INSULATION SYSTEM FOR ELECTRICAL APPARATUS CONTAINING LIQUID DIELECTRICS

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The present invention relates to insulated electrical apparatus containing liquid dielectrics comprising oil and has particular reference to wire enamel insulating compositions which are suitable for use in such apparatus in combination with stabilized cellulose insulation.

Certain kinds of electrical apparatus such as transformers contain liquid dielectrics comprising oil and cellulose insulating materials such as paper, cotton cloth, cotton tape and wood. These cellulose materials deteriorate rapidly at temperatures of about 100° C, particularly when in contact with oil. For this reason, electrical apparatus employing cellulose insulation generally is not operated continually at temperatures above 105° C.

U.S. Patent No. 2,722,561, to McCulloch, discloses that substances like urea or non-acidic compounds derived from urea, when added to oil-filled transformers, greatly improve the thermal life of the cellulose insulation contained therein. The patent discloses that the addition of approximately 0.3% of urea to the oil, based on the total weight of the oil, provides paper having about the same life at 125° C. as it has at 100° C. without the urea stabilizer being present. The life is measured in terms of retention of tensile strength and crease resistance.

Urea and non-acidic compounds derived from urea provide excellent stabilizing materials in oil-filled transformers employing conductors insulated with cellulose materials. However, attempts to use, in this type of apparatus, conductors insulated with the ordinary enamel compositions have not been completely satisfactory. Thus, many enamels are attacked under start-up conditions by substances like urea and its decomposition products at elevated temperatures. When polyester wire enamels, for example, are employed in a closed system containing a liquid dielectric, urea and cellulose materials, the enamel may be dissolved or stripped completely from the wire, under some conditions of urea concentration, in a period of one week at a temperature of about 150° C.

The object of this invention is to provide electrical apparatus capable of use at temperatures above 100° C. for long periods of time, the apparatus comprising in combination, an electrical conductor with a heat hardened flexible wire enamel composition applied thereto, cellulose insulation, oil and urea or non-acidic compounds derived from urea.

Another object of the present invention is to provide wires insulated with a stable wire enamel composition which may be immersed at elevated temperatures for long periods of time in liquid dielectrics in contact with cellulose insulation stabilized with urea or non-acidic compounds derived from urea.

Another object is to provide electrical apparatus including, in combination, an electrical conductor provided with a cured wire enamel insulation comprising a mixture of a glycidyl polyester and urea-aldehyde or melamine-aldehyde resin, a liquid dielectric, cellulose insulation and a stabilizer for the cellulose insulation comprising urea or non-acidic compounds derived from urea.

Still another object of the present invention is to provide electrical apparatus including, in combination, an electrical conductor provided with a cured wire enamel insulation comprising a mixture of a heat hardenable organosiloxane resin and a specific polyamide reaction product, a liquid dielectric, cellulose insulation, and a stabilizer for the cellulose insulation comprising urea or non-acidic compounds derived from urea.

Yet another object of the present invention is to provide electrical apparatus including, in combination, an electrical conductor provided with a cured wire enamel insulation comprising a polyvinyl formal resin, a liquid dielectric, cellulose insulation, and a stabilizer for the cellulose insulation comprising urea or non-acidic compounds derived from urea.

Other and further objects of the invention will, in part, be obvious and will, in part, appear hereinafter.

For a more complete understanding of the present invention, reference is made to the accompanying drawings, the single figure of which is a view in elevation, partly in cross section, illustrating a transformer.

In the attainment of the foregoing objects and in accordance with the present invention there is provided electrical apparatus comprising electrical conductors insulated with a heat hardenable flexible wire enamel composition containing the particular resins described herein. Such an enamel composition, when applied to an electrical conductor and cured, provides an insulating conductor which may be employed in liquid dielectric-filled apparatus to provide a log-lived assemble suitable for use in combination with cellulose insulating materials associated with a stabilizer comprising urea or non-acidic compounds derived from urea.

Enamels which are suitable for use in this invention include cured heat-hardenable enamels which remain tough and flexible without softening at temperatures up to at least 250° C. It is also particularly important that the enamels be resistant to attack by alkalies or alkaline materials with which they may come in contact in the apparatus. If, for example, the enamel stabilizer employed in the herein described oil-filled transformers break down or decompose during use, ammonia and/or ammonium hydroxide will result. To be satisfactory, the enamels must resist attack from this ammonia and/or ammonium hydroxide. Furthermore, the enamel must be resistant to the abrasion to which wire conductors normally are subjected during conventional coil-winding operations. Also, the enamels must be sufficiently thermally stable to decompose upon subjection to temperatures at least as high as 250° C.

