables development of dielectric, triglyceride fluids, in line with a preferred embodiment of the present invention, for power and/or electrical applications. The dielectric triglyceride fluids as per the present invention may exhibit reduced viscosity, improved insulation, reduced pour point, improved oxidation stability, permittivity, biodegradability, as well as other highly attractive properties, for instance resulting in improved personnel health and safety, negligible environmental impact, and facilitated and safer handling.

[0040] In a preferred embodiment, the present invention relates to a naturally derived triglyceride comprising one, two, or three carbon-carbon double bonds. Said naturally derived triglyceride may preferably be reacted with cyclopentadiene or cyclopentadiene substituted with alkyl, alkenyl, and/or alkynyl, generating a chemically modified triglyceride having increased fluidity, implying improved properties in terms of inter alia reduced viscosity, improved insulation, reduced pour point, improved oxidation stability, permittivity, and biodegradability.

[0041] In another embodiment, the dielectric triglyceride fluid may have a permittivity value in the range between approximately 2.2 and approximately 4.5, in order to provide a dielectric triglyceride fluid with optimized properties.

[0042] One aspect of the present invention pertains to a method for preparing a dielectric, triglyceride fluid. The method comprises the steps of providing a triglyceride composition having a fatty acid composition of between approximately 10% and approximately 100% fatty acids having at least one carbon-carbon double bond. The at least one carbon-carbon double bond is subsequently reacted with at least one conjugated diene, normally in the presence of a catalyst, resulting in the formation of the dielectric triglyceride fluids in accordance with the present invention. The method for preparing dielectric, triglyceride fluids enables facile and inexpensive production of fluids with highly desirable properties in terms of inter alia oxidation stability, fluidity, insulation, permittivity, reduced pour point, and reduced viscosity.

[0043] In one embodiment, the catalyst is a Lewis acid, i.e. any substance capable of accepting a pair of electrons. In yet another embodiment, the Lewis acid may for instance be selected from the group comprising aluminium chloride, ethylaluminium dichloride, and/or ethylaluminium sesquichloride.

[0044] As per an additional embodiment of the present invention, the reaction step may be carried out at between approximately 100°C and 200°C, preferably approximately 160°C. In yet another embodiment, the reaction step may be carried out at between approximately 1000 MPa (10 kbar) and approximately 1600 Mpa (16 kbar), preferably approximately 1300 MPa (13 kbar), during, in a further embodiment, between approximately 20 h and approximately 30 h, preferably approximately 24 h.

[0045] One aspect of the present invention relates to an electrical and/or power apparatus comprising the dielectric triglyceride fluid of the present invention. In one embodiment, the dielectric fluid functions as an insulating medium, as a result of its superior properties in terms of inter alia oxidation stability, fluidity, insulation, permittivity, reduced pour point, reduced viscosity, etc.

[0046] Another aspect of the present invention pertains to various uses of the dielectric triglyceride fluid for instance in electrical apparatuses, and/or in apparatuses for power applications, or in components utilized in said apparatuses. Apparatuses of interest as per the present invention may for instance be transformers, capacitors, switchgear, bushings, etc., as well components and/or parts utilized in power or electrical applications. In one embodiment, the dielectric fluid may be utilized in for instance paints and coatings, printing inks, lubricants, surfactants, or within the food and/or cosmetics industry.

[0047] In yet another aspect, the present invention relates to the use of a chemically modified triglyceride in a dielectric fluid, wherein said chemically modified triglyceride is obtainable by reacting at least one carbon-carbon double bond of a triglyceride fatty acid moiety with at least one conjugated diene

[0048] In one embodiment, the at least one conjugated diene may optionally further comprise at least one second moiety that further increases triglyceride fluidity. As per a further embodiment, the at least one second moiety may be a saturated or unsaturated, branched, linear and/or cyclic hydrocarbon, optionally substituted with at least one heteroatom. In yet another embodiment, the at least one conjugated diene may be selected from the group comprising cyclopentadiene, cyclopentadiene substituted with alkyl, alkenyl, and/or alkynyl.

Examples

Cyclopentadiene-modified triglycerides

[0049] Cyclopentadiene is added to a solution comprising triglycerides having a fatty acid composition of between approximately 10% and approximately 100% fatty acids having at least one carbon-carbon double bond. The cyclopentadiene is reacted with the carbon-carbon double bond in the presence of a Lewis acid catalyst, which most likely mediates a Diels-Alder reaction between the dieneophile (i.e. the carbon-carbon double bond) and the diene (i.e. the cyclopentadiene). Said reaction produces a modified triglyceride displaying improved properties in terms of increased fluidity, insulation, permittivity, reduced pour point, reduced viscosity, improved oxidation stability, etc.

