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(54) **ELECTRICAL EQUIPMENT INSULATED WITH A BIODEGRADABLE DIELECTRIC FLUID**

(57) The present invention belongs to the field of the insulation and cooling of electrical systems, it specifically relates to electrical equipment comprising a biodegradable dielectric fluid that is highly resistant to oxidation consisting of an oil or a mixture of vegetable oils with a

very high oleic acid content which substantially conserve all their natural tocopherols and containing a metal de-activator.

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DescriptionField of the Invention

5 **[0001]** The present invention belongs to the field of the insulation and cooling of electrical systems, it specifically relates to electrical equipment comprising a biodegradable dielectric fluid that is highly resistant to oxidation consisting of an oil or a mixture of vegetable oils with a very high oleic acid content which substantially conserve all their natural tocopherols and containing a metal deactivator.

10 Background of the Invention

[0002] Dielectric fluids which are used in the electrical industry generally consist of gases or liquids the most important mission of which is to achieve the electrical insulation between live parts, as well as to serve as a cooling means. The liquids which are used as dielectric media can have different origins.

15 **[0003]** The liquids most used as a dielectric fluid are mineral oils derived from petroleum. The considerable use of mineral oils is due to their low cost and easy availability, as well as to their dielectric properties, cooling properties, to the low viscosity at high temperatures and to their excellent behavior at very low temperatures. Likewise, they have a high oxidation stability. But on the other hand, mineral oils involve the drawback that due to their chemical composition, their biodegradability is very low, whereby a spillage of said oil can cause damage in the ecosystem and can remain in the environment for many years. Likewise, mineral oils have a high combustion power and have a very low fire point, whereby they involve a high risk in the event of fire and/or explosion.

20 **[0004]** Current regulations furthermore require any dielectric fluid intended for use as a coolant to not be classified as inflammable. According to the use of the fluid and the degree of risk, one or more safety measures can be required. A recognized safety option is to substitute mineral oils with less inflammable or non-inflammable liquids. The less inflammable liquids must have a fire point equal to or greater than 300°C. Thus, dielectric liquids with a high fire point (equal to or greater than 300°C), such as for example silicone oils, high molecular weight hydrocarbons (HMWHs) or synthetic esters are occasionally used. However, silicone oils and high molecular weight hydrocarbons (HMWHs) are characterized, like mineral oils, by their null or low biodegradability. Likewise, all these liquids have a higher cost than that of mineral oils.

25 **[0005]** Among the alternatives to the aforementioned liquids which have appeared in recent years, natural esters from vegetable oils must be emphasized. Natural esters are obtained from oils with a plant origin through suitable refining and purification processes.

30 **[0006]** Vegetable oils are essentially made up of triacylglycerols and of other components in a lower proportion such as for example monoacylglycerols, diacylglycerols, free fatty acids, phosphatides, sterols, oil-soluble vitamins, tocopherols, pigments, waxes, long-chain alcohols etc.

35 **[0007]** Triacylglycerols occurring in vegetable oils are triesters formed by three fatty acids chemically bonded to glycerin. The general formula of a triacylglycerol is:



50 wherein R, R', R'' can be the same or different fatty acids normally with C₁₄ to C₂₂ carbon chains and with unsaturation levels of 0 to 3.

[0008] The main differences between the different vegetable oils are caused by the different fatty acid contents present in the composition of their triacylglycerols.

55 **[0009]** There are several fatty acids, including myristic, palmitic, stearic, oleic, linoleic, linolenic, arachidic, eicosenoic, behenic acid, erucic, palmolitic, docosadienoic, lignoceric, tetracosenoic, margaric, margaroleic, gadoleic, caprylic, capric, lauric, pentadecanoic and heptadecanoic acids. They differ from one another by the number of carbon atoms and by the number of unsaturations (carbon-carbon double bonds).