In preparing the wire enamel compositions for this invention any one of several resins may be used. For example, resin comprising a mixture of a glycidyl polyester and urea aldehyde or melamine aldehyde resin may be used. A second resin which may be used comprises a mixture of a heat hardenable organosiloxane and a specific polyamide reaction product. Moreover, a polyvinyl formal-phenol-aldehyde resin may be employed in forming the enameled wire of the present invention.

In those wire enamel compositions wherein a resin comprising a mixture of a glycidyl polyester and urea aldehyde or melamine aldehyde resins is employed, the urea-aldehyde and/or melamine-aldehyde resins appear to react with and promote the curing of the glycidyl polyester or epoxide resin. It has been determined that enamels of high hardness may be obtained by additionally incorporating therein a phenol-aldehyde resin in amounts up to about 15% by weight, based on the total weight of the enamel resins. Such latter enamels are extremely resistant to the scraping and abrasion frequently encountered in coil winding and other manufacturing operations. When it is desired to coat rectangular wire it has been found to be advantageous to incorporate a polyvinyl formal resin in the enamel composition in amounts up to about 10% to 30% by weight, based on the total weight of the enamel resins. The polyvinyl formal resin serves
to modify the coating properties, including increasing the viscosity of the enamel composition, whereby to permit the deposition of a satisfactorily thick enamel coating on the corners of the article, in which coating does not pull away from the corners during curing.

The resinous glycylid polymers employed in the enamel compositions of the present invention may be prepared by reacting predetermined amounts of at least one polyhydric phenol and at least one epichlorohydrin in an alkaline medium. Phenols which are suitable for use in preparing such resinous polymeric epoxides include those which contain at least two phenolic hydroxy groups per molecule. Polynuclear phenols which have been found to be particularly suitable include those wherein the phenol nuclei are joined by carbon bridges, such for example as 4,4'-dihydroxy-diphenyl-dimethylmethane (referred to hereinafter as bis-phenol “A”) and 4,4'-dihydroxy-diphenyl-methane. In admixture with the named polynuclear phenols, use also may be made of those polynuclear phenols wherein the phenol nuclei are joined by sulfur bridges such, for example, as 4,4'-dihydroxy-diphenyl-sulfone.

While it is preferred to use epichlorohydrin as the epichlorohydrin in the preparation of the resinous polymeric epoxide starting materials of the present invention, homologues thereof, for example, epibromohydrin and the like also may be used advantageously.

In the preparation of the resinous polymeric epoxides, aqueous alkali is employed to combine with the halogen of the epichlorohydrin reactant. The amount of alkali employed should be substantially equivalent to the amount of halogen present and preferably should be employed in an amount somewhat in excess thereof. Aqueous mixtures of alkali metal hydroxides, such as potassium hydroxide and lithium hydroxide, may be employed although it is preferred to use sodium hydroxide since it is relatively inexpensive.

The resinous polymeric epoxide, or glycylid polyether of a dihydric phenol, suitable for use in this invention has a 1,2-epoxy equivalency greater than 1.0. By epoxy equivalency reference is made to the average number of 1,2-epoxy groups contained in the average molecule of the glycylid ether. Owing to the method of preparation of the glycylid polyethers and the fact that they are ordinarily a mixture of chemical compounds having somewhat different molecular weights and contain some compounds wherein the terminal glycylid radicals are in hydrated form, the epoxy equivalency of the product is not necessarily the integer 2.0. However, in all cases it is a value greater than 1.0. The 1,2-epoxy equivalency of the polyethers is thus a value between 1.0 and 2.0.

Resinous polymeric epoxides or glycylid polyethers suitable for use in accordance with this invention may be prepared by admixing and reacting from one to two mols proportions of epichlorohydrin, preferably epichlorohydrin, with about one mol proportion of bis-phenol “A” in the presence of at least a stoichiometric excess of alkali based on the amount of halogen.

