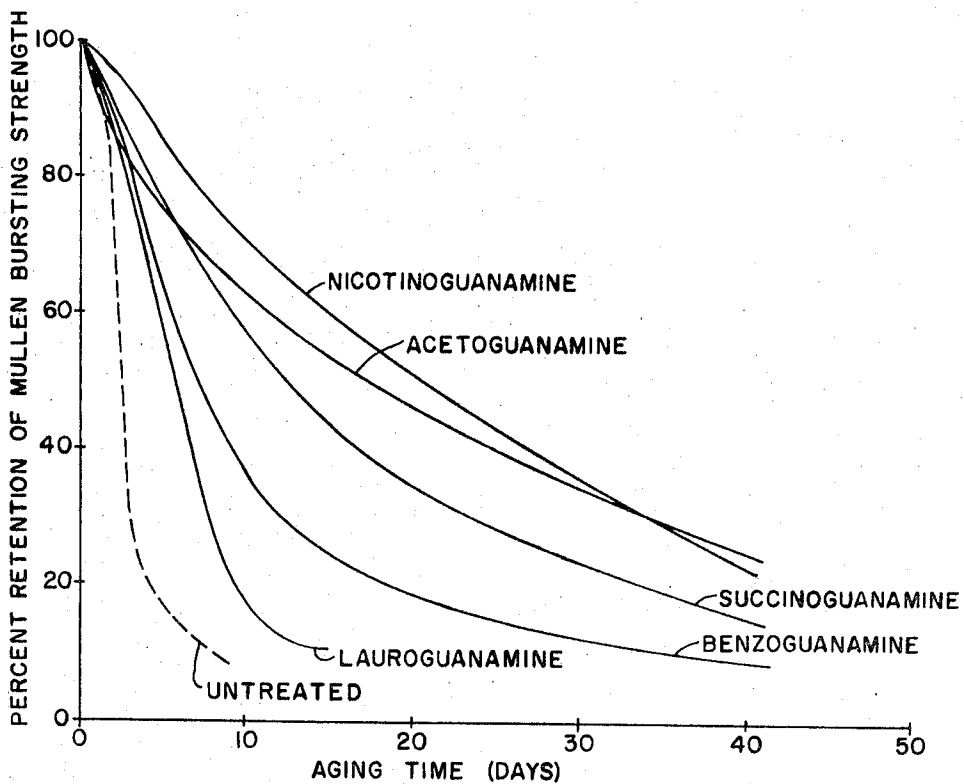


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THERMALLY STABILIZED CELLULOSE IN ELECTRICAL
APPARATUS AND METHOD FOR MAKING SAME
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3,469,219



AGING OF S-TRIAZINE TREATED KRAFT PAPER UNDER
TRANSFORMER OIL AT 150°C. WITH LIMITED ENTRY OF AIR.

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THERMALLY STABILIZED CELLULOSE IN ELECTRICAL APPARATUS AND METHOD FOR MAKING SAME

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5 Claims

ABSTRACT OF THE DISCLOSURE

A cellulosic insulating material such as kraft paper which is pretreated with an organic solution containing from about 0.1% to 10% by weight of a derivative of 2,4-diamino-s-triazine, whereby the material has improved thermal stability and is suitable for use at temperatures up to 150° C. when submerged in transformer oil.

This invention relates to thermal stabilization of cellulosic insulation and more particularly it pertains to the stabilization of cellulosic fibers as insulating material in electrical equipment.

The thermal stability of the electrical insulation in electrical equipment is a limiting factor in its design. In many instances the electrical insulation consists wholly or partially of cellulosic materials such as paper, paperboard, cotton, linen, and wood. The design temperature limit for cellulose insulation materials is about 105° C. When higher operating temperatures are desired, the practice at present is to employ other insulating materials which possess higher thermal stabilities but which are also more expensive than cellulose.