Alkene-modified triglycerides

[0050] A (C₁-C₃₀)alkyl having two carbon-carbon double bonds in conjugated positions (i.e. a conjugated diene) is added to a solution comprising triglycerides having a fatty acid composition of between approximately 40% and approximately 100% fatty acids comprising at least one carbon-carbon double bond. The conjugated diene may be reacted with the carbon-carbon double bond of the triglyceride in the presence of a Lewis acid catalyst, which most likely mediates a Diels-Alder reaction between the dieneophile (i.e. the carbon-carbon double bond present on the fatty acid moiety of the triglyceride) and the diene (i.e. the two carbon-carbon double bonds located in conjugated positions on the (C₁-C₃₀) alkyl). Said reaction produces a modified triglyceride displaying improved properties in terms of increased fluidity, insulation, permittivity, reduced pour point, reduced viscosity, improved oxidation stability, etc.

Claims

- 5
1. A dielectric, triglyceride fluid obtained by reacting the at least one carbon-carbon double bond of a dielectric triglyceride fluid having a fatty acid composition of between 10% and 100% fatty acids having at least one carbon-carbon double bond with at least one conjugated diene.
 2. The dielectric triglyceride fluid according to claim 1, wherein the at least one conjugated diene optionally further comprises at least one second moiety that further increases triglyceride fluidity.
 - 10 3. The dielectric triglyceride fluid according to claim 2, wherein the at least one second moiety is a saturated or unsaturated, branched, linear and/or cyclic hydrocarbon, optionally substituted with at least one heteroatom.
 4. The dielectric triglyceride fluid according to claim any one of claims 1-3, wherein the at least one conjugated diene is selected from the group comprising cyclopentadiene, cyclopentadiene substituted with alkyl, alkenyl, and/or alkyl-
15 nyl.
 5. The dielectric triglyceride fluid according to any one of the preceding claims, further comprising less than 20% saturated fatty acids, less than 40% di-unsaturated fatty acids, less than 20% tri-unsaturated fatty acids, and more than 0% of other fatty acids.
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 6. A method for preparing the dielectric triglyceride fluid according to any one of the preceding claims, comprising the steps of:
 - a. providing a triglyceride composition having a fatty acid composition of between 10% and 100% fatty acids having at least one carbon-carbon double bond;
25 b. reacting said at least one carbon-carbon double bond with at least one conjugated diene, in the presence of a catalyst;thereby obtaining said dielectric, triglyceride fluid.
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 7. The method according to claim 6, wherein the catalyst is a Lewis acid.
 8. The method according to claim 7, wherein the Lewis acid is aluminium chloride.
 - 35 9. The method according to any one of claims 6 to 8, wherein step (b) is carried out at between 100°C and 200°C, preferably 160°C, and at between 1000 MPa (10 kbar) and 1600 MPa (16 kbar), preferably 1300 MPa (13 kbar), for between 20 h and 28 h, preferably 30 h.
 - 40 10. An electrical and/or power apparatus comprising the dielectric triglyceride fluid according to any one of claims 1 to 5.
 11. The electrical and/or power apparatus according to claim 10, wherein the dielectric fluid composition functions as an insulating medium.
 - 45 12. Use of the dielectric triglyceride fluid according to any one of claims 1 to 5 in an electrical apparatus.
 13. Use of a chemically modified triglyceride in a dielectric fluid, wherein said chemically modified triglyceride is obtainable by reacting at least one carbon-carbon double bond of a triglyceride fatty acid moiety with at least one conjugated diene
 - 50 14. Use according to claim 13, wherein the at least one conjugated diene optionally further comprises at least one second moiety that further increases triglyceride fluidity.
 15. Use according to claim 14, wherein the at least one second moiety is a saturated or unsaturated, branched, linear and/or cyclic hydrocarbon, optionally substituted with at least one heteroatom.
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 16. Use according to any one of claims 12 to 15, wherein the at least one conjugated diene is selected from the group comprising cyclopentadiene, cyclopentadiene substituted with alkyl, alkenyl, and/or alkynyl.

