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J. DAZZI

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ELECTRICAL DEVICES

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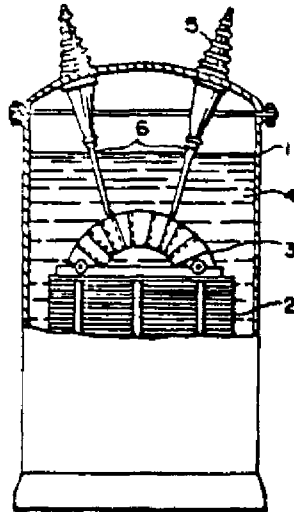


FIG - 1

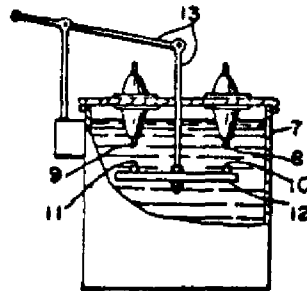


FIG - 2

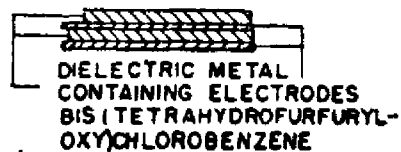


FIG - 4



FIG - 5

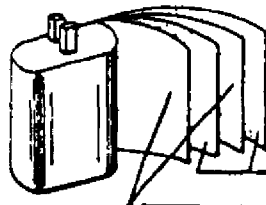


FIG - 3

METAL FOIL
PAPER IMPREGNATED WITH
2-(DICHLOROPHENOXY) METHYL-
TETRAHYDROFURAN

INVENTOR

JOACHIM DAZZI

BY

Andrew Phares

ATTORNEY

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2,945,994

ELECTRICAL DEVICES

Joseph Dazzi, Dayton, Ohio, assignor to Monsanto Chemical Company, St. Louis, Mo., a corporation of Delaware

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6 Claims (Cl. 317-258)

The present invention relates to electrical devices and more particularly deals with apparatus comprising a combination of electricity conducting elements and dielectric insulating media.

The use of a dielectric is required in certain electrical equipment for the purpose of removing heat and of allowing the making of electrical contact in the absence of air or of explosive mixtures. The requirements for such dielectrics are, among other things, very high resistance to the flow of electric currents, high stability to atmospheric conditions at ordinary and at somewhat elevated temperatures, high resistance to thermal decomposition, low vapor pressure, low congealing temperature, low inflammability and high flash point. Preferably the dielectric should be a mobile liquid even at relatively low temperatures and should be a good heat transfer agent.

In commercial practice, high boiling fractions of petroleum distillates have been largely used for this purpose. These liquids do not satisfy all of the above-stated requirements. They are relatively poor heat transfer agents and under the conditions of their use they gradually decompose with the formation of undesirable products which adversely influence the electrical properties. Some of these products are tarry, and others are appreciably soluble and may present fire and explosion hazards.

Another disadvantage of the mineral oils is that they tend to form deposits generally known as "sludge" during the period of their use. This is due to oxidation and decomposition and also results to some extent in the formation of acids which is equally undesirable. The sludging of dielectrics during use is a serious disadvantage and requires either replacement of the oil or treatment to remove the sludge and revivify the dielectric. A satisfactory dielectric liquid should not sludge or undergo substantial deleterious change during use and it is one of the objects of the invention to provide a liquid which does not possess this undesirable disadvantage characteristic of the mineral oils.

The undesirable effect of decomposition is further manifested when the mineral oils are used as capacitor impregnants. Then, under high operating temperatures and high current voltages, capacitors impregnated therewith show a characteristic type of deterioration which results in an ever increasing leakage current, a short capacitor life, visible localized decomposition of the dielectric and corrosion of the electrodes. Moreover, in the case of capacitors operating on alternating current, the decomposition sometimes results in an excessive increase in the power factor of the dielectric material.

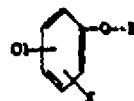
It is, therefore, an object of the present invention to provide a method for the insulation of elements in electrical apparatus wherein the above objectionable properties are either completely eliminated or substantially reduced.

