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(54) Fatty acid and fatty acid alkyl ester oil additives

(57) The present invention pertains to dielectric oil additives and dielectric oils obtainable from naturally occurring sources. Further, the present invention relates to the use of the dielectric oil additives and/or the dielectric oils in electrical and/or power applications, electrical and/or power apparatuses comprising the dielectric oil additives and/or the dielectric oils, as well as methods for preparing said dielectric oil additives and/or the dielectric oils. Moreover, the present invention relates to the use chemically modified fatty acids and/or fatty acid alkyl esters in dielectric fluids.

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Description

Technical field

[0001] The present invention pertains to fatty acid- and/or fatty acid alkyl ester-based dielectric oil additives, methods for preparing said additives, as well as uses thereof.

Technical background

[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 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 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 μs) is considered as the most important parameter from an electrical 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 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 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 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 properties, the fluid has to be inert with many different materials, should not contain sulphur and halogens, should 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.

[0007] 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 availability 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 oil.

[0008] 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 good alternatives 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 and vegetable oil derivatives are not utilized to any greater extent for power and/or electrical applications, neither as the main insulating oil component nor as insulating oil additives, as a result of a number of disadvantageous chemical and/or physical properties.

Summary of the invention

[0009] There are consequently substantial needs in the art for finding novel ways of utilizing the abundant source of renewable material obtainable from vegetable oils, i.e. triglyceride-based fluids, and fatty acids and/or fatty acid alkyl esters obtainable from triglycerides. Thus, the present invention aims at providing novel uses of fatty acids and/or fatty acid alkyl esters, obtainable from naturally occurring triglycerides, in improving the performance of fluids for power and/or electrical applications. In particular, dielectric oil additives obtainable from triglycerides may provide a novel way of modifying the properties of the rather disadvantageous insulation fluids currently utilized within the industry, as well as other vegetable oil-based insulation fluids under development.

[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 the cooling point of view. This leads to a requirement for a lower value of viscosity of vegetable based fluids, or, alternatively, the development of naturally derived dielectric oil additives for modulating the properties of insulating oils.

[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, which can be achieved using the dielectric oil additives of the present invention.

[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, but the addition of dielectric oil additives with desirable oxidation stability may be an alternative way of addressing issues pertaining to oxidation stability.

[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. Again, addition of dielectric oil additives based on modified fatty acids and/or fatty acid alkyl esters may endow insulation fluids with improved properties relating to specific heat and thermal conductivity.

[0014] There is consequently a substantial need in the art for providing dielectric fluid additives, preferably derived from renewable resources, having the capability of modulating numerous desirable properties in terms of inter alia reduced viscosity, improved heat transfer, 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.

[0015] The present invention fulfils the above-identified needs, as it provides, inter alia, dielectric, dielectric oil additives based on modified fatty acids and/or fatty acid alkyl esters bestowing insulation oils with improved 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 oil additives, as well as their uses in electrical and/or power apparatuses, in addition to the electrical and/or power apparatuses per se comprising said dielectric oil additives.

[0016] In a first aspect, the present invention pertains to a dielectric oil additive comprising a fatty acid and/or a fatty acid alkyl ester comprising at least one carbon-carbon double bond. The dielectric oil additive is obtained by reacting said at least one carbon-carbon double bond with at least one alkyl halide and/or at least one acyl halide.

[0017] In a second aspect, the present invention relates to a method for preparing dielectric oil additives. The method comprises the steps of providing a suitable fatty acid and/or a fatty acid alkyl ester, preferably naturally derived, comprising at least one carbon-carbon double bond. Subsequently, the at least one carbon-carbon double bond is reacted with at least one alkyl halide and/or at least one acyl halide, normally in the presence of a catalyst, generating the dielectric oil

additives in accordance with the present invention.

[0018] In a third aspect, the present invention concerns a method for preparing a dielectric oil, wherein the method comprises the steps of providing a suitable fatty acid and/or a fatty acid alkyl ester comprising at least one carbon-carbon double bond, subsequently reacting the at least one carbon-carbon double bond with at least one alkyl halide and/or at least one acyl halide, and finally adding to alkylated and/or acylated fatty acid and/or fatty acid alkyl ester to a suitable oil. The reaction may take place in the presence of a catalyst.