To prepare the resinous polymeric epoxides, aqueous alkali, bis-phenol “A” and epichlorohydrin are introduced into and admixed in a reaction vessel. The aqueous alkali serves to dissolve the bis-phenol “A” with the formation of the alkali salts thereof. If desired, the aqueous alkali and bis-phenol “A” may be admixed first and then the epichlorohydrin added thereto, or an aqueous solution of alkali and bis-phenol “A” may be added to the epichlorohydrin. In any case, the mixture is heated in the vessel to a temperature within the range of about 80° C. to 110° C., for a period of time varying from about one-half hour to three hours, or more, depending upon the quantities of reactants used.

Upon completion of heating, the reaction mixture separates into two layers. The upper aqueous layer is withdrawn and discarded, and the lower layer is washed with hot water to remove unreacted alkali and halogen salts, in this case, sodium chloride. If desired, dilute acids, for example, acetic acid or hydrochloric acid, may be employed during the washing procedure to neutralize the excess alkali.

Glycidyl polymers may be prepared in either solid or liquid form. The commercially available glycidyl polymers which are solids are less expensive than the liquid grades, thus the use of the solid materials affords a substantial cost saving when used in accordance with this invention. Usually, the liquid polyethers have very few, if any hydroxyl groups. The solid polyethers, on the other hand, have a substantial number of hydroxyl groups per molecule.

The following example illustrates the preparation of a glycylid polyether suitable for use in this invention.

EXAMPLE 1

Into a suitable reaction vessel there was introduced two liters of water, 160 parts of sodium hydroxide and 685 parts of bis-phenol “A.” This mixture was agitated for several minutes at a temperature of about 50° C. Thereafter, a mixture of approximately 280 parts of epichlorohydrin and 85 parts of bi-flash naphtha was added to the reaction mixture. This formulation contains a ratio of one mol of epichlorohydrin to one mol of bis-phenol “A,” with about 15% of sodium hydroxide and about 10% of solvent. The reaction mixture was maintained at a temperature of about 95° C. to 100° C. for a period of about two hours. The resin so produced was washed free of alkali and salt by successive washings with hot water at 100° C. After four separate washings the solution was neutralized with sulfurous acid and washed once with water. As much water as was possible was removed from the kettle by distillation and the resin was dried by heating to 150° C. The hot resin was then poured into a pan and permitted to cool.

A typical urea-aldehyde resin suitable for use with the glycidyl polyether so prepared is the reaction product of one mol of urea with two mols of an aldehyde such as formaldehyde. Ordinarily, the reaction is carried out in an alcohol such as butanol, and the reaction product is an alcoholic urea-resin, for instance, butylated urea-aldehyde resin. The preparation of urea-aldehyde resins is well known in the art and need not be detailed herein. When preparing the enamel compositions of this invention, the clarified and dehydrated urea-aldehyde in the solvent soluble stage or A-stage is dissolved in a suitable solvent or mixture of solvents and blended with the other enamel components.

The melamine-aldehyde resins which may be used with the glycidyl polymers may be prepared by reacting from two to six mols of an aldehyde, such as formaldehyde, with one mol of melamine under alkaline conditions.

The number of substituted methyol groups occurring in the product is generally dependent upon the mol ratio of the reactants. Thus, it is possible to react formaldehyde or another aldehyde with melamine in mol ratios sufficient to give mono-, di-, tri-, tetra-, penta-, and hexa-

methylated melamines or mixtures thereof. Any of these derivatives or mixtures thereof are satisfactory in preparing the resins of this invention.

Aldehydes other than formaldehyde may be used in preparing the urea-aldehyde and/or melamine-aldehyde resins of this invention. For example, acetaldehyde, propionaldehyde, butyraldehyde, benzaldehyde, and the like may be used to replace a part or even all of the formaldehyde, with satisfactory results being obtainable.

Another resinous composition suitable for use in preparing wire enamels for this invention may be prepared.
by admixing (A) from 1 part to 50 parts by weight of a heat-hardenable organosiloxane resin with (B) 100 parts by weight of a specific polyamide reaction product. This resin and enamels prepared therefrom are described in a copending application Serial No. 634,275, filed January 15, 1957, which application is assigned to the same assignor as the present invention.

The organosiloxane resins that have been found particularly satisfactory are the phenyl methyl polysiloxanes having from 1.3 to 1.95 phenyl and methyl groups per silicon atom. Particularly good results are obtained with organosiloxanes having a total of from 1.5 to 1.8 phenyl and methyl groups per silicon atom. It has been found that the phenyl groups may be replaced with up to 50% of diphenyl groups with equally good results. It will be understood that other organic groups other than phenyl and methyl groups may be present in the siloxane. Thus, the phenyl methyl organosiloxanes may comprise a small proportion, for example, up to 10 mol percent of other organic groups such as tolyl, allyl, ethyl, and the like.