Another additional object is to provide transformers, capacitors, circuit breakers, cables, switches, fuses, reactors, reactors and the like wherein the deleterious action com-

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mon to the prior art dielectric materials such as the deterioration of paper insulation and metal parts is eliminated or materially reduced. Still another object is to provide electrical apparatus having a long, useful life and good dielectric stability.

According to the invention, these and other objects which will be hereinafter disclosed are provided by the following invention wherein there is provided electrical apparatus comprising, in combination, conducting elements disposed in spaced relationship to each other and adapted during operation of the apparatus, to have a difference in electrical potential therebetween and, interposed between said elements for insulating one from the other, a liquid dielectric medium comprising an ether of the formula



in which R is selected from the class consisting of the furfuryl and the tetrahydrofurfuryl radicals and X is selected from the class consisting of chlorine and the radical —O—R .

Compounds having the above formula are readily prepared by heating trichlorobenzene with furfuryl or tetrahydrofurfuryl alcohol in the presence of an alkali metal hydroxide, i.e., sodium, potassium or lithium hydroxide.

One class of compounds of the above formula includes the 2-(dichlorophenoxyethyl)furan or the 2-(dichlorophenoxyethyl)-tetrahydrofuran, e.g., 2-(2,3-dichlorophenoxyethyl)furan, 2-(3,5-dichlorophenoxyethyl)furan, 2-(2,6-dichlorophenoxyethyl)furan, 2-(3,4-dichlorophenoxyethyl)-tetrahydrofuran, 2-(2,5-dichlorophenoxyethyl)-tetrahydrofuran, 2-(3,5-dichlorophenoxyethyl)furan, 2-(3,4-dichlorophenoxyethyl)furan, etc.

Another presently useful class of compounds having the above formula and prepared by the condensation of a trichlorobenzene with furfuryl or tetrahydrofurfuryl alcohol includes the bis(furfuryloxy)chlorobenzenes and the bis(tetrahydrofurfuryloxy)chlorobenzenes, e.g., 2,3-bis(furfuryloxy)chlorobenzene, 3,5-bis(furfuryloxy)chlorobenzene, 2,5-bis(furfuryloxy)chlorobenzene, 3,4-bis(furfuryloxy)chlorobenzene, 2,5-bis(tetrahydrofurfuryloxy)chlorobenzene, 2,4-bis(furfuryloxy)chlorobenzene, 2,3-bis(furfuryloxy)chlorobenzene, etc.

Formation of the present ethers occurs by replacement of one or two of the chlorine atoms of the trichlorobenzene by one or two furfuryloxy radicals. The replacement reaction takes place readily by heating the trichlorobenzene with furfuryl or tetrahydrofurfuryl alcohol in the presence of an alkali metal hydroxide. Since the reaction may result in the replacement of more than one chlorine atom, when desiring a preponderance of the substitution of only one chlorine atom by the furfuryloxy or tetrahydrofurfuryloxy radical, it is generally advisable to use a large excess of the trichlorobenzene. On the other hand, when the major product to be obtained is the diether, an excess of the furfuryl or tetrahydrofurfuryl alcohol is advantageously used. The quantity of alkali metal hydroxide employed is also somewhat controlling in the type of product obtained. Hydrogen chloride is liberated in the replacement of the nuclear chlorine by the furfuryloxy or tetrahydrofurfuryloxy moiety of the alcohol and in order to obtain good yields of either the mono-ether or the di-ether, there should be present in the reaction mixture enough of the alkali

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to neutralize the liberated acid. Usually from one to two moles of the alkali metal hydroxide per mole of the furfuryl or tetrahydrofurfuryl alcohol is used. An excess of sodium hydroxide is not detrimental to the reaction, whereas a molar quantity which is substantially less than that of the alcohol is conducive to lower yields of ether product.

The reaction time and temperature appears to have little, if any, effect on the nature of the ether product. Although a primarily formed mono-ether will react with another mole of furfuryl or tetrahydrofurfuryl alcohol to yield a di-ether, higher temperatures or continued heating do not suffice in effecting substantial conversion to the di-ether. An excess of one of said alcohols over that required for replacement of one chlorine atom should be present in order to obtain any substantial formation of the di-ether. Whether the reactant quantities present are those which favor mono-substitution (excess of trichlorobenzene) or whether the properties are such as to favor di-substitution (excess of one of said alcohols), ether formation occurs after heating at a temperature of from 100° C. to 250° C., and preferably of from 125° C. to 200° C. for a time of, say, several hours to a day. The progress of the reaction can be generally followed by noting the alkalinity or the quantity of water being formed. While provision for removal of water during the reaction is not required, better yields of ether product and a ready means of determining reaction rate are afforded by operating in a reaction vessel which is equipped with some water-removing facility, e.g., a water trap or take-off head.

