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J. E. MILLINGTON

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THERMOSTABLE DIELECTRIC MATERIAL

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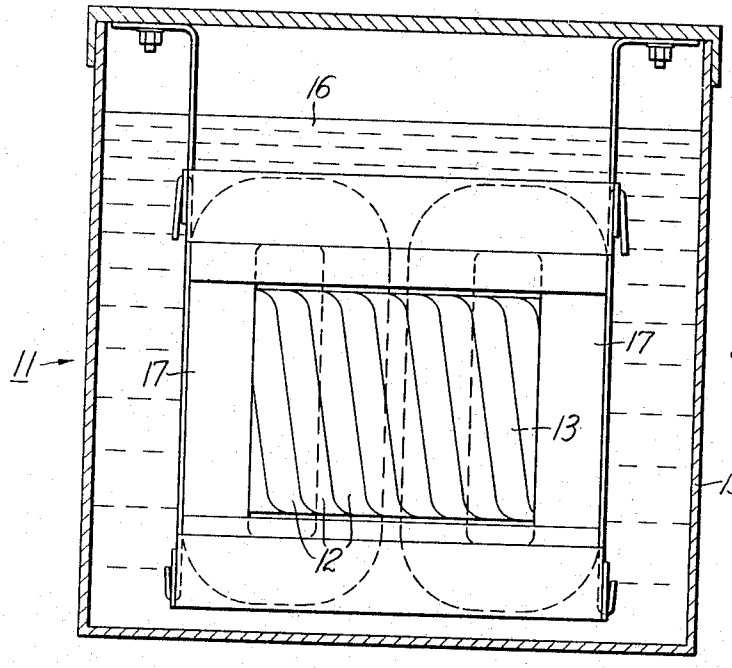

Fig. 1

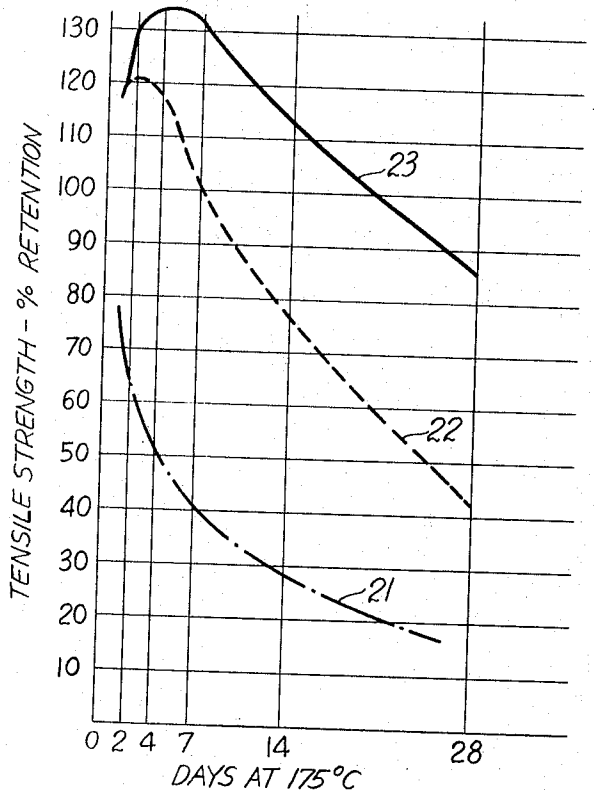

Fig. 2

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THERMOSTABLE DIELECTRIC MATERIAL

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7 Claims. (Cl. 252—63.7)

This invention relates to a dielectric material and in particular to a dielectric material for electrical apparatus containing an insulating liquid, and is a continuation in part of my application Ser. No. 161,171 filed Dec. 21, 1961, now abandoned.

It has frequently been the practice to immerse certain types of electrical apparatus, such as transformers, in a housing containing an insulating liquid. Perhaps the most common of all insulating liquids used for this type of electrical apparatus is petroleum oil. In addition to the liquid insulation, there is also dielectric sheet material or paper which is used to insulate the various electrical components. A long recognized problem has been the manner in which the dielectric sheet material deteriorates when immersed in the insulating liquid. The deterioration of this material is particularly noticeable when the insulating liquid is substantially heated.