The polyamide employed in preparing the resinous composition of this invention has the generic formula

$$R^1 \cdot H \cdot R^2 \cdot \left( -N^\gamma - R^3 - N^\beta - (C\text{H}_2)_{n} - \right) \cdot N^\gamma - R^4 \cdot H$$

where $n$ represents an integer having a value of two or more, and $n$ is 0 or an integer. $R$ represents the residue of an ethylenically unsaturated dicarboxylic acid after removal of the hydroxyl groups. $R'$ represents the residue of isophthalic acid, terephthalic acid, or an aliphatic dicarboxylic acid with the hydroxyl groups removed, said aliphatic dicarboxylic acid having no ethylenically unsaturation and having at least two and not more than eight non-carboxyl carbon atoms.

The polyamide is derived by admixing and heating to reaction ($a$) at least one acidic compound selected from the group consisting of ethylenically unsaturated dicarboxylic acids and anhydrides thereof and ($b$) at least one diamino compound selected from the group consisting of primary hydrocarbon diamines and polyamide reaction products derived by reacting a primary hydrocarbon diamine and at least one dicarboxylic acid having terminal amino groups, said acid being selected from the group consisting of isophthalic acid, terephthalic acid and saturated aliphatic dicarboxylic acids having from 2 to 10 non-carboxyl carbon atoms. For each mol of diamino compound there is provided from about 1 mol to 2 mol of the acidic compound.

Examples of suitable ethylenically unsaturated dicarboxylic acids and anhydrides thereof are maleic acid, maleic anhydride, fumaric acid, citraconic acid, and aconitic anhydride. It will be understood that esters of the above-mentioned acids and anhydrides may be substituted for all or a part of the acids in the reaction with the diamin compound. For example, dibutylmalonate may be substituted for all or a part of maleic acid.

The primary hydrocarbon diamines employed should have at least two and no more than six methylene groups. Examples of suitable primary diamines are ethylene diamine, 1,3-propane diamine, 1,4-butanedi amine and hexamethylenediamine.

The polyamide reaction products having terminal amino groups that may be employed in place of the above-mentioned primary diamines are those derived by reacting an excess of at least one of the primary diamines mentioned above with an aliphatic dicarboxylic acid or anhydride thereof having at least two and no more than eight non-carboxyl carbon atoms and having no other reactive groups than the carboxyl groups or anhydride groups. Examples of these are adipic, sebacic and glutaric acids. The above-mentioned dicarboxylic acids may be replaced in whole or in part by isophthalic acid or terephthalic acid.

The preparation of the above-mentioned polyamide re-
vent resistance desired in a good enamel, some other property or properties will be so poor that such composition will not be satisfactory in all properties for commercial use in electrical apparatus containing liquid dielectrics and urea stabilized cellulose insulating materials. The wire enamel compositions of this invention may be applied not only to bare copper wire, but they may be applied to cotton covered wire, asbestos covered wire, glass fiber covered wire, and wire carrying other fibrous or cellulosic materials to provide for good electrical insulating coatings. The fibrous materials may be applied before or after the enamel is applied, or concurrently therewith, as desired.

Electrical conductors insulated with the enamels described hereinabove are suitable for use in oil-filled transformers containing cellulose insulation stabilized with urea or non-acidic compounds derived from urea. The non-acidic compounds have the formula

\[
\text{R} - \text{C} = \text{N} - \text{R}'
\]

wherein \( R \) is selected from the group consisting of hydrogen, monovalent hydrocarbon radicals, \(-\text{CN}\) radicals, and methylol radicals, and \( R' \) is selected from the group consisting of oxygen, sulfur, hydrogen, and \(-\text{NH} \) radicals, there being a total of at least two hydrogen atoms attached directly to the \( C \) and \( N \) atoms, to reduce greatly the rate of loss of strength of the cellulose insulation.