Although, as above stated, reaction of the trichlorobenzene and the furfuryl or tetrahydrofurfuryl alcohol can be so directed as to result in a preponderance of either mono- or diether formation, generally the product contains mixture of the two in varying proportions. These can be readily separated from each other and from any unreacted initial material and/or from any diluent by fractional distillation. While the present condensation reaction takes place in the absence of any extraneous solvent or diluent, reaction may be facilitated by operating in the presence of an inert liquid as solvent or diluent, e.g., toluene, xylene, etc.

I have found that the present furfuryl or tetrahydrofurfuryl chloro-substituted phenyl ethers serve as very useful dielectric media when interposed in electrical apparatus between metallic conducting elements that have a difference in potential during operation of the apparatus because they are very stable liquids which possess good dielectric strength, low power factor and good ohm resistivity. They are particularly valuable as liquid impregnants in capacitor and cable manufacture, as transformer coolants, and in the fabrication of switch gear.

Characteristics of the present chloro-ethers are such as to render them particularly valuable as impregnants for cellulosic insulating materials. It is known in the art that impregnation of cellulosic materials, e.g., wood pulp paper, cotton, cotton fabric, cellulose acetate fibers and textiles, by certain liquid dielectrics provides an insulating material having a dielectric constant which is much higher than that of either the cellulosic material before impregnation or of the liquid dielectric. Some of the first liquids used for this purpose were mineral oils, the dielectric strength of oil impregnated paper having been reported by Bailey (Radio Engineering, 17 17, 35 (1937)) to be 15 times as high as that of the oil alone. However, because mineral oils are readily oxidized, their usefulness as insulating media and as impregnating agents for cellulosic materials has been limited in that exposure to air, sunlight or moisture often leads to gas formation, gaseous ionization and formation of wax. These changes affect power factor stability.

Although wood pulp paper, alone, has good insulating properties, it is also affected by exposure to air, particularly at higher temperatures. While the rate of me-

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chanical deterioration is reduced by impregnating the insulation with oil, this was of little advantage as noted above. Accordingly, the art resorted to other impregnating agents, particularly the highly chlorinated aromatic hydrocarbons. These materials have dielectric strengths which are higher than those of the mineral oils. In addition, they are non-flammable and more stable to the influence of air, moisture and light. However, their general utility has been somewhat hampered in that under high operating temperatures and voltages decomposition of said highly chlorinated hydrocarbons is manifested. Hydrogen chloride is evolved; and this attacks not only the paper which had been impregnated but also the metal portions of the capacitor.

The presently provided ethers are high-boiling materials which possess high resistivities and low power factors. Their stability to high temperatures is evidenced by little or no change in power factor readings after heating for 24 hours at 100° C. Their stability is further illustrated by continued high resistivities, which indicates freedom from conducting ions which would be present if decomposition of the ethers had occurred. The present ethers remain liquid at low temperatures, whereby there is avoided a decrease in dielectric constant due to freezing of the dipoles.

The above characteristics thus speak for eminent suitability of these ethers as impregnating agents for cellulosic materials, and as embodiment of the present invention is the provision of improved cellulosic insulating agents comprising porous materials derived from cellulose, e.g., pulps, fibers, textiles or papers derived from wood, cotton or linen, which porous products have been impregnated with said ethers. A noteworthy feature of the present invention is the provision of a capacitor comprising a pair of electrodes and an insulating agent associated with each of the electrodes and isolating them from each other, said insulating agent comprising a cellulosic material impregnated with the present ethers.

Examples of electrical apparatus in which the present furfuryl or tetrahydrofurfuryl chloro-substituted phenyl ethers are valuable components are shown in the accompanying drawing.

Fig. 1 is a front elevation partly in section of a transformer; Fig. 2 illustrates a switch in a similar manner; Fig. 3 represents a rolled capacitor; Fig. 4 shows a sectional view of a portion of the electrodes and dielectric sheets of Fig. 3; and Fig. 5 is a side view of a cable, the casing being partly removed to permit the interior of the parts to be seen.