Consequently, the maximum output for certain types of heat producing electrical apparatus such as transformers is limited in order to avoid overheating the dielectric material. The duration and extent of transformer overloads are limited primarily by this insulation aging factor. It has been generally accepted in the transformer industry that the rate of aging of dielectric insulation doubles with an 0° to 10° C. rise. The bulk oil temperature for continuous operation of the transformer should not exceed 105° C. if excessive aging of the transformer is to be avoided. Likewise, the maximum temperature for the hottest point in the transformer should not exceed 135° C. At greater temperatures, the dielectric material will deteriorate at a much faster rate and consequently the life of the transformer will be substantially reduced. However, it is apparent that if the dielectric material can be thermally upgraded and be less subject to aging at high temperatures, the life of the apparatus will not be so severely affected when operating at heavy overloads.

Thus, it is an object of this invention to provide a thermally upgraded dielectric sheet material which has greater retention of tensile strength and folding endurance as compared to present day dielectric materials when immersed in hot insulating liquids.

Another object of this invention is to provide a new and improved transformer capable of withstanding greater loads at longer intervals.

Objects and advantages other than those mentioned above will be apparent upon reading the folowing description in connection with the drawing in which a transformer is illustrated with dielectric material and immersed in an oil filled housing.

Referring to FIG. 1, a transformer **11** is illustrated containing insulation paper **12** treated in accordance with this invention which is applied to windings **13**. The transformer is contained in a tank **115** containing a dielectric liquid **16** such as petroleum ol.

Degradation of insulating paper in electrical apparatus is generally based on the paper's reduction of certain mechanical properties including tensile strength and folding endurance, i.e., flexibility. As the paper becomes weak and brittle, its value as insulating material for transformers is lessened. This is because the insulation is subjected to mechanical forces despite the fact that the transformer is static. Minute vibrations from the core **17** plus the forces from electrical surges in windings **13** stress the insulation **12**.

Degradation of insulation **12** is generally attributed to a reaction between the insulation and the hot insulating liquid. As transformer **11** begins to heat, its petroleum oil **16** likewise becomes heated. In the presence of moisture, acids such as formic acid and acetic acid are produced. A hydrolytic reaction occurs between the acid and the insulating material **12** which is generally of a cellulose composition. As a result of this hydrolytic reaction, a new cellulose is produced by chain scission which has a lower molecular weight than the original material. This new cellulose has a reduced tensile strength and the apparatus is substantially weakened in its life expectancy. Because the fibers of the new cellulose have also taken on a brittle characteristic, the cellulose likewise has a reduced flexibility.

Even in the absence of a petroleum oil, cellulose decomposes at elevated temperatures (for example 135° C.) by the intra-molecular and inter-molecular loss of water. My data has demonstrated that cellulose treated with an hydroxyalkylamine degrades at a much slower rate.

The present invention combats degradation of the insulating paper through a plasticizing effect on the paper fibers and also by scavenging the acids before they affect the paper. This is accomplished by treating the paper with an aliphatic amine having one or more primary, secondary, or tertiary amino functional groups and at least one hydroxy functional group. This group includes the compounds ethanolamine, diethanolamine, triethanolamine, methylethanolamine, methyldiethanolamine, 1,1-dimethylamino-2-propanol, t-butylaminoethanol, trishydroxymethylaminomethane, tetrakis - (2 - hydroxyethyl)-ethylenediamine, tetra (2 - hydroxypropyl) ethylenediethylenediamine, tetra - (2-hydroxypropyl) - ethylenediamine, 9-diethylamino-10-hydroxysterylamine, and 1,9 bis-(diethylamino)-10-hydroxyoctadecane. It has been found that any of the compounds in the above group, when properly applied to a cellulose insulating paper, reacts in such a manner as to provide an unexpected improvement in the thermostability of the insulating paper in the presence of hot insulating oil, thereby greatly increasing the paper's dielectric life.