Examples of the stabilizing compounds suitable for this purpose are urea, substitution derivatives of urea, and reaction products of urea and aldehydes such as urea-formaldehyde resins. Excellent results have been had using the alkyl substitution derivatives in which one or more aliphatic hydrocarbon groups are substituted for hydrogen in both urea and thiourea, for example, methyl, ethyl, butyl propyl, amyl and octyl radicals. Examples of such compounds are thiourea, hexamethyleneetramine, guanidine carbonate, tertbutyl urea, tertamyl urea, n-butyl urea, 1,1-diethyl urea, 1,3-diethyl thiourea, 1,3-disopropyl thiourea, 1,3-dimethyl urea, 1,3-dibutyl urea, diacylendiamide, methyol urea, and butyl urea. The term "non-acidic compounds," as used in the present specification and claims, refers to compounds which when placed in water in amounts of about 1% and warmed for a few hours produce aqueous solutions of a pH of 7 or higher. Thus, water with 0.2% by weight of urea has a pH of approximately 10. Dicyandiamide under the same conditions gives a pH of 8, while thiourea gives a solution having a pH of 7. On the other hand, dibutyluret gives a pH of 5 and uramid a pH of about 1, and each of these latter have been found to be useless in retarding the rate of deterioration of cellulose materials in liquid dielectrics.

In order to increase the thermal stability of cellulose insulation in contact with liquid dielectrics, thereby greatly reducing its rate of loss of strength, a small quantity of the stabilizing compound is introduced into the liquid dielectric or otherwise placed in contact with the liquid dielectric. The quantity of the compound may be quite small. For example, a quantity equal to 0.01% by weight of the liquid dielectric is sufficient; however, a larger amount does no harm and may be desirable in some cases. One or more of the compounds may be present in an amount of up to 10% of the weight of the dielectric. The compound may be finely divided. The compound needs to be appreciably soluble in the dielectric. In fact it was found that even though urea is only very slightly soluble in cold oil, it produced excellent results. At higher temperatures as, for example, at 135° C., urea will melt and disperse readily in oils.

The stabilizer for the cellulose insulation also may be placed in the paper either added to the furnish of the paper before it is formed into sheet, or is sifted or otherwise applied as the paper is wrapped on the conductors or coils, in the oil, or in both. Since the solubility of substances like urea and non-acidic compounds derived therefrom is very slight, less than 0.1%, in cold transformer oil, and since oil circulation through tightly wound coils is very slow, it is particularly advantageous to incorporate the stabilizer in the paper itself at some stage during the manufacture of the paper. Addition of about 3% of urea or derivative thereof, based on the weight of the paper, provides satisfactory stabilizing results.

Referring to the drawing, there is illustrated a transformer in accordance with the present invention. The transformer comprises a tank carrying a support internally on which magnetic core and a coil is disposed. Coil 16 comprises a high voltage winding 18 and a low voltage winding 20 each insulated with the wire enamel composition of the present invention. The windings also are insulated from one another by cellulose insulation 22 which comprises paper, cotton, or other cellulosic material. An exterior cellulose wrapping 24 of cloth or paper may be applied to the coil 16. In some cases, pressboard, wood, or cardboard spacers or various other cellulosic products may be applied to the electrical windings. A liquid dielectric 26 is disposed within the tank 10 to cover the core 14 and coil 16 in order to insulate them and to dissipate the heat produced in operation. The liquid dielectric may be any suitable dielectric such as oil.

In applying the enamel compositions on electrical conductor wire to be used in the apparatus of the present invention it has been found that an enamel coating composition having a resin solids content of from 15% to 30% is suitable for use in most enamelling machines. If enamel coating dies are employed, a more viscous solution having a higher resin solids content may be employed, for example, a 50% solids content. The wire enamel so prepared may be applied by a flowing or by a dipping process or other suitable method of applying a film or a coating of the enamel solution to an electrical conductor. To drive off the solvent and to cure or copolymerize the enamel composition, the coated wires are heated or baked. The baking temperature may be varied within a wide range, since for most satisfactory application the temperature within the tower adjacent the wire must be correlated with the speed of the wire through the enamelling tower as well as the size of the tower. Thus, in a small high speed tower, a temperature of approximately 450° C. may be satisfactory, while in a larger tower with slower wire travel speeds a temperature of about 250° C. may be more suitable.

In order to indicate more fully the advantages and capabilities of the present invention the following specific examples are set forth. The parts given are by weight unless otherwise indicated.