[0010] The three fatty acids in a triacylglycerol molecule can all be the same or can be two or three different fatty acids. The fatty acid composition of triacylglycerols varies between plant species and less between strains of a particular

species. The vegetable oils derived from a single strain essentially have the same fatty acid composition in their triacylglycerols. Each triacylglycerol has unique properties depending on the fatty acids that it contains. For example, some triacylglycerols are more susceptible to oxidation than others. In this sense, the oils formed by triacylglycerols with mono-unsaturated (with a single C=C double bond) fatty acids have a higher oxidation stability than oils formed by triacylglycerols with fatty acids with two or three carbon-carbon double bonds. Likewise, the oils formed by triacylglycerols with saturated (no C=C double bond) fatty acids will have an even higher oxidation stability than mono-unsaturated fatty acids but their minimum pour point would be much higher.

[0011] The greatest advantages of the use of vegetable oils as dielectric fluids are summarized in their excellent biodegradability, their obtaining from renewable natural sources, their non-toxicity, their high fire point ($\cong 360\text{ }^{\circ}\text{C}$) and their low cost compared to other options with a high fire point such as synthetic esters. All the environmental, health and safety trends have reinforced the idea of using dielectric fluids based on vegetable oils.

[0012] However, vegetable oils or their derivatives are not free of problems in their application as dielectric fluids in electrical equipment.

[0013] For example, the freezing point (or minimum pour point) of vegetable oils is a property to be taken into account. The freezing point defines the temperature at which a liquid passes to the solid state, with the consequent loss of cooling properties. According to the only existing standard specifying the properties of a vegetable oil for its use as a dielectric fluid, American standard ASTM D6871-03, the freezing point must be $-10\text{ }^{\circ}\text{C}$ at most. It is therefore important for the dielectric fluid to be based on vegetable oils ensuring that it remains as a flowing liquid even when the dielectric fluid is subjected to moderately low temperatures (less than $-15\text{ }^{\circ}\text{C}$). Additives are usually used to reduce the freezing point and achieve dielectric liquids that are more resistant to the low temperatures. For example additives such as PMA (polymethacrylate), oligomers and polymers of polyvinyl acetate and/or acrylic oligomers and polymers, diethylhexyl adipate, polyalkylmethacrylate have been used.

[0014] Other problematic factors in the properties of vegetable oils are the presence of water, microbial growth, the presence of solids, etc.

[0015] But in fact one of the most important problems of vegetable oils is that of oxidation. Vegetable oils are normally susceptible to polymerization when they are exposed to oxygen. The exposure to oxygen activates the non-saturated bonds present in the fatty acids of the triacylglycerols of the oils, causing oxidative polymerization of the oil, with potentially adverse effects on the properties of the actual dielectric fluid. Their susceptibility to oxidation is an important obstacle to their use as a dielectric.

[0016] The problem of the oxidation of oils has usually been solved by means of adding synthetic antioxidant oils such as BHA (butylated hydroxyanisole), BHT (butylated hydroxytoluene), TBHQ (tertiary butylhydroquinone), THBP (tetrahydrobutrophenone), ascorbyl palmitate (rosemary oil), propyl gallate etc. On the other hand, the problem of the oxidation of dielectric fluids based on vegetable oils is emphasized in electrical apparatuses due to the catalytic activity of copper or of other metals present in this type of apparatus.

[0017] All the aforementioned problems have been previously set forth in patents EP1365420, US 2004069975, US6613250, US6340658, US6645404, US6280659, JP2000090740 and JP2005317259, with different solutions.

[0018] The inventors of the present invention propose electrical equipment comprising a dielectric liquid providing an alternative technical solution to the problem of oxidation and providing very advantageous features to the liquid for its application as an insulator and coolant of electrical apparatuses.