[0019] In a fourth aspect, the present invention relates to an electrical apparatus comprising the dielectric oil additive and/or the dielectric oil of the present invention.

[0020] In a fifth aspect, the present invention pertains to various uses of the dielectric oil additive and/or the dielectric oil 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.

[0021] In a sixth aspect, the present invention relates to the use of a chemically modified fatty acid and/or fatty acid alkyl ester in a dielectric fluid, wherein said chemically modified fatty acid and/or fatty acid alkyl ester is obtainable by reacting at least one carbon-carbon double bond of the fatty acid and/or of the fatty acid alkyl ester with at least one alkyl halide and/or at least one acyl halide.

Detailed Description of the Invention

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

[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 acyl halides 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 carboxylic acids with aliphatic tails, for instance, but 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, and lignoceric acid. The fatty acids may be saturated or un-saturated, branched or linear, conjugated or un-conjugated, and optionally having additional moieties attached to any part of the molecule.

[0026] 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.

[0027] 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.

[0028] The fatty acids 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.

[0029] The term "alkyl" or "alkylene", as used herein, is a (C_1-C_{50})alkyl or (C_1-C_{50})alkylene moiety, e.g. a (C_2-C_{30}) alkyl or (C_{10}-C_{40})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.

[0030] In a first aspect, the present invention relates to a dielectric oil additive comprising a fatty acid and/or a fatty acid alkyl ester comprising at least one carbon-carbon double bond. The dielectric oil additive is obtained by reacting said at least one carbon-carbon double bond with at least one alkyl halide and/or at least one acyl halide.

[0031] The reaction between the fatty acids and/or the fatty acid alkyl ester comprising at least one carbon-carbon double bond and the at least one alkyl halide and/or at least one acyl halide may take place through a Friedel-Crafts reaction mechanism, or a radical mechanism, or through any other reaction mechanism, known and/or unknown. Said reaction between a fatty acid and/or a fatty acid alkyl ester comprising at least one carbon-carbon double bond and the at least one alkyl halide and/or at least one acyl halide, leads to inter alia reduced viscosity of oils comprising the dielectric oil additive, as well as increased permittivity, increased oxidation stability, and reduced pour point, etc.

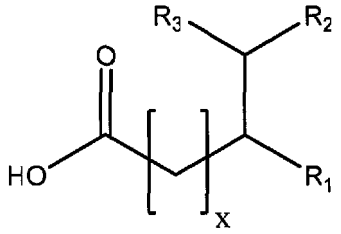
[0032] In one embodiment of the present invention, the fatty acids and/or the fatty acid alkyl ester comprising at least one carbon-carbon double bond are obtained from naturally derived oils and/or fluids, inter alia vegetable oil and/or oil from animal sources. The fatty acids and/or the fatty acid alkyl esters may be obtained through numerous different procedures, for instance acid-catalyzed hydrolysis of naturally derived triglycerides, and/or base-catalyzed hydrolysis of naturally derived triglycerides, and/or enzymatic treatments, and/or by any other chemical and/or physical means. Further, the number of unsaturations in the fatty acids and/or the fatty acid alkyl esters may be reduced or increased, depending on the desired characteristics of the resultant dielectric oil additive, and the fatty acids may additionally also be esterified into for instance methyl, ethyl, propyl, isopropyl, butyl, and essentially any type of alkyl esters.

[0033] In one embodiment in accordance with the present invention, the at least one alkyl halide and/or the at least one acyl halide optionally further comprise at least one moiety that further increases fatty acid and/or a fatty acid alkyl ester fluidity. In further embodiments, said moiety increasing the fatty acid and/or a fatty acid alkyl ester fluidity may be saturated or unsaturated, branched, linear and/or cyclic hydrocarbon, optionally substituted with at least one heteroatom. Said moiety that further increases the fatty acid and/or a fatty acid alkyl ester fluidity may be attached to any part of alkyl the moiety of the alkyl halide and/or any part of the acyl moiety of the acyl halide, and, in yet another embodiment, said moiety may for instance be selected from the group comprising inter alia branched or linear, and/or cyclic, (C_1-C_{50})alkyl, (C_1-C_{50})alkenyl, and (C_1-C_{50})alkynyl, any hydrocarbyl, 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, phosphine, phosphodiester, phosphono, phosphate, phenyl, benzyl, aryl, etc., or any combinations thereof.