**EXAMPLE I**

An enamel composition was prepared by dissolving 75 parts of the glycidyl polyether as described in Example 1 in 150 parts of Linseed Oil (C油H油) and 125 parts of xylene. This solution was mixed with 50 parts of a butylated urea-formaldehyde solution containing 50% solids in a mixture composed of 30 parts of butanol and 20 parts of xylene. The wire enamel so prepared was coated 1.5 mils thick on number 17 A.W.G. copper wire at a rate of 28 feet per minute at 430° C. in a 15 foot coating tower. The enamel composition coated smoothly and had good flexibility over bends. Twisted samples of wire coated at this coating rate and temperature were tested for thermal stability according...
to American Institute of Electrical Engineering Test No. 57 at 200° C. The thermal life of this enamel as determined from an average of 5 samples tested was 336 hours at 200° C. The enamel had a scrape hardness of 40 to 43 ounces using a 9 millimeter diameter knife edge when tested in the tester described in U.S. Patent 2,372,093, and had a dielectric strength of from 4,500 to 6,500 volts.

EXAMPLE III

A wire enamel composition was prepared by dissolving 65 parts of the glycidyl polyether as described in Example I in 130 parts of methyl Cellulose acetate and 130 parts of xylene. This solution was blended with 70 parts of a butylated urea-formaldehyde solution containing 50% solids dissolved in a mixture composed of 30 parts of butanol and 20 parts of xylene. This wire enamel was coated on No. 17 A.W.G. copper wire at an average rate of 25 feet per minute at 430° C. Twisted samples of wire coated at these various coating rates and temperatures were tested for thermal stability according to American Institute of Electrical Engineering Test No. 57 at 200° C. The thermal life of this enamel was 436 hours at 200° C. The enamel coated smoothly and had good flexibility. The enamel had a scrape hardness of from 39 to 44 and exhibited dielectric strengths as high as 9,000 volts.

EXAMPLE IV

To 75 parts of the glycidyl polyether prepared as described in Example I dissolved in 150 parts of cresol and 125 parts of xylene was added 50 parts of butylated urea-formaldehyde solution containing 50% solids in 30 parts of butanol and 20 parts of xylene. The enamel was coated on No. 17 A.W.G. copper wire at a rate of 25 feet per minute at 430° C. The cured enamel had a scrape hardness of from 39 to 42 ounces and had a dielectric strength varying from 4,000 to 9,500 volts. A wire enamel of essentially the same characteristics is obtained when 275 parts of methyl Cellulose acetate is used in place of the cresol-xylene solvent.

Example IV was repeated increasing the urea-formaldehyde resin content to 70 parts, on a solids basis, and decreasing the glycidyl polyether content to 65 parts. This had the effect of increasing the scrape hardness of the cured enamel to 45±2 ounces without adversely affecting any of the other properties.

EXAMPLE V

A wire enamel composition was prepared by admixing (1) 20 parts of a polyvinyl formal resin of medium molecular weight dissolved in 225 parts of cresol, (2) 52 parts of the glycidyl polyether of Example I dissolved in 104 parts of methyl Cellulose acetate and 310 parts of xylene, and (3) 56 parts of a 50% solids, basis, urea-formaldehyde resin solution dissolved in 30 parts of butanol and 20 parts of xylene. This wire enamel composition was coated on No. 17 A.W.G. copper wire at a rate of 28 feet per minute at 430° C. The cured wire enamel had excellent flexibility characteristics and excellent heat shock resistance. The enamel had a scrape hardness of 53 to 54 ounces and a dielectric strength varying from 6,000 to 11,000 volts. This enamel is particularly well suited for coating on rectangular wire.

EXAMPLE VI

An enamel was prepared by dissolving (1) 58.5 parts of the glycidyl polyether of Example I, (2) 63 parts of a 50%, solids basis, urea-formaldehyde solution in 30 parts of butanol and 20 parts of xylene, and (3) 10 parts of a polyvinyl formal resin of medium molecular weight in 117 parts of methyl Cellulose acetate. 95 parts of cresol, and 83 parts of xylene. This wire enamel was coated on No. 20 A.W.G. copper wire at the rate of 28 feet per minute at 430° C. The enamel had a scrape hardness of from 34 to 37 ounces and a dielectric strength of from 5,500 to 10,500 volts. This wire enamel composition was particularly well suited for coating on rectangular wire.