[0019] The solution to the problem of the oxidation of the dielectric fluid inside electrical equipment comes from the use of oils with a very high oleic acid content, and obtained by refining processes which allow conserving the natural tocopherols present in said vegetable oils in a high percentage, given that traditional refining processes involve the loss of a considerable amount of their tocopherols. An example of a suitable process for the purposes of the present invention is described in patent US 5928696. The inventors have discovered that certain vegetable oils with very high oleic acid contents and low linoleic contents and which conserve their natural tocopherols to a great extent have enough antioxidant power to prevent having to add antioxidant additives, such as for example non-biodegradable synthetic antioxidant additives, as was being done up until now. Tocopherols, however, in addition to being substantially biodegradable, are substances which are naturally present in the composition of oils and which have important antioxidant properties. There are four types of tocopherols, α -, β -, γ - and δ -tocopherol, having different antioxidant power and which are present in different proportions depending on the type of vegetable oil and on the variety from which it is obtained.

[0020] Furthermore, to solve the problem of the acceleration of oxidation due to the catalytic activity of metals present in electrical equipment, the inventors of the present invention provide the incorporation of metal deactivators such as derivatives of triazole, of benzotriazole, of dimercaptothiadiazole, etc

Object of the Invention

[0021] A first object of the invention is electrical equipment for an electric power distribution network comprising a vat or envelopment integrating one or more electrical elements insulated in a biodegradable dielectric fluid free of added

antioxidant additives, synthetic or not, comprising an oil or a mixture of vegetable oils with an oleic acid (C18:1) content greater than 75%, a natural tocopherol content greater than 200 ppm and incorporating a metal deactivator additive in a proportion less than 1% by weight.

[0022] The second object of the invention is a method for insulating and cooling electrical elements in a power distribution network comprising submerging or enveloping said electrical elements in a biodegradable dielectric fluid free of synthetic antioxidant additives added thereto comprising an oil or a mixture of vegetable oils with an oleic acid (C18:1) content greater than 75%, with a natural tocopherol content greater than 200 ppm and a metal deactivator additive in a proportion less than 1%.

Detailed Description of the Invention

[0023] The invention relates in the first place to electrical equipment for an electric power distribution network comprising a vat or envelopment integrating one or more electrical elements insulated in a biodegradable dielectric fluid free of synthetic antioxidant additives added thereto comprising an oil or a mixture of vegetable oils with an oleic acid (C18:1) content greater than 75%, characterized by having a natural tocopherol content greater than 200 ppm and a metal deactivator additive in a proportion less than 1%.

[0024] In a preferred embodiment of the invention the natural tocopherol content of the fluid is greater than 300 ppm and in an even more preferred embodiment it is greater than 400 ppm.

[0025] In a preferred embodiment of the invention the oleic acid content of the oil or vegetable oils making up the dielectric fluid is greater than 80% and in an even more preferred embodiment said content is greater than 90%.

[0026] Since in electrical equipment the dielectric liquids are usually in contact with metals, the dielectric fluid includes as an additive a metal deactivator to prevent copper or another metal in contact with the oil from acting as a catalyst of the oxidation reactions thereof. Therefore, it is suitable to include in the composition of the dielectric liquid a metal deactivator such as for example any derivative of triazole, of benzotriazole or of dimercaptothiadiazole.

[0027] Furthermore, the dielectric fluid incorporated in the electrical equipment of the invention preferably comprises:

- a) a linoleic acid (C18:2) content less than 3.5%
- b) a linolenic acid (C18:3) content less than 1%
- c) a palmitic acid (C16:0) content less than 4%
- d) a stearic acid (C18:0) content less than 2.5%

[0028] Oils or mixtures of sunflower, rapeseed, soybean, cotton, jojoba, safflower, olive or olive-pomace oils with a high oleic content are especially suitable for their use as a dielectric fluid in the context of the present invention, although the preferred embodiment of the invention involves the use of high oleic sunflower oil. These oils, in addition to high oleic acid levels, naturally have a large amount of tocopherols which are mostly lost in normal refining processes. The refining of said oils according to methods capable of conserving their natural tocopherols to a great extent contributes to these oils being very suitable for their use as dielectric fluids without the risk of oxidation thereof. For example, the methods described in patent US 5928696 allow obtaining oils with tocopherol concentrations greater than 400 ppm and with low phosphatide, free fatty acid and wax contents.