The cellulosic paper may either be subsequently treated with a particular compound or, if preferred, the compound may be added to the paper during one of the steps as the paper is being manufactured, that is to say prior to forming the cellulosic fibers into a sheet. Thus, conventional kraft paper may be immersed in an aqueous solution containing one of the forementioned compounds. Immersion of the paper in a 10 percent by weight solution for a period that permits from about 50 to 100 percent wet pickup of the solution has been found to be quite satisfactory. The term wet pickup as used herein describes the weight gain in percent of the wetted paper as compared to the dry paper. The paper is subsequently dried.

A method for adding the particular compound during the manufacture of the paper comprises running the paper sheet through a bath of liquid solution comprising about a 10 percent concentration of the compound. After the pulp has been properly beaten to form the desired fiber length, the slurry is put on a Fourdrinier wire. Application of a vacuum removes part of the water, and moisture content is further reduced by passing the sheet over steam heated rollers. At this point the pulp has formed into a sheet which may be passed through a chemical bath (size press) containing one of the above compounds. The sheet may then be run through an additional drying section and calender stack to provide a dry paper. Just as the concentration of the solution may vary from 10 percent, the rate of travel of the paper through the bath or its time exposure to the bath may be varied. For most

satisfactory results the dry treated paper should have an optimum nitrogen content of 0.2 percent and 0.6 percent although as much as 1.0 percent is acceptable. The paper is now ready for direct application on an electrical apparatus such as shown in FIG. 1, in the usual manner.

Another method for combining the chemical with paper is during the pulp stage. The concentration of the chemical in the pulp solution may vary from approximately 3 to 10 percent for best results. Papers manufactured with this built-in chemical treatment on a hand sheet production basis have generally had a nitrogen content ranging from approximately .02 percent to 1 percent. From a commercial standpoint this procedure is less efficient since a large percent by weight of the pulp is water, thereby requiring a large amount of the treating chemical in order to maintain the desired ratio.

In determining the effect of the above amines on cellulosic paper, accelerated tests were run in which conditions were controlled to closely simulate a transformer operating at high overloads. Thus, the various treated papers were immersed in petroleum oil at 175° C. and aged for 24 hours. In each instance the treated paper was obtained by soaking untreated paper in an aqueous solution of the requisite compound. The following table illustrates the manner in which the amines affected the tensile strength and folding endurance of these treated papers. Folding endurance was determined on a standard M.I.T. folding endurance tester.

Treatment on Kraft Paper	Percent Retention of Tensile Strength	Percent Retention of Folding Endurance
Untreated kraft paper	79	2
Ethanolamine	139	48
Diethanolamine	111	44
Triethanolamine	115	74
Methylethanolamine	116	46
Methyldiethanolamine	114	93
1,1-diethylamino-2-propanol	97	22
t-Butylaminoethanol	99	21
Tetrakis-(2-hydroxyethyl)-ethylenediamine	106	109
Tris-hydroxymethylaminomethane	106	----------

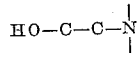
It can be seen that in each case the percent of tensile strength retention is substantially greater in the treated papers than in an untreated paper. Likewise the percent retention of folding endurance was a substantial multiple of the retention of untreated paper.

In FIG. 2 results are shown in graph form based on an extended 28 day period during which the tested papers were immersed in 175° C. petroleum oil. The lowest curve **21** represents a standard untreated kraft paper. Its retention of tensile strength was about 15 percent after 28 days. Curves **22** and **23** illustrate how the treatment of kraft paper with a solution of triethanolamine greatly improves retention of tensile strength. Curves **22** and **23** show a substantial difference between each other because of the difference in their fiber makeup. Whereas curve **22** represents a treated southern pine kraft paper, curve **23** represents a treated northern pine spruce-balsam kraft paper.

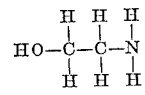
The above test results can be summarized by saying that whereas untreated kraft paper will have only about 17 percent retention of tensile strength after being in a transformer which has been in continuous operation approximately 21 years, a paper treated with triethanolamine will have a retention of 42 to 86 percent, depending upon the type of paper stock used. This is based on the transformer operating at 95° C. or an average of 55° C. over ambient, which is generally taken as 40° C. It is further based on the rule for rate of aging where the rate of aging doubles for each 10° C. rise. If the rate of aging is considered to double for each 8° C. rise then the 28 day-175° C. test period represents an even longer period than 21 years.