Patentansprüche

- 5 1. Dielektrisches Triglyzerid-Fluid, erhalten durch Umsetzung der wenigstens einen Kohlenstoff-Kohlenstoff-Doppelbindung eines dielektrischen Triglyzerid-Fluids, welches eine Fettsäurezusammensetzung von zwischen 10 % und 100 % Fettsäuren aufweist, die zumindest eine Kohlenstoff-Kohlenstoff Doppelbindung aufweisen, mit wenigstens einem konjugierten Dien.
- 10 2. Dielektrisches Triglyzerid-Fluid gemäß Anspruch 1, wobei das wenigstens eine konjugierte Dien optional weiterhin wenigstens einen zweiten Rest umfasst, der die Fluidität des Triglyzerids weiter steigert.
3. Dielektrisches Triglyzerid-Fluid gemäß Anspruch 2, wobei der wenigstens eine zweite Rest ein gesättigter oder ungesättigter, verzweigter, linearer und/oder zyklischer Kohlenwasserstoff ist, der optional mit wenigstens einem Heteroatom substituiert ist.
- 15 4. Dielektrisches Triglyzerid-Fluid gemäß einem der Ansprüche 1-3, wobei das wenigstens eine konjugierte Dien ausgewählt ist aus der Gruppe, umfassend: Cyclopentadien, Cyclopentadien substituiert mit Alkyl, Alkenyl, und/oder Alkynyl.
- 20 5. Dielektrisches Triglyzerid-Fluid gemäß einem der vorstehenden Ansprüche, weiterhin umfassend: weniger als 20 % gesättigte Fettsäuren, weniger als 40 % di-ungesättigte Fettsäuren, weniger als 20 % tri-ungesättigte Fettsäuren, und mehr als 0 % anderer Fettsäuren.
- 25 6. Verfahren zur Herstellung des dielektrischen Triglyzerid-Fluids gemäß einem der vorstehenden Ansprüche, umfassend die Schritte:
 - a. Bereitstellen einer Triglyzeridzusammensetzung, die eine Fettsäurezusammensetzung von zwischen 10 % und 100 % Fettsäuren aufweist, welche wenigstens eine Kohlenstoff-Kohlenstoff Doppelbindung aufweisen;
 - b. Umsetzen der wenigstens einen Kohlenstoff-Kohlenstoff Doppelbindung in Gegenwart eines Katalysators mit wenigstens einem konjugierten Dien, wodurch das dielektrische Triglyzerid-Fluid erhalten wird.
- 30 7. Verfahren gemäß Anspruch 6, wobei der Katalysator eine Lewis-Säure ist.
8. Verfahren gemäß Anspruch 7, wobei die Lewis-Säure Aluminiumchlorid ist.
- 35 9. Verfahren gemäß einem der Ansprüche 6 bis 8, wobei Schritt (b) ausgeführt wird bei zwischen 100°C und 200 °C, vorzugsweise 160 °C, und bei zwischen 1000 MPa (10 kbar) und 1600 MPa (16 kbar), vorzugsweise 1300 MPa (13 kbar), für zwischen 20 h und 28 h, vorzugsweise 30 h.
- 40 10. Elektrisches und/oder Energie-Gerät umfassend das dielektrische Triglyzerid-Fluid gemäß einem der Ansprüche 1 bis 5.
11. Elektrisches und/oder Energie-Gerät gemäß Anspruch 10, wobei die dielektrische Fluidzusammensetzung als ein isolierendes Medium fungiert.
- 45 12. Verwendung des dielektrischen Triglyzeridfluids gemäß einem der Ansprüche 1 bis 5 in einem elektrischen Gerät.
13. Verwendung eines chemisch modifizierten Triglyzerids in einer dielektrischen Flüssigkeit, wobei das chemisch modifizierte Triglyzerid durch Umsetzung wenigstens einer Kohlenstoff-Kohlenstoff Doppelbindung eines Triglyzerid-Fettsäurerestes mit wenigstens einem konjugierten Dien erhältlich ist.
- 50 14. Verwendung gemäß Anspruch 13, wobei das wenigstens eine konjugierte Dien optional weiterhin wenigstens einen zweiten Rest umfasst, der die Fluidität des Triglyzerids weiter steigert.
- 55 15. Verwendung gemäß Anspruch 14, wobei der wenigstens eine zweite Rest ein gesättigter oder ungesättigter, verzweigter, linearer und/oder zyklischer Kohlenwasserstoff ist, der optional mit wenigstens einem Heteroatom substituiert ist.
16. Verwendung gemäß einem der Ansprüche 12 bis 15, wobei das wenigstens eine konjugierte Dien ausgewählt ist

aus der Gruppe umfassend: Cyclopentadien, Cyclopentadien substituiert mit Alkyl, Alkenyl, und/oder Alkynyl.