Although cellulosic materials deteriorate relatively rapidly at temperatures in excess of 100° C. when in contact with air, they deteriorate at a greater rate at such elevated temperatures when the materials are in contact with liquid dielectrics such as transformer oil that may be oxidized. It is for that reason that electrical apparatus employing cellulosic insulation generally is not operated continually at temperatures above 105° C.

A factor involved in determining the maximum temperature at which electrical apparatus may be operated safely is the ability of the cellulosic insulation to retain appreciable mechanical and electrical strength after being operated at such maximum temperatures. That limitation applies to cellulosic insulation in contact with or immersed in liquid dielectric as well as cellulosic insulation in contact with air.

Patent No. 2,722,561 discloses that the addition of a nonacidic compound such as about 3% of urea to oil based upon the total weight of the oil, provides the paper with improved thermal life; that is, a paper having about the same life at 125° C. as it would have at 100° C. without the urea stabilizer being added. The life of the paper is measured in terms of retention of tensile strength and crease resistance.

In accordance with the present invention, it has been found that the thermal stability of electrical insulating paper may be greatly enhanced by pretreatment of the paper with or by addition during the manufacture of the paper, an organic chemical compound of the group known as 2,4-diamino-s-triazine compounds, to provide from 0.1% to 10% by weight of at least one compound in the paper which treatment renders the paper more resistant to deterioration at higher temperatures. It has been found that one or more of the s-triazine compounds can be impregnated into the cellulosic material either during manufacture in the paper mill or in the finished paper.

Accordingly, it is a general object of this invention to provide a cellulosic insulating material for use in electrical equipment which material has improved thermal stability at elevated operating temperatures.

It is another object of this invention to provide kraft paper as an electrical insulation material which possesses higher thermal stabilities when in contact with or immersed in liquid dielectric used in electrical apparatus.

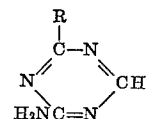
It is another object of this invention to increase the life of paper as an insulation material more than three-fold over the life of untreated paper.

Finally, it is an object of this invention to accomplish the foregoing objects and desiderata in a simple and effective manner.

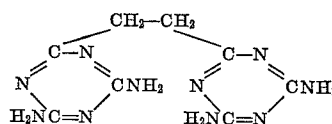
Briefly, the present invention provides an electrical apparatus comprising in combination an electrical winding developing heat during use of the apparatus, cellulosic insulation being present in the apparatus in contact with the winding and subject to loss of physical strength with the passage of time at the temperatures developed, a liquid dielectric consisting essentially of petroleum oil applied to the winding and in contact with the cellulosic insulation to dissipate the heat developed therein, and the cellulosic insulation being permeated with a derivative of 2,4-diamino-s-triazine with different substituents in the 6-position.

For a better understanding of the nature and objects of this invention reference is made to the drawing which is a chart illustrating the progressive loss of bursting strength during the aging process wherein percent retention of initial Mullen bursting strength is plotted against time in days.

In accordance with the present invention the thermal stability of electrical insulation consisting wholly or partially of cellulosic materials such as paper, paperboard, cotton, linen, and wood may be improved by treating the material with organic chemical compounds known as s-triazines. With such treatment the "life" of the material may be increased more than threefold over the "life" of untreated material subjected to the same operating conditions. For that purpose a cellulosic material such as kraft paper is impregnated such as by immersion in a solution containing at least one derivative of 2,4-diamino-s-triazine with different substituents in the 6-position. Such substituted derivatives of 2,4-diamino-s-triazine are commonly called guanamines. The general formula for such guanamines is:



where R is a monovalent nonacidic organic radical such as alkyl and monocyclic radicals having from 1 to about 11 carbon atoms, examples being C₁₁H₂₃ in lauroguanamine, —CH₃ in acetoguanamine, —C₆H₅ in benzoguanamine, a heterocyclic radical such as —C₅H₄N in nicotoguanamine, and —CH₂— in an ethylene linked group in succinoguanamine. The last named derivative is believed to contain two s-triazine rings because it is made by a reaction involving succinonitrile which furnishes difunctionality and the general formula for succinoguanamine is:



The various s-triazine solutions are used to impregnate electrical grade kraft paper such as by dipping in the solution or spraying the solution on the paper. The sol-

vents used in making the solutions are generally different according to the particular s-triazine being used. The choice of solvent is determined by its ability to dissolve a sufficient amount of the s-triazine so that when the paper is treated and later dried, it will contain at least 0.1% and preferably from 0.5% to 10% of the guanamine derivative based on the dry weight of the paper. The preferred s-triazine content of the dry, treated paper is about 4% by weight. Obviously, the dipping or spraying treatment can be repeated several times if necessary to build up the s-triazine content to the extent desired.

The following solvents have been found to be useful in making up lauroguanamine solutions: acetone, methanol, methyl ethyl ketone, and denatured ethyl alcohol. Lauroguanamine dissolves in acetone to the extent of about 1.3% by weight; in methanol, about 2% by weight; in methyl ethyl ketone, about 2.3% by weight; and in denatured ethyl alcohol, about 8.2% by weight. Denatured ethyl alcohol because of its higher solvent power for lauroguanamine is the preferred solvent for this s-triazine when used to impregnate the electrical grade kraft paper. Kraft paper dipped into an 8% solution of lauroguanamine in denatured ethyl alcohol and later dried were found to have increased 4.3% in weight (dry basis), presumably as a result of the added weight of the benzoguanamine.

Acetoguanamine was found to be poorly soluble in methanol, methyl ethyl ketone, denatured ethyl alcohol, dimethyl formamide, and cold water. However, it was readily soluble in hot water and in a hot solvent mixture consisting of 50 parts by volume of denatured ethyl alcohol and 50 parts by volume of distilled water. The last named solvent mixture retained about 5% acetoguanamine in solution based on the weight of the solution on cooling to room temperature. The preferred composition

insoluble in this solvent at room temperature. It was also found to be soluble in dimethylformamide to at least 5% by weight at room temperature and was not tested for solubility in greater percentages. A satisfactory improvement in the thermal stability of the kraft paper was obtained when the paper was impregnated with nicotinoguanamine by dipping in a 5 parts by weight solution of the compound in 95 parts of dimethylformamide.

Succinoguanamine was found to be relatively insoluble in hot or cold methanol and in hot or cold methyl ethyl ketone. It was readily soluble in hot water and slightly soluble in cold water and cold denatured ethyl alcohol. Dimethylformamide was able to dissolve at least 5% by weight of succinoguanamine at room temperature and was not tested for its ability to dissolve higher percentages. As with the previously mentioned nicotinoguanamine, a satisfactory improvement in the thermal stability of the kraft paper was found when the paper was impregnated with succinoguanamine by dipping the paper in a solution containing 5 parts by weight of the compound in 95 parts of formamide.

For each solution the treated paper samples were first dried in room air after which any final traces of solvent were removed by heating the samples in a forced air oven for three hours at about 125° C.

After cooling to room temperature the impregnated paper was subjected to a temperature of about 150° C. for the purpose of age testing in transformer oil for various lengths of time up to 42 days. For each time, certain of the specimens were removed and tested for Mullen bursting strength in accordance with a procedure prescribed by the ASTM. The results of aging tests performed on treated and untreated paper samples are shown for the various solutions used in the following table.

TABLE

[Effect of s-triazine impregnation on aging of Kraft paper under oil at 150° C. with limited admission of air]

	Ave. Mullen bursting strength, p.s.i.						
	Initial	Aged 1 day	Aged 4 days	Aged 7 days	Aged 14 days	Aged 28 days	Aged 42 days
Untreated paper.....	63.3	58.7	12.9	7.8	(E)		
Treatment in—						(E)	
Lauroguanamine.....	62.5	59.3	44.5	24.8	7.0		
Acetoguanamine.....	74.8	68.4	58.5	53.0	41.0	28.8	17.0
Benzoguanamine.....	61.0	59.3	49.5	32.8	15.0	9.0	5.5
Nicotinoguanamine.....	61.1	56.2	60.0	49.0	38.0	23.6	13.0
Succinoguanamine.....	63.5	60.8	64.9	49.0	30.0	16.2	9.0

(E)—Test discontinued, paper too weak to test further.