The transformer illustrated in Fig. 1 comprises a casing 1, core 2, coils 3 insulated with manila paper, kraft paper, cotton or other fibrous insulation, insulating and cooling medium 4, lead-in bushings 5, and suitable leads 6 connected to the coil assembly. The insulating and cooling medium may consist of an ether such as 2-(dichlorophenoxymethyl)tetrahydrofuran which may be employed as such or in combination with a highly chlorinated biphenyl such as "Aroclor" (manufactured by Monsanto Chemical Co., St. Louis, Mo.). These two components may be employed in proportions such as from 50% to 90% by weight of one or more of the present ethers with the balance being the Aroclor. Liquid hydrocarbons or other halogenated hydrocarbons or mixtures thereof may also be used in combination with the furfuryl or tetrahydrofurfuryl chloro phenyl ethers as dielectric media, e.g., petroleum oil, halogenated compounds of naphthalene, toluene, benzene, nitrophenyl or diphenyl oxide.

The switch shown in Fig. 2 comprises a casing 7, fixed contacts 8 and 9, and movable contacts 10 and 11 which co-operate therewith. The movable contacts are mounted upon a support 12 which in turn is operatively connected to actuating levers 13. A suitable arc-quenching liquid which may be used in this device, either as the sole dielectric, or in combination with a minor proportion of a petroleum oil or a halogenated hydrocarbon such as

Tetra-
benzene
To a 2
and Deca-
of 1,2,4-
distilled
C/20-25
and 250
C within
C for 5 h
and 140 h
resulting
phenolphor-
hydrochlori-
luted with
nitric acid
was then
tered. Af-
layer which
was washed
and prod-
and 1.0 ml
liquid thus
pure 2 (1
130°-150° C
ether, b.p.
192-204° C
134-140° C

highly chlorinated biphenyl, is bis(tetrahydrofurfuryloxy)chlorobenzene.

The capacitor shown in Fig. 3 is made up of alternate layers of metal foil such as aluminum or tin foil separated by sheets of dielectric material. Fig. 4 shows a section of one turn of the finished rolled capacitor illustrating the alternate electrodes and dielectric layers. Details of the construction of the paper capacitor are set forth here by way of illustration.

Three sheets of tissue paper (preferably kraft capacitor tissue), are stacked upon each other, and a thin aluminum foil (about 0.0003" in thickness) is laid on the top sheet of tissue. The foil is then covered with three more sheets of the tissue and another sheet of the foil is placed thereon so that the two sheets of metal foil are separated from each other by the paper. The stack of alternating layers of metal foils and tissues thus obtained is wound into a cylindrical roll. This is placed in a container, and at this point electrical connecting means, e.g., wire or bar conductors, depending upon the size of the assembly, may be connected to the metal foil in a known manner. After drying, preferably in a heated vacuum oven one of the present ethers, such as 2-(dichlorophenoxy)methyltetrahydrofuran, is added to the container in a quantity sufficient to impregnate thoroughly the paper content thereof. The container is then sealed.

Alternatively, and particularly in the manufacture of the small items, which for the sake of economy are housed in paper tubes rather than in leak-proof containers, the tissue paper is impregnated with said tetrahydrofuran compound previous to interleaving with the metal foil in the manner described above.

The cable of Fig. 5, comprises a core 14, cable conductors 15, insulation consisting of paper or other suitable material 16 and a casing 17. The space between the insulated conductors and the casing is filled with one of the present ethers, e.g., 2-[(dichlorophenoxy)methyl]tetrahydrofuran, or a mixture of said furan compound with substantially an equal part by weight of partially chlorinated biphenyl having from 50 to 55% by weight of combined chlorine.

The invention is further illustrated but not limited by the following examples.