[0034] In a further embodiment, the at least one alkyl halide may for instance be selected from the group comprising any alkyl halide, isopropyl chloroformate, isobutyl chloroformate, butyl chloroformate, octyl chloroformate, alkyl chloroformate, alkyl haloformate, cyclohexyl chloroformate, cyclohexyl haloformate, and di-tert-butylpyrocarbonate.

[0035] As per another embodiment of the present invention, the at least one acyl halide may for instance be selected from the group comprising any acyl halide, propanoyl chloride, butanoyl chloride, alkanoyl chloride, alkenoyl chloride, alkynoyl chloride, alkanoyl halogen, alkenoyl halogen, alkynoyl halogen.

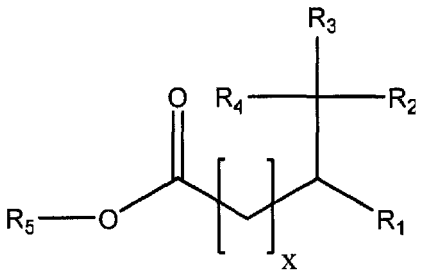
[0036] In one embodiment, the dielectric oil additive may comprise inter alia a fatty acid exemplified in a non-limiting manner by the following structural formula (I), drawn merely in a schematic manner, as will be immediately recognized by a person skilled in the art:



(I)

wherein x may be selected from integers of 0-50, R_1 may be selected from the group comprising saturated or unsaturated, branched, linear, and/or cyclic (C_0-C_{50})alkyl, each R_2 and R_3 may be independently selected from hydroxy, hydroxyalkyl, hydroxyalkoxy, hydroxyalkoxyalkyl, hydroxypolyoxyalkylene, alkoxy, alkoxyalkyl, polyoxyalkylene, carboxy, carboxyalkyl, carboxyalkoxy, carboxyalkoxyalkyl, carboxypolyoxyalkylene, alkoxycarbonyl, alkoxycarbonylalkyl, alkoxycarbonylalkoxy, alkoxycarbonylalkoxyalkyl, 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)(cartboxy)polyoxyalkylene, (alkylamino)(carboxy)polyoxyalkylene, (dialkylamino)(carboxy)polyoxyalkylene, (alkoxycarbonyl)(amino)alkyl, (alkoxycarbonyl)(alkylamino)alkyl, (alkoxycarbonyl)(dialkylamino)alkyl, (alkoxycarbonyl) (amino) alkoxy, (alkoxycarbonyl)(alkylaπiino)alkoxy, (alkoxycarbonyl) (dialkylamino) alkoxy, (alkoxycarbonyl) (amino) alkoxyalkyl, (alkoxycarbonyl) (alkylamino)alkoxyalkyl, (alkoxycarbonyl)(dialkylamino)alkoxyalkyl, (alkoxycarbonyl)(amino)polyoxyalkylene, (alkoxycabonyl)(alkylamino)polyoxyalkylene, (alkoxycabonyl)(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 the alkyl and/or acyl moieties introduced by the reaction between fatty acids having at least one carbon-carbon double bond and at least one alkyl halide and/or at least one acyl halide (e.g.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 acid side or on the alkyl side of the introduced alkyl(s) and/or acyl(s)), and the length and the branching of the fatty acid chains (e.g. the presence of branches either on the acid side and/or on the alkyl side of the introduced alkyl(s) and/or acyl(s)), the length of the alkyl chains on the acid side and on the alkyl side of the introduced alkyl(s) and/or acyl(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 the alkyl(s) and/or acyl(s) increases the fluidity of the fatty acids, 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 fatty acid fluidity may correspond to any one of R_2 and/or R_3, in accordance with structural formula (I) above.