The particularly effective way in which the listed hydroxyalkylamines prevent thermal degradation of cellulose

papers in oil is believed to be attributed to their general structural makeup. In each instance the amine has at least one hydroxyl group and an amino function. The amino function may be in a primary, secondary or tertiary form. Thus, the general formula is

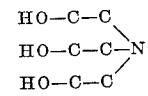


For ethanolamine the formula is



with the amino function being in the primary NH_2 group.

For triethanolamine the formula is



with the nitrogen in the tertiary amino group.

Since it is believed that the reactions of treated papers containing the above amines with the acids formed from the petroleum oil and cellulose are substantially the same, only one example need be fully explained. Taking ethanolamine as an example, the acid in the oil is scavenged through the combination of an OH group in the acetic acid with an H atom in the ethanolamine to form water, the residue being the amide-2-hydroxyethylacetamide. The chemical equations for this reaction and including an intermediate stage are:

$$HOCH_2CH_2NH_2 + CH_3COOH \longrightarrow$$

(ethanolamine) (acetic acid)

$$[HOCH_2CH_2NH_3]+CH_3COO^- \longrightarrow$$

$$HOCH_2CH_2NHOCCH_3 + H_2O$$

(2-hydroxyethylacetamide)

Consequently, the tensile strength of the treated paper is not so severely affected. The flexibility or folding endurance of the paper is retained through a plasticizing effect on the fibers. Whereas fibers in untreated paper become brittle after aging, the fibers of the treated paper remain relatively flexible.

Thus, it is clear that the particular above amines have an unusual thermostabilizing effect on insulating paper immersed in petroleum oil. While the above table relates to treatments of lignocellulose pulp, the results are also applicable to other material including alpha cellulose pulp (rag stock) and rope stock.

Tests have also assured the compatibility of these treated papers with oil and with epoxy coated copper wire. Specific amounts of the oil, insulated wire and treated paper were combined to simulate the approximate ratio of these elements in a transformer. Upon completing the aging tests the dielectric strength of the oil and wire were tested. It was found that in each instance the dielectric strengths were not significantly affected, thereby assuring the compatibility of the treated papers with these elements.

Although only several embodiments of this invention have been disclosed in full, it will be apparent to those skilled in the art that other embodiments are available within the spirit of the invention and scope of the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A thermally upgraded cellulosic paper dielectric for transformers of the type operated in a petroleum oil environment comprising a cellulosic paper dielectric impregnated with an amine selected from the group consisting of ethanolamine, diethanolamine, triethanolamine, methylethanolamine, methyldiethanolamine, 1,1-dimethylamino-2-propanol, t-butylaminoethanol, tetrakis-(2-hydroxyethyl)-ethylenediamine tris-hydroxymethylaminome-

thane, tetra (2-hydroxypropyl) ethylenediamine, 9-diethanolamine-10-hydroxystearylamine, and 1,9-bis (diethanolamino) 10-hydroxyoctadecane in an amount such that said cellulosic paper dielectric has an amino nitrogen content of from about 0.2% to about 1.0% by weight.

2. The method of extending the useful life of a cellulose paper dielectric for insulating coils of electrical transformers of the type operated in a petroleum oil environment comprising impregnating the cellulose fibers with an amine selected from the group consisting of ethanolamine, diethanolamine, triethanolamine, methylethanolamine, methyldiethanolamine, 1,1-dimethylamino-2-propanol, t-butylaminoethanol, tetrakis(2-hydroxyethyl)-ethylenediamine tris-hydroxymethylaminomethane, tetra (2-hydroxypropyl) ethylenediamine, 9-diethanolamino-10-hydroxystearylamine, and 1,9-bis (diethanolamino) 10-hydroxyoctadecane in an amount sufficient to give the cellulose fibers an amino nitrogen content of from about 0.2% to about 1.0% by weight.