Example 1

Tetrahydrofurfuryl alcohol was reacted with trichlorobenzene as follows:

To a 2-liter, 3-neck flask equipped with stirrer, column and Dean-Stark trap there was charged 2.5 moles (454 g.) of 1,2,4-trichlorobenzene, 3.75 moles (383 g.) of re-distilled tetrahydrofurfuryl alcohol, B.P. 75° C./80° C./20-25 mm., 3 moles (120 g.) of sodium hydroxide and 250 g. of toluene. The mixture was heated to 152° C. within about 2.0 hours and at from 152° C. to 180° C. for 5 hours. During the heating period 56 cc. of water and 140 g. of toluene was collected. After allowing the resulting reaction mixture to cool, it was neutralized to phenolphthalein by treatment with 18 ml. of concentrated hydrochloric acid (equal to 0.22 mole of HCl) and diluted with 500 ml. of water, whereupon most of the precipitated sodium chloride went into solution. The whole was then diluted with about 700 ml. of ether, and filtered. After allowing the filtrate to stratify, the organic layer which formed was separated and the aqueous layer was washed with ether. The ether extract thus obtained was combined with the first organic layer, and the combined product was washed with about 100 ml. of water and 150 ml. of brine. Distillation of the washed, orange liquid thus obtained gave (I) 549 g. of the substantially pure 2-(dichlorophenoxy)methyltetrahydrofuran, B.P. 107°-150° C./0.4-1.0 mm. and (II) 41.1 g. of the ether, bis(tetrahydrofurfuryloxy)chlorobenzene, B.P. 92-204° C./0.8-1.0 mm. A narrow cut of (I) B.P. 94-140° C./0.6-0.8 mm., analyzed as follows:

	Found	Calcd for $C_{12}H_{10}Cl_2O_2$
C.....percent..	63.84	63.40
H.....do.....	4.92	4.64
Cl.....do.....	28.77	28.77

The diether fraction, i.e., (II) analyzed as follows:

	Found	Calcd for $C_{12}H_{10}Cl_2O_2$
C.....percent..	61.86	61.8
H.....do.....	6.81	6.73
Cl.....do.....	11.4	11.4

Based on the charged 1,2,4-trichlorobenzene there was obtained 89.4 percent conversion to mono-ether and 5.0 percent to di-ether. The 2-(dichlorophenoxy)methyltetrahydrofuran thus obtained was found to have a volume resistivity of 55×10^9 ohm-cm. at 25° C., a pour point of minus 35° C., and the following dielectric constant and power factor values at the frequencies and temperatures noted below:

Test Frequency	Dielectric Constant		Power Factor	
	25° C.	100° C.	25° C.	100° C.
10 kc.....	2.0	2.3	0.35	1.70
100 kc.....	2.0	2.1	0.05	0.05

The low power factor values at both test frequencies and at both test temperatures show very good stability of the 2-(dichlorophenoxy)methyltetrahydrofuran. Power capacitors in which the present ether is employed for impregnating the paper are particularly useful in that they may be used without freezing of the dipoles at temperatures which approximate the low pour point of this ether.

Testing of (II), i.e., the bis(tetrahydrofurfuryloxy)chlorobenzene, also gave good results, the dielectric constant and power factor values of (II) being found to be 10.5 and 1.1% respectively at 100 kc. and 25° C. It is advantageously employed as an arc-quenching dielectric in the manufacture of switches (see Fig. 2). Because (II) has a solidifying point which is approximately that of (I), a mixture of (I) and (II) may be employed as the impregnating agent in the preparation of paper capacitors as transformer coolants.

Example 2

This example describes the reaction of 1,2,4-trichlorobenzene with tetrahydrofurfuryl alcohol using greater quantities of reactant than those employed in Example 1. A mixture consisting of 6.75 moles (1,220 g.) of the trichlorobenzene, 10.15 moles (1,035 g.) of said alcohol, 8 moles (320 g.) of sodium hydroxide and 200 ml. of toluene was heated at a temperature of 140-172° C. for about 7 hours while collecting 154 ml. of water of reaction as it was formed. The reaction mixture was then diluted with 1 liter of water and neutralized with 0.38 mole of hydrogen chloride. The organic layer which separated was washed with water and brine and made alkaline to phenolphthalein in order to remove any phenol which might still be present. After subsequent neutralizing, filtering, and heating of the filtrate at 150° C./18 mm. in order to remove water and other low boiling materials, the residue was fractionated to get 1125 g. of (I) the substantially pure 2-(dichlorophenoxy)methyltetrahydrofuran, B.P. 135-142° C./0.6-0.7 mm. analyzing 53.38% C, 4.96% H, and 28.07% Cl, and 88 g. of (II) bis(tetrahydrofurfuryloxy)chlorobenzene, B.P. 180-200° C./0.8 mm. analyzing 61.00% C, 6.73% H, and 11.44% Cl. Based on the charged 1,2,4-trichlorobenzene, there was obtained 89.5 percent conversion to the mono-ether and 3.7 percent to the di-ether.