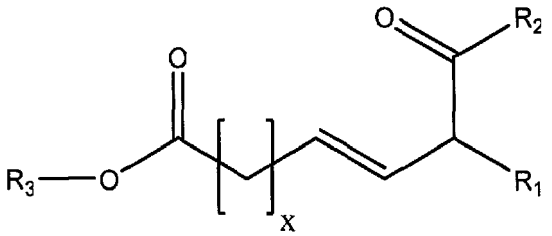
[0037] In yet another embodiment, the dielectric oil additive may comprise inter alia a fatty acid alkyl ester exemplified in a non-limiting manner by the following structural formula (II), drawn merely in a schematic manner, as will be immediately recognized by a person skilled in the art:



(II)

wherein x may be selected from integers of 0-50, R_1 and R_5 may each be independently selected from the group comprising saturated or unsaturated, branched, linear, and/or cyclic (C_0-C_{50})alkyl, each R_2, R_3, and R_4 may be independently selected from hydroxy, hydroxyalkyl, hydroxyalkoxy, hydroxyalkoxyalkyl, hydroxypolyoxyalkylene, alkoxy, alkoxyalkyl, polyoxyalkylene, carboxy, carboxyalkyl, carboxyalkoxy, carboxyalkoxyalkyl, carboxypolyoxyalkylene, alkoxycarbonyl, alkoxycarbonylalkyl, alkoxycarbonylalkoxy, alkoxycarbonylalkoxyalkyl, 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)(cατboxy)polyoxyalkylene, (alkylamino)(carboxy)polyoxyalkylene, (dialkylamino)(carboxy)polyoxyalkylene, (alkoxycarbonyl)(amino)alkyl, (alkoxycarbonyl)(alkylamino)alkyl, (alkoxycarbonyl)(dialkylamino)alkyl, (alkoxycarbonyl) (amino) alkoxy, (alkoxycarbonyl)(alkylaπiino)alkoxy, (alkoxycarbonyl) (dialkylamino) alkoxy, (alkoxycarbonyl) (amino) alkoxyalkyl, (alkoxycarbonyl) (alkylamino)alkoxyalkyl, (alkoxycarbonyl) (dialkylamino)alkoxyalkyl, (alkoxycarbonyl)(amino)polyoxyalkylene, (alkoxycabonyl) (alkylamino)polyoxyalkylene, (alkoxycabonyl)(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 the alkyl and/or acyl moieties introduced by the reaction between fatty acid alkyl esters having at least one carbon-carbon double bond and at least one alkyl halide and/or at least one acyl halide (e.g. the position along the fatty acid chain), the number and locations of unsaturations of the fatty acid alkyl ester 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 introduced alkyl(s) and/or acyl(s)), and the length and the branching of the fatty acid alkyl ester chains (e.g. the presence of branches either on the ester side and/or on the alkyl side of the introduced alkyl(s) and/or acyl(s)), the length of the alkyl chains on the ester side and on the alkyl side of the introduced alkyl(s) and/or acyl(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 the alkyl(s) and/or acyl(s) increases the fluidity of the fatty acid alkyl esters, 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 fatty acid alkyl ester fluidity may correspond to any one of R_2, R_3, and/or R_4, in accordance with structural formula (II) above.

[0038] In yet another embodiment, the dielectric oil additive may comprise inter alia a fatty acid alkyl ester exemplified in a non-limiting manner by the following structural formula (III), drawn merely in a schematic manner, as will be immediately recognized by a person skilled in the art:



(III)

wherein x may be selected from integers of 0-50, R_1 and R_3 may each be independently selected from the group comprising saturated or unsaturated, branched, linear, and/or cyclic (C_0-C_{50})alkyl, R_2 may be independently selected from hydroxy, hydroxyalkyl, hydroxyalkoxy, hydroxyalkoxyalkyl, hydroxypolyoxyalkylene, alkoxy, alkoxyalkyl, polyoxyalkylene, carboxy, carboxyalkyl, carboxyalkoxy, carboxyalkoxyalkyl, carboxypolyoxyalkylene, alkoxycarbonyl, alkoxycarbonylalkyl, alkoxycarbonylalkoxy, alkoxycarbonylalkoxyalkyl, 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)(caτtboxy)polyoxyalkylene, (alkylamino)(carboxy) polyoxyalkylene, (dialkylamino)(carboxy)polyoxyalkylene, (alkoxycarbonyl)(amino)alkyl, (alkoxycarbonyl)(alkylamino) alkyl, (alkoxycarbonyl)(dialkylamino)alkyl, (alkoxycarbonyl) (amino) alkoxy, (alkoxycarbonyl)(alkylaτiino)alkoxy, (alkoxycarbonyl) (dialkylamino) alkoxy, (alkoxycarbonyl) (amino) alkoxyalkyl, (alkoxycarbonyl) (alkylamino)alkoxyalkyl, (alkoxycarbonyl)(dialkylamino)alkoxyalkyl, (alkoxycarbonyl)(amino)polyoxyalkylene, (alkoxy-cabonyl)(alkylamino)polyoxyalkylene, (alkoxycabo-nyl)(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 the alkyl and/or acyl moieties introduced by the reaction between fatty acid alkyl esters having at least one carbon-carbon double bond and at least one alkyl halide and/or at least one acyl halide (e.g. the position along the fatty acid chain), the number and locations of unsaturations of the fatty acid alkyl ester chain (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 introduced alkyl(s) and/or acyl(s)), and the length and the branching of the fatty acid alkyl ester chains (e.g. the presence of branches either on the ester side and/or on the alkyl side of the introduced alkyl(s) and/or acyl(s)), the length of the alkyl chains on the ester side and on the alkyl side of the introduced alkyl(s) and/or acyl(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 the alkyl(s) and/or acyl(s) increases the fluidity of the fatty acid alkyl esters, 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 fatty acid alkyl ester fluidity may correspond to R_2, in accordance with structural formula (III) above.

[0039] The above-outlined structural formulas merely depict exemplary embodiments according to the present invention. A person skilled in the art would hence immediately realize that the above structural formulas I-III are primarily meant for illustrative purposes and that other structures and moieties not specifically mentioned and/or illustrated above are encompassed by the present invention.

[0040] Another aspect of the present invention pertains to a dielectric oil comprising the dielectric oil additives as per the present invention. In one embodiment, the dielectric oil comprises at least one triglyceride, or a triglyceride composition having properties that needs to be enhanced in various ways, using the oil additive of the present invention. The dielectric oil may preferably be naturally derived, for instance oil and/or fluid from vegetable and/or animal sources.

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

[0042] Yet another aspect as per the present invention relates to a method for preparing dielectric oil additives. The

method comprises the steps of providing a suitable fatty acid and/or a fatty acid alkyl ester, preferably naturally derived, comprising at least one carbon-carbon double bond. Subsequently, the at least one carbon-carbon double bond is reacted with at least one alkyl halide and/or at least one acyl halide, normally in the presence of a catalyst, generating the dielectric oil additives in accordance with the present invention.

[0043] In one embodiment, the catalyst is a Lewis acid, and, in yet another embodiment, the Lewis acid may be selected from the group comprising aluminium chloride, ethylaluminium dichloride, and/or ethylaluminium sesquichloride.

[0044] In a further embodiment, the reaction step may be carried out at ambient temperature.

[0045] In a preferred embodiment, the present invention relates to a naturally derived fatty acid and/or fatty acid alkyl ester having one, two, or three carbon-carbon double bonds. The fatty acid and/or fatty acid alkyl ester may for instance be oleic acid or an oleic acid methyl or ethyl ester. Said carbon-carbon double bond of the naturally derived oleic acid and/or oleic acid alkyl ester may preferably be reacted with isopropyl chloroformate, cyclohexyl chloroformate, propanoyl chloride, or butanoyl chloride, di-tert-butylpyrocarbonate, in order to generate a modified fatty acid and/or fatty acid alkyl ester having increased fluidity, implying improved properties in terms of reduced viscosity, improved insulation, reduced pour point, improved oxidation stability, permittivity, and/or biodegradability.