[0029] The oil or oils resulting from the mentioned methods can be subjected to a subsequent vacuum distillation process, using a combination of heat and vacuum, to eliminate most of their moisture. The dehumidification of the oil is necessary due to the fact that the oil can have an initial moisture level making it unsuitable to be used as a dielectric liquid. The vegetable oil is thus processed for the purpose of eliminating the excessive moisture to a level less than 50 ppm.

[0030] The oils thus obtained are characterized by having induction times longer than 25 hours in the Rancimat test (EN 14112) and a biodegradability index greater than 99% after 21 days (CEC-L-33-A-93). In other words, dielectric fluids with a high quality and excellent yield satisfying or exceeding the safety standards and which in turn are not toxic, are harmless to the environment and have a lower cost than other dielectric fluids are achieved by using the mentioned oils or their mixtures.

[0031] The dielectric fluid incorporated to the apparatus of the invention can further have additional additives depending on the type of application to which it is going to be subjected.

[0032] For applications in electrical equipment present in environments in which the temperature can drop to temperatures less than -15°C , it is recommendable to further add an additive to reduce the freezing point, preferably of the polyalkylmethacrylate type. The use of these additives allows obtaining dielectric fluids with freezing points equal to or less than -18°C .

[0033] In a particular embodiment of the invention the electrical equipment of the invention can be switchgear and/or protection cubicles, transformers, self-protected transformers with current-limiting fuses or transformation centers with multiple switchgear elements and multiple protection devices.

[0034] The second aspect of the invention relates to a method for insulating and cooling electrical elements in an

electric power distribution network comprising submerging or enveloping said electrical elements in a biodegradable electrical fluid free of synthetic antioxidant additives added thereto comprising an oil or mixture of vegetable oils with an oleic acid (C18:1) content greater than 75%, with a natural tocopherol content greater than 200 ppm and a metal deactivator additive in a proportion less than 1%. As is obvious, all the optional and additional elements and features herein described and referring to the dielectric fluid are applicable in the method for insulating and cooling electrical elements in a distribution network herein described.

Preferred Embodiment of the Invention

[0035] The special fatty acid composition of the triacylglycerols of the vegetable oils used and the process for obtaining them, as well as their final drying, confer to the resulting liquid specific physical properties making it particularly suitable for its use as a dielectric liquid.

[0036] A preferred example of the invention consists of a transformer in which a dielectric liquid with the following composition is included as an insulator and coolant:

Sunflower oil with a high oleic acid content with:

a) natural tocopherols

	ppm
α-tocopherol	402.0
β-tocopherol	17.1
γ-tocopherol	8.6
δ-tocopherol	
Total	427.7

b) triacylglycerols, with the following fatty acid composition

	%
C16:0	< 4.0
C18:0	< 2.5
C18:1	> 90
C18:2	< 3.5
C18:3	< 1.0

c) 5000 ppm of a metal deactivator additive derived from dimercaptiothiadiazole (Additin RC 8210 of Rhein Chemie) corresponding to less than 1% by weight of the total of the composition.

[0037] The dielectric liquid with the composition indicated above has the following properties:

Property	Value
Water content	< 50 ppm
Dielectric strength	> 40 kV
ignition pt.	> 350°C
flash pt. (open cup)	> 300°C
freezing pt.	< -15°C
oxidation stability - Rancimat EN14112 (110°C, 10L/h air)	> 25 hours
oxidation stability - Rancimat EN14112 (110°C, 10L/h air) with copper(*)	> 6.5 hours

[0038] Optionally, for some more demanding embodiments, in places where the electrical equipment is subjected to extremely low temperatures, the pour point can be further reduced by adding an additive to the oil to obtain a lower freezing point. Commercially available additives which are compatible with vegetable oils, such as for example the product known as Viscoplex 10-310, can thus be used.