EXAMPLE VII

The following were introduced into a closed reaction vessel provided with a condenser:

<table>
<thead>
<tr>
<th>Parts</th>
<th>310 (2.0 mols)</th>
<th>200</th>
<th>200 (1.2 mols)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexamethylenediamine, 80% aqueous solution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cresol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isophthalic acid</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The mixture was stirred and heated slowly until the temperature of the mixture reached 240° C. This temperature was maintained until substantially all the water had been removed from the mixture by operation of the condenser. The mixture was cooled to approximately 190° C. and then sparged with nitrogen until all the air was replaced by the nitrogen while the temperature of 190° C. was maintained. After the sparging had been completed, 273 parts (1.2 mols) of dibutylmaleate dissolved in 250 parts of cresol were added to the mixture. The mixture was then heated to approximately 165° C., which temperature was maintained for about 1½ hours. The temperature of the mixture was then gradually increased to 185° C. during the succeeding two hours, during which time between 60 parts and 80 parts of butanol distilled off.

One hundred parts of a 60% solution of phenyl-diphenyl-methyl siloxane resin in xylene were then added to the mixture to form a resinous composition. The R to Si ratio was about 1.5 and the phenyl, diphenyl and methyl groups were present in approximately equal proportions. The resinous composition was then diluted by adding 300 parts dichlorobenzene and 600 parts of butyl alcohol.

No. 13 (A.W.G.) copper wire was coated with six dips in the diluted resinous composition in a wire enameling tower having an oven maintained at 825° F. The cured resin enamel on the wire was smooth and hard, and it had a scab test value of from 45 to 55 ounces as determined on the scab tester described in Patent 2,372,093. The enamelled wire successfully passed the quick jar and heat shock tests, and it showed high resistance to hot impregnating varnishes and varnish solvents such as toluene. The enamelled wire was wound around a mandrel having the same diameter of the enamelled wire and was aged for four weeks at 200° C. without cracking or otherwise exposing the copper wire.

EXAMPLE VIII

A wire enamel containing a polyvinyl formal-phenol-formaldehyde resin may be prepared according to the method disclosed in U.S. Patent No. 2,307,585, which disclosure is incorporated herein. Briefly, such a wire enamel may be prepared by mixing 16% by weight of resins and 84% by weight of solvents. The resins include about 5.5% cresol-formaldehyde resin and 10.5% polyvinyl formal and the solvent includes about 25.5% cresol and 58.5% naphtha.

The data set forth in the following table illustrate the improved results obtainable when employing the insulation system of the present invention as compared with other systems. The data was obtained from tests run on three coils. Coils I and II were wound with wire insulated with an enamel containing a polyester-polyamide resin. Coil III was wound with wire insulated with an enamel containing a resin comprising a mixture of a glycidyl polyether (epoxy resin) and a urea formaldehyde resin. Cellulosic layer varnish insulation was applied to each coil between each layer of wire wound about the coils. In coil I the layer insulation was kraft paper. In coils II and III the layer insulation was urea treated kraft paper comprising 3% by weight of urea. Each of
the three coils was placed in a transformer tank partially filled with transformer oil. The coils were completely covered by the oil in each tank. A cover was placed on each tank and current was applied to each coil in an amount sufficient to generate a coil hot spot temperature of 150°C. This temperature was maintained for five days, the duration of the test.

The test data show that in coil I, employing plain kraft paper with polyester-polyamide enamel, the enamel was not degraded but that the paper was degraded as evidenced by a greatly reduced breaking strength. In coil II, where urea was added to the paper, the paper was greatly improved but the polyester-polyamide enamel was practically completely dissolved off the wire in deep coil portions. When a combination of urea, paper and glycidyl polyester-urea-formaldehyde enamel was used, coil III, both the paper and enamel were satisfactory after the accelerated test and suffered no significant deterioration.

**Table**

<table>
<thead>
<tr>
<th>Materials Used</th>
<th>Test Results</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Coil</strong></td>
<td><strong>Layer Insulation</strong></td>
</tr>
<tr>
<td>I</td>
<td>Kraft Paper</td>
</tr>
<tr>
<td>II</td>
<td>Kraft + Urea</td>
</tr>
<tr>
<td>III</td>
<td>Kraft + Urea</td>
</tr>
</tbody>
</table>

Bend test: Wire diameter Smallest mandrel diameter bend without cracking of enamel.

While the present invention has been described with respect to the insulation of an oil-filled transformer it will be understood by those skilled in the art that it is equally applicable to other electrical apparatus such as capacitors, reactors, cables, switchgear and the like in which liquid dielectrics are in contact with cellulosic insulation and with electrical conductors provided with enamel insulation.