[0046] A further aspect of the present invention pertains to a method for preparing an dielectric oil, wherein the method comprises the steps of providing a suitable fatty acid and/or a fatty acid alkyl ester comprising at least one carbon-carbon double bond, subsequently reacting the at least one carbon-carbon double bond with at least one alkyl halide and/or at least one acyl halide, and finally adding to alkylated and/or acylated fatty acid and/or fatty acid alkyl ester to a suitable oil. The reaction may take place in the presence of a catalyst, and the catalyst may, in accordance with one embodiment of the present invention, be a Lewis acid.

[0047] In a further embodiment, the Lewis acid may be selected from the group comprising aluminium chloride, ethylaluminium dichloride, and/or ethylaluminium sesquichloride. As per another embodiment, the reaction step may be carried out at ambient temperature.

[0048] In yet another embodiment, the oil comprises at least one triglyceride, and said oil may optionally be naturally derived.

[0049] One aspect of the present invention relates to an electrical apparatus comprising the dielectric oil additive of the present invention. A further aspect pertains to an electrical apparatus comprising the dielectric oil as per the present invention.

[0050] Another aspect of the present invention pertains to various uses of the dielectric oil additive and/or the dielectric oil 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 oil additive and/or the dielectric oil may be utilized in for instance paints and coatings, printing inks, lubricants, surfactants, or within the food and/or cosmetics industry.

[0051] Yet another aspect of the present invention relates to the use of a chemically modified fatty acid and/or fatty acid alkyl ester in a dielectric fluid, wherein said chemically modified fatty acid and/or fatty acid alkyl ester is obtainable by reacting at least one carbon-carbon double bond of the fatty acid and/or of the fatty acid alkyl ester with at least one alkyl halide and/or at least one acyl halide.

[0052] In one embodiment, the at least one alkyl halide and/or the at least one acyl halide may optionally further comprise at least one moiety that further increases fatty acid and/or a fatty acid alkyl ester fluidity. In yet another embodiment, the at least one moiety that further increases fatty acid and/or a fatty acid alkyl ester fluidity may comprise a saturated or unsaturated, branched, linear and/or cyclic hydrocarbon, optionally substituted with at least one heteroatom.

[0053] As per a further embodiment, the at least one alkyl halide may be selected from the group comprising isopropyl chloroformate, isobutyl chloroformate, butyl chloroformate, octyl chloroformate, alkyl chloroformate, alkyl haloformate, cyclohexyl chloroformate, cyclohexyl haloformate, and di-tert-butylpyrocarbonate. In accordance with yet another embodiment, the at least one acyl halide is selected from the group comprising propanoyl chloride, butanoyl chloride, alkanoyl chloride, alkenoyl chloride, alkynoyl chloride, alkanoyl halogen, alkenoyl halogen, and alkynoyl halogen.

Examples

Isopropylation of fatty acids and fatty acid alkyl esters

[0054] At least one carbon-carbon double bond of a suitable fatty acid or a suitable fatty acid alkyl ester is reacted with isopropyl chloroformate at ambient temperature in the presence of ethylaluminium sesquichloride ($Et_3Al_2Cl_3$), with CH_2Cl_2 as the solvent. After a reaction time of 2 h, fatty acids or fatty acid alkyl esters having a isopropyl-alkylated fatty acid chain are formed. The isopropylated fatty acids and fatty acid alkyl esters generated through the alkylation reaction has increased fluidity, rendering a composition comprising the isopropyl-alkylated compounds less viscous, with higher

oxidation stability, increased permittivity, and reduced pour point.

Cyclohexyl-alkylation of fatty acids and fatty acid alkyl esters

[0055] At least one carbon-carbon double bond of a suitable fatty acid or a suitable fatty acid alkyl ester is reacted with cyclohexyl chloroformate at ambient temperature in the presence of $Et_3Al_2Cl_3$, with CH_2Cl_2 as the solvent. After a reaction time of 2 h, fatty acids or fatty acid alkyl esters comprising at least one cyclohexyl moiety are generated. The cyclohexylated fatty acids or fatty acid alkyl esters have increased fluidity, rendering a composition comprising cyclohexylated fatty acids or fatty acid alkyl esters-based dielectric oil additive less viscous, with higher oxidation stability, increased permittivity, and reduced pour point.