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Claims

- 10 1. Electrical equipment for an electric power distribution network comprising a vat or envelopment integrating one or more electrical elements insulated in a biodegradable dielectric fluid free of synthetic antioxidant additives added thereto comprising an oil or a mixture of vegetable oils with an oleic acid (C18:1) content greater than 75%, with a natural tocopherol content greater than 200 ppm and a metal deactivator additive in a proportion less than 1 %.
- 15 2. Electrical equipment according to claim 1, wherein the dielectric fluid comprises an oil or mixture of oils with an oleic acid (C18:1) content greater than 80%.
3. Electrical equipment according to claim 1, wherein the dielectric fluid comprises an oil or mixture of oils with a oleic acid (C18:1) content greater than 90%.
- 20 4. Electrical equipment according to claim 1, **characterized in that** the natural tocopherol content of the electric fluid is greater than 300 ppm.
5. Electrical equipment according to claim 1, **characterized in that the** natural tocopherol content of the dielectric fluid is greater than 400 ppm.
- 25 6. Electrical equipment according to any of the previous claims, **characterized in that** the dielectric fluid has a fire point greater than 350°C.
7. Electrical equipment according to any of the previous claims, **characterized in that** the dielectric fluid comprises oil or vegetable oils comprising:
 - a) a linoleic acid (C18:2) content less than 3.5%
 - b) a linolenic acid (C18:3) content less than 1 %
 - c) a palmitic acid (C16:0) content less than 4%
 - 35 d) a stearic acid (C18:0) content less than 2.5%
8. Electrical equipment according to any of the previous claims, **characterized in that** the dielectric fluid comprises an additive to reduce the freezing point.
- 40 9. Electrical equipment according to claim 8, **characterized in that** the additive is of the methacrylicpolyalkyl type.
10. Electrical equipment according to claims 8 and 9, **characterized in that** the dielectric fluid has a freezing point equal to or less than -18°C.
- 45 11. Electrical equipment according to any of the previous claims, wherein the metal deactivator of the dielectric fluid is a derivative of triazole, of benzotriazole or dimercaptotriadiazole.
12. Electrical equipment according to claim 11, wherein the metal deactivator is a derivative of dimercaptotriadiazole.
- 50 13. Electrical equipment according to any of the previous claims, **characterized in that** the oil or mixture of vegetable oils of the dielectric fluid can be of sunflower, rapeseed, soybean, cotton, jojoba, safflower, olive or olive-pomace oils with a high oleic content
- 55 14. Electrical equipment according to any of the previous claims selected from switchgear and/or protection cubicles, transformers, self-protected transformers with current-limiting fuses or transformation centers with multiple switch-gear elements and multiple protection devices.
15. Method for isolating and cooling electrical elements in a power distribution network comprising submerging or

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enveloping said electrical elements in a biodegradable dielectric fluid free of synthetic antioxidant additives added thereto comprising an oil or a mixture of vegetable oils with an oleic acid (C18:1) content greater than 75%, with a natural tocopherol content greater than 200 ppm and a metal deactivator additive in a proportion less than 1 %.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER see extra sheet According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) H01B, H01F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CIBEPAT, EPODOC, WPI, HCAPLUS, BIOSIS, XPESP, NPL, EMBASE		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006/0030499 A1 (OOMMEN, T.V. & CLAIBORNE, C.C.) 09.03.2006, the whole document.	1-15
A	WO 2000/011682 A1 (ABB POWER T & D COMPANY, INC.) 02.03.2000, claims.	1-15
A	EP 1365420 A1 (COOPER INDUSTRIES, INC.) 26.11.2003, the whole document.	1-15
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"P" document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family
Date of the actual completion of the international search 20 September 2007 (20.09.2007)	Date of mailing of the international search report (22/11/2007)	
Name and mailing address of the ISA/ O.E.P.M. Paseo de la Castellana, 75 28071 Madrid, España. Facsimile No. 34 91 3495304	Authorized officer G. Esteban García Telephone No. +34 91 349 54 25	

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CLASSIFICATION OF SUBJECT MATTER

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REFERENCES CITED IN THE DESCRIPTION

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