Example 3

A mixture consisting of 9 moles (882 g.) of furfuryl alcohol, 6 moles (1086 g.) of 1,2,4-trichlorobenzene, 9.3 moles (521 g.) of potassium hydroxide and 150 ml. of toluene was charged to a 5-liter, 4-neck flask equipped with a stirrer, thermometer and column bearing a head for removal of condensed vapors. The mixture was heated, with stirring, for about 11.5 hours at a pot temperature of from 130° C to 159° C. During the first 5.5 hours of heating there was collected 191 cc. of water. When heating was discontinued, about 2 liters of water were added to the reaction mixture, and the whole was filtered. After allowing the filtrate to stratify, the organic layer which formed was separated and washed with water. Water was removed from the washed material by heating to 60° C. at a pressure of 30-35 mm. of mercury. Subsequent distillation of the heated material gave 179 g. of the substantially pure 2-(dichlorophenoxyethyl)furan, B.P. 80° C./115° C./0.1-0.3 mm., and analyzing as follows:

	Found	Calcd. for C ₁₂ H ₁₀ O ₂
C, percent	84.94	84.19
H, percent	4.18	5.79

The 2-(dichlorophenoxyethyl)furan is advantageously employed as impregnating agent in the manufacture of cables (see Fig. 5).

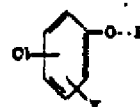
Although the present ethers are particularly valuable as impregnating agents for cellulosic materials adapted for use as dielectrics, because of their very good electrical properties, their thermal stability and their ability to remain liquid at low temperatures they are of general utility as liquid dielectrics. As hereinbefore disclosed the furfuryl or tetrahydrofurfuryl chlorine-substituted phenyl ethers may be employed per se as the dielectric liquid media of electrical apparatus, or they may be combined with up to substantially equal parts by weight of one or more other dielectric liquids, such as certain liquid petroleum hydrocarbons, the partially chlorinated biphenyls, trichlorobenzene, benzene, chlorinated naphthalene, chlorinated diphenyl ketone, chlorinated diphenyl oxide, chlorinated diphenylmethane, chlorinated diphenylethane, chlorinated benzene, chlorinated toluene, chlorinated nitrophenyl, chlorinated alkylated benzene, chlorinated alkylated biphenyl, ether trichlorobenzene, ether tetrachlorobenzene, ethyl pentachlorobenzene,

chlorinated terphenyls, chlorinated quaterphenyls, chlorinated paraffinic hydrocarbons, chlorinated alicyclic hydrocarbons, chlorinated oxygen-containing organic compounds, chlorinated rubber, chlorinated polymers, chlorinated fats, chlorinated vegetable oils, chlorinated animal oils, chlorinated mineral oils or mixtures of one or more of these.

This application is a continuation-in-part of my co. pending application, Serial No. 550,238, filed November 30, 1955, and now issued as Patent No. 2,870,169.

What I claim is:

1. Electrical apparatus comprising, in combination, metallic conducting elements disposed in spaced relationship to each other and adapted during operation of the apparatus to have a difference in electrical potential therebetween and, interposed between said elements for insulating one from the other, a liquid dielectric medium consisting of at least 50% by weight of an ether of the formula



in which R is selected from the class consisting of the furfuryl and the tetrahydrofurfuryl radicals and X is selected from the class consisting of chlorine and the radical -O-R.

2. A capacitor comprising a pair of electrodes and insulating agent associated with each of the electrodes and isolating them from each other, said insulating agent comprising the dielectric medium defined in claim 1.

3. A capacitor comprising a pair of electrodes and an insulating agent associated with each of the electrodes and isolating them from each other said insulating agent comprising a cellulosic material impregnated with 2-(dichlorophenoxyethyl)tetrahydrofuran.

4. An electrical switch comprising a pair of electrodes and bis(tetrahydrofurfuryloxy)chlorobenzene associated with each of said electrodes and isolating them from each other.

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