Butyl-pyrocarbonate-alkylation of fatty acids and fatty acid alkyl esters

[0056] At least one carbon-carbon double bond of a suitable fatty acid or a suitable fatty acid alkyl ester is reacted with di-tert-butylpyrocarbonate at ambient temperature in the presence of $Et_3Al_2Cl_3$, with CH_2Cl_2 as the solvent. After a reaction time of 2 h, a fatty acids or fatty acid alkyl esters having at least one tert-butyl-alkylated moiety are formed. The fatty acids or fatty acid alkyl esters generated through the alkylation reaction has increased fluidity, rendering a composition comprising the tert-butyl-alkylated fatty acids or fatty acid alkyl esters less viscous, with higher oxidation stability, increased permittivity, and reduced pour point.

Propanoyl chloride acylation of fatty acids and fatty acid alkyl esters

[0057] Suitable fatty acids or fatty acid alkyl esters comprising at least one carbon-carbon are reacted with propanoyl chloride at ambient temperature in the presence of ethylaluminium dichloride. After a reaction time of 3 h, fatty acids or fatty acid alkyl esters having at least one propanoylated fatty acid chain are formed. The fatty acids or fatty acid alkyl esters generated through the alkylation reaction have increased fluidity, rendering a composition comprising the propanoylated fatty acids or fatty acid alkyl esters less viscous, with higher oxidation stability, increased permittivity, and reduced pour point.

Butanoyl chloride acylation of fatty acids and fatty acid alkyl esters

[0058] Suitable fatty acids or fatty acid alkyl esters comprising at least one carbon-carbon are reacted with butanoyl chloride at ambient temperature in the presence of ethylaluminium dichloride. After a reaction time of 3 h, fatty acids or fatty acid alkyl esters having at least one butanoylated fatty acid chain are formed. The fatty acids or fatty acid alkyl esters generated through the alkylation reaction have increased fluidity, rendering a composition comprising the butanoylated fatty acids or fatty acid alkyl esters less viscous, with higher oxidation stability, increased permittivity, and reduced pour point.

Claims

1. An dielectric oil additive comprising a fatty acid and/or a fatty acid alkyl ester comprising at least one carbon-carbon double bond, **characterized in that** said dielectric oil additive is obtained by reacting said at least one carbon-carbon double bond with at least one alkyl halide and/or at least one acyl halide.

2. The dielectric oil additive according to claim 1, wherein the at least one alkyl halide and/or the at least one acyl halide optionally further comprise at least one moiety that further increases fatty acid and/or a fatty acid alkyl ester fluidity.

3. The dielectric oil additive according to claim 2, wherein the at least one moiety that further increases fatty acid and/or a fatty acid alkyl ester fluidity comprises a saturated or unsaturated, branched, linear and/or cyclic hydrocarbon, optionally substituted with at least one heteroatom.

4. The dielectric oil additive according to any one of the preceding claims, wherein the at least one alkyl halide is selected from a group comprising isopropyl chloroformate, isobutyl chloroformate, butyl chloroformate, octyl chloroformate, alkyl chloroformate, alkyl haloformate, cyclohexyl chloroformate, cyclohexyl haloformate, and di-tert-butylpyrocarbonate.

5. The dielectric oil additive according to any one of the preceding claims, wherein the at least one acyl halide is selected from a group comprising propanoyl chloride, butanoyl chloride, alkanoyl chloride, alkenoyl chloride, alkynoyl chloride, alkanoyl halogen, alkenoyl halogen, and alkynoyl halogen.

6. The dielectric oil additive according to any one of the preceding claims, wherein the at least one fatty acid and/or a fatty acid alkyl ester is selected from the group comprising synthetically modified or native oleic acid, linoleic acid, α-linolenic acid, myristoleic acid, arachidonic acid, icosapentaenoic acid, palmitoleic acid, erucic acid, 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, and lignoceric acid, and alkyl esters thereof.