Revendications

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1. Fluide diélectrique à base de triglycérides, que l'on a obtenu en faisant réagir avec au moins un diène conjugué la double liaison carbone-carbone, au nombre d'au moins une, d'un fluide diélectrique à base de triglycérides qui comportait, dans sa composition en acides gras, entre 10 % et 100 % d'acides gras dotés d'au moins une double liaison carbone-carbone.

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2. Fluide diélectrique à base de triglycérides, conforme à la revendication 1, dans lequel ledit diène conjugué au nombre d'au moins un comporte en outre, en option, au moins un deuxième fragment qui fait encore augmenter la fluidité des triglycérides.

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3. Fluide diélectrique à base de triglycérides, conforme à la revendication 2, dans lequel ledit deuxième fragment au nombre d'au moins un est un fragment hydrocarboné saturé ou insaturé, linéaire, ramifié et/ou cyclique, et en option, porteur d'au moins un substituant hétéroatomique.

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4. Fluide diélectrique à base de triglycérides, conforme à l'une des revendications 1 à 3, pour lequel ledit diène conjugué au nombre d'au moins un est choisi dans l'ensemble comprenant le cyclopentadiène et les dérivés de cyclopentadiène porteurs de substituant(s) alkyle, alcényle et/ou alcynyle.

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5. Fluide diélectrique à base de triglycérides, conforme à l'une des revendications précédentes, qui comprend en outre moins de 20 % d'acides gras saturés, moins de 40 % d'acides gras di-insaturés, moins de 20 % d'acides gras tri-insaturés, et plus de 0 % d'autres acides gras.

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6. Procédé de production d'un fluide diélectrique à base de triglycérides conforme à l'une des revendications précédentes, lequel procédé comporte les étapes suivantes :

- a) prendre une composition de triglycérides comportant, dans sa composition en acides gras, entre 10 % et 100 % d'acides gras dotés d'au moins une double liaison carbone-carbone ;
- b) et faire réagir ladite double liaison carbone-carbone au nombre d'au moins une avec au moins un diène conjugué, en présence d'un catalyseur ;

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ce qui donne ledit fluide diélectrique à base de triglycérides.

7. Procédé conforme à la revendication 6, dans lequel le catalyseur est un acide de Lewis.

8. Procédé conforme à la revendication 7, dans lequel l'acide de Lewis est du chlorure d'aluminium.

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9. Procédé conforme à l'une des revendications 6 à 8, dans lequel on met l'étape (b) en oeuvre à une température de 100 à 200 °C et de préférence de 160 °C, sous une pression de 1000 MPa (10 kbar) à 1600 MPa (16 kbar) et de préférence de 1300 MPa (13 kbar), et durant 20 à 30 heures et de préférence 24 heures.

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10. Appareil électrique et/ou de fourniture d'énergie, comprenant un fluide diélectrique à base de triglycérides conforme à l'une des revendications 1 à 5.

11. Appareil électrique et/ou de fourniture d'énergie, conforme à la revendication 10, dans lequel la composition de fluide diélectrique joue le rôle de milieu isolant.

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12. Utilisation d'un fluide diélectrique à base de triglycérides, conforme à l'une des revendications 1 à 5, dans un appareil électrique.

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13. Utilisation d'un triglycéride chimiquement modifié dans un fluide diélectrique, pour laquelle ledit triglycéride chimiquement modifié est accessible par réaction d'au moins une double liaison carbone-carbone d'un fragment acide gras de triglycéride avec au moins un diène conjugué.

14. Utilisation conforme à la revendication 13, pour laquelle ledit diène conjugué au nombre d'au moins un comporte

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en outre, en option, au moins un deuxième fragment qui fait encore augmenter la fluidité des triglycérides.

5 **15.** Utilisation conforme à la revendication 14, pour laquelle ledit deuxième fragment au nombre d'au moins un est un fragment hydrocarboné saturé ou insaturé, linéaire, ramifié et/ou cyclique, et en option, porteur d'au moins un substituant hétéroatomique.

10 **16.** Utilisation conforme à l'une des revendications 12 à 15, pour laquelle ledit diène conjugué au nombre d'au moins un est choisi dans l'ensemble comprenant le cyclopentadiène et les dérivés de cyclopentadiène porteurs de substituant(s) alkyle, alcényle et/ou alcynyle.

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 6274067 B [0008]