3. The method of extending the useful life of an electrical transformer cellulose paper dielectric of the type being immersed in a petroleum oil environment comprising impregnating said paper dielectric with an amine selected from the group consisting of ethanolamine, diethanolamine, triethanolamine, methylethanolamine, methyldiethanolamine, 1,1-dimethylamino-2-propanol, t-butylaminoethanol, tetrakis-(2-hydroxyethyl) ethylenediamine tris-hydroxymethylaminomethane, tetra (2-hydroxypropyl) ethylenediamine, 9-diethanolamino-10-hydroxystearylamine, and 1,9-bis (diethanolamino)-10-hydroxyoctadecane so that the cellulose dielectric paper has an amino nitrogen content of from about 0.2% to about 1.0% by weight.

4. The method of producing a thermally upgraded cellulosic dielectric material for electrical transformers of the type operated within a petroleum oil environment comprising pulping a cellulosic material, immersing the pulped material into a bath of an aqueous solution of an amine selected from the group consisting of ethanolamine, diethanolamine, triethanolamine, methylethanolamine, methyldiethanolamine, 1,1-dimethylamino-2-propanol, t-butylaminoethanol, tetrakis(2-hydroxyethyl)-ethylenediamine tris-hydroxymethylaminomethane, tetra (2-hydroxypropyl) ethylenediamine, 9-diethanolamino-10-hydroxystearylamine, and 1,9-bis (diethanolamino) 10-hydroxyoctadecane; picking up sufficient amine to give the dried cellulosic material an amino nitrogen content of from about 0.2% to about 1.0% by weight; removing the pulp from the amine bath; removing the excess amine solution from the pulp; forming the pulp into a paper; and drying said paper.

5. The method of producing a thermally upgraded cellulosic dielectric paper for electrical transformers of the type operated within a petroleum oil environment comprising the steps of immersing the paper into a bath of an aqueous solution of an amine selected from the group consisting of ethanolamine, diethanolamine, triethanolamine, methylethanolamine, methyldiethanolamine, 1,1-

dimethylamino-2-propanol, t-butylaminoethanol, tetrakis-(2 - hydroxyethyl)-ethylenediamine tris-hydroxymethylaminomethane, tetra (2-hydroxypropyl) ethylenediamine, 9-diethanolamino-10-hydroxystearylamine, and 1,9-bis (diethanolamino)-10-hydroxyoctadecane; the concentration of the amine in said bath being adjusted to a level such that the finished cellulosic dielectric paper has a nitrogen content of between 0.2 to 1.0% nitrogen by weight; removing the paper from said bath and drying said paper.

6. The method of producing a thermally upgraded cellulosic dielectric paper for electrical transformers of the type housed in a petroleum oil environment comprising the steps of pulping a cellulosic material; immersing the pulped cellulosic material into a bath of an aqueous solution of an amine selected from the group consisting of ethanolamine, diethanolamine, triethanolamine, methylethanolamine, methyldiethanolamine, 1,1-dimethylamino-2-propanol, t-butylaminoethanol, tetrakis-(2-hydroxyethyl)-ethylenediamine tris-hydroxy-methylaminomethane, tetra (2-hydroxypropyl) ethylenediamine, 9-diethanolamino-10-hydroxystearylamine, and 1,9-bis (diethanolamino)-10-hydroxyoctadecane; adjusting the concentration of the amine in said aqueous solution to a level such that the finished cellulosic dielectric material has a nitrogen content of between 0.2 and 1.0% by weight; removing the pulp from said bath; extracting the excess solution from said pulp; forming said pulp into a paper, and drying said paper.

7. The method of producing a thermally upgraded cellulosic dielectric paper for electrical transformers of the type operated within a petroleum oil environment comprising the steps of immersing the paper into a bath of an aqueous solution of an aliphatic amine having at least one amino functional group and at least one hydroxy functional group; the concentration of the amine in said bath being adjusted to a level such that the finished cellulosic dielectric paper has a nitrogen content of between 0.2 to 1.0% nitrogen by weight; removing the paper from said bath and drying said paper.

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