7. A dielectric oil comprising the dielectric oil additive according to any one of the preceding claims.

8. The dielectric oil according to claim 7, wherein said oil comprises at least one triglyceride.

9. A method for preparing the dielectric oil additive according to any one of claims 1 to 6, comprising the steps of:

(a) providing a fatty acid and/or a fatty acid alkyl ester comprising at least one carbon-carbon double bond;
(b) reacting said at least one carbon-carbon double bond with at least one alkyl halide and/or at least one acyl halide, in the presence of a catalyst;

thereby obtaining said dielectric oil additive.

10. The method according to claim 7, wherein the catalyst is a Lewis acid.

11. The method according to claim 8, wherein the Lewis acid is selected from the group comprising aluminium chloride, ethylaluminium dichloride, and/or ethylaluminium sesquichloride.

12. The method according to any one of claims 9 to 11, wherein step (b) is carried out at ambient temperature.

13. A method for preparing an dielectric oil according to any one of claims 7 to 8, comprising the steps of:

(c) providing a fatty acid and/or a fatty acid alkyl ester comprising at least one carbon-carbon double bond;
(d) reacting said at least one carbon-carbon double bond with at least one alkyl halide and/or at least one acyl halide, in the presence of a catalyst;
(e) adding the product obtained in step (b) to a suitable oil.

14. The method according to claim 13, wherein the catalyst is a Lewis acid.

15. The method according to claim 14, wherein the Lewis acid is selected from the group comprising aluminium chloride, ethylaluminium dichloride, and/or ethylaluminium sesquichloride.

16. The method according to any one of claims 13 to 15, wherein step (b) is carried out at ambient temperature.

17. The method according to any one of claims 13 to 16, wherein the suitable oil comprises at least one triglyceride.

18. An electrical apparatus comprising the dielectric oil additive according to any one of claims 1 to 6.

19. An electrical apparatus comprising the dielectric oil according to any one of claims 7 to 8.

20. Use of the dielectric oil additive according to any one of claims 1 to 6 in an electrical apparatus.

21. Use of the dielectric oil according to any one of claims 7 to 8 in an electrical apparatus.

22. Use of a chemically modified fatty acid and/or fatty acid alkyl ester in a dielectric fluid, wherein said chemically modified fatty acid and/or fatty acid alkyl ester is obtainable by reacting at least one carbon-carbon double bond of the fatty acid and/or of the fatty acid alkyl ester with at least one alkyl halide and/or at least one acyl halide.

23. Use according to claim 22, wherein the at least one alkyl halide and/or the at least one acyl halide optionally further

comprise at least one moiety that further increases fatty acid and/or a fatty acid alkyl ester fluidity.

24. Use according to claim 23, wherein the at least one moiety that further increases fatty acid and/or a fatty acid alkyl ester fluidity comprises a saturated or unsaturated, branched, linear and/or cyclic hydrocarbon, optionally substituted with at least one heteroatom.

25. Use according to any one of claims 22 to 24, wherein the at least one alkyl halide is selected from the group comprising isopropyl chloroformate, isobutyl chloroformate, butyl chloroformate, octyl chloroformate, alkyl chloroformate, alkyl haloformate, cyclohexyl chloroformate, cyclohexyl haloformate, and di-tert-butylpyrocarbonate.

26. Use according to any one of claims 22 to 25, wherein the at least one acyl halide is selected from the group comprising propanoyl chloride, butanoyl chloride, alkanoyl chloride, alkenoyl chloride, alkynoyl chloride, alkanoyl halogen, alkenoyl halogen, and alkynoyl halogen.

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EUROPEAN SEARCH REPORT

Application Number
EP 10 16 8019

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	US 4 187 188 A (MILLER DENNIS P [US]) 5 February 1980 (1980-02-05) * column 1, line 8 - column 3, line 34 * * examples 1-7 * -----	1-26	INV. H01B3/24

TECHNICAL FIELDS SEARCHED (IPC)

H01B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	3 September 2010	Stinchcombe, John

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 10 16 8019

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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03-09-2010

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4187188 A	05-02-1980	NONE	

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