We claim as our invention:

1. In electrical apparatus, the combination comprising an electrical conductor winding developing heat during use of the apparatus, cellulosic insulation present in the apparatus and in contact with the winding and normally being subject to loss of physical strength with passage of time at the temperatures developed, a liquid dielectric consisting essentially of petroleum oil applied to the winding and to the cellulosic insulation to dissipate the heat developed therein, and, in the liquid dielectric to maintain the physical strength of the cellulosic insulation, a non-acidic compound having the formula

![Image](image_url)

where R is selected from the group consisting of hydrogen, monovalent hydrocarbon radicals, —CN radicals, and methyl radicals and R' is selected from the group consisting of oxygen, sulfur, hydrogen, and —NH radicals, there being a total of at least two hydrogen atoms attached directly to the C and N atoms, the electrical conductor winding being provided with a hard, tough, flexible enamel coating which is resistant to attack by ammonia, ammonium hydroxide, and other decomposition products of said non-acidic compounds, and which does not soften at temperatures up to about 250°C, the coating comprising from 50 to 85 parts by weight of a glycidyl polyether of a dihydric phenol having a 1,2-epoxy equiva-

2. In electrical apparatus, the combination comprising an electrical conductor winding developing heat during use of the apparatus, cellulosic insulation present in the apparatus and in contact with the winding and normally being subject to loss of physical strength with passage of time at the temperature developed, a liquid dielectric consisting essentially of petroleum oil applied to the winding and the cellulosic insulation to dissipate the heat developed therein, and, in the liquid dielectric to maintain the physical strength of the cellulosic insulation, a non-acidic compound having the formula

![Image](image_url)

where R is selected from the group consisting of hydro-

3. In electrical apparatus, the combination comprising an electrical conductor winding developing heat during use of the apparatus, cellulosic insulation present in the apparatus and in contact with the winding and normally being subject to loss of physical strength with passage of time at the temperature developed, a liquid dielectric consisting essentially of petroleum oil applied to the winding and the cellulosic insulation to dissipate the heat developed therein, and, in the liquid dielectric to maintain the physical strength of the cellulosic insulation, a non-acidic compound having the formula

![Image](image_url)

where R is selected from the group consisting of hydro-

4. In electrical apparatus, the combination comprising an electrical conductor winding developing heat during use of the apparatus, cellulosic insulation present in the apparatus and in contact with the winding and normally being subject to loss of physical strength with passage of time at the temperature developed, a liquid dielectric consisting essentially of petroleum oil applied to the winding and the cellulosic insulation to dissipate the heat developed therein, and, in the liquid dielectric to maintain the physical strength of the cellulosic insulation, a non-acidic compound having the formula

![Image](image_url)

where R is selected from the group consisting of hydro-
gen, monovalent hydrocarbon radicals, —CN radicals, and methyol radicals and R’ is selected from the group consisting of oxygen, sulfur, hydrogen, and —NH radicals, there being a total of at least two hydrogen atoms attached directly to the C and N atoms, the electrical conductor winding being provided with a hard, tough, flexible enamel coating which is resistant to attack by ammonia, ammonium hydroxide, and other decomposition products of said non-acidic compounds, and which does not soften at temperatures up to about 250° C., the coating comprising (1) 100 parts by weight of a polyamide resin composition derived by admixing and heating (f) from about 1 to 2 mols of an unsaturated acidic compound selected from the group consisting of maleic acid, maleic anhydride, fumaric acid and the monomethyl substitution derivatives for the non-carboxyl hydrogen thereof for (ii) each one mol of a diamino compound selected from the group consisting of primary hydrocarbon diamines having from 2 to 6 carbon atoms and polyamide reaction products having terminal amino groups and having an average molecular weight of not in excess of 1500 and from (2) one part to 50 parts by weight of a solvent soluble, heat-hardenable organosilicone resin having from 1.3 to 1.95 hydrocarbon groups per silicon atom.

4. In electrical apparatus, the combination comprising an electrical conductor winding developing heat during use of the apparatus, cellulosic insulation being present in the apparatus and in contact with the winding and normally being subject to loss of physical strength with passage of time at the temperatures developed, a liquid dielectric consisting essentially of petroleum oil applied to the winding and to the cellulosic insulation to dissipate the heat developed therein, and, in the liquid dielectric to main-

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