NOTE.—About 4% of the guanamine was present in the treated paper.

tion of the acetoguanamine is thus about 5 parts by weight of acetoguanamine dissolved in 95 parts by weight of a solvent mixture consisting of 50 parts by volume of denatured ethyl alcohol and 50 parts by volume of distilled water.

Benzoguanamine was found to be relatively insoluble in acetone, benzene, cyclohexanone, denatured ethyl alcohol, methanol, and methyl ethyl ketone. However, when dimethyl formamide was added to the methyl ethyl ketone in the proportions of one part by weight of dimethyl formamide to two parts by weight of methyl ethyl ketone, the resulting solvent mixture dissolved benzoguanamine to the extent of about 8.1% based on the weight of the solution. Kraft papers dipped into the foregoing solution and later dried were found to have increased 6.9% in weight based on the weight of the dry papers before treatment. The preferred composition of the benzoguanamine solution for impregnating the paper with 4% of the compound in the dipping process is thus about 5 parts by weight of benzoguanamine dissolved in 95 parts of a solvent mixture containing about 31.7 parts by weight dimethylformamide and about 63.3 parts by weight methyl ethyl ketone.

Nicotinoguanamine was found to be relatively insoluble in hot or cold methanol, hot or cold methyl ethyl ketone, and hot or cold water. It was soluble to about 2% by weight in hot denatured ethyl alcohol but was apparently

The results of the table are shown graphically in the drawing in which the percent retention of the initial Mullen bursting strength in psi is plotted against the aging time in days. A comparison of the aging test data in the foregoing table shows the prolongation of life of kraft paper resulting from incorporating the derivatives of 2,4-diamino-s-triazine with different substituents in the 6-position. Untreated kraft paper was too weak to test after 9 days. With the exception of the lauroguanamine, the s-triazine derivatives extended the "end point" to 42 days or longer. The least effective of the derivatives is the lauroguanamine treatment which extended the life of kraft paper to only 15 days.

The following examples are illustrative of the present invention.

EXAMPLE I

Fifty squares of electrical grade kraft paper, each square being four inches by four inches in area and 0.005 inch thick, were first dried for 3 hours in a circulating air oven at 120° C. A solution of about 8 parts by weight of lauroguanamine in about 92 parts by weight of denatured alcohol, U.S. Formula SD #1, was prepared at room temperature. After cooling the paper squares were dipped into the solution one at a time. The time of immersion was long enough to wet each paper square completely. After removal from the solution the squares

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were hung in room air to dry. When dried to touch the squares were then returned to the oven at about 120° C. for an additional 3 hours to remove all traces of the denatured alcohol solvent.

After cooling to room temperature the dried paper squares were placed in a one-liter beaker containing 850 milliliters of uninhibited transformer oil. Thirty minutes later two paper squares were removed and after blotting off excess oil they were tested for bursting strength according to ASTM D-774, otherwise known as "Mullen bursting strength" test. The average of the two values thus obtained was designated as the initial or unaged bursting strength. The beaker with its contents was placed in a sealable can with a petcock in the cover which could be opened to release any built-up gas pressure and also allow limited access of air. The can with the petcock open was placed in a recirculating air oven at a temperature of about 150° C. and after the can and its contents reached oven temperature the petcock was closed. The can was allowed to remain in the oven for 22 hours. The petcock was then opened to allow entry of air and the can was removed from the oven and allowed to stand at room temperature for 2 hours. Two paper squares were then removed and tested for the Mullen bursting strength to obtain an average value of 1 day aging. Thereafter the cycle of 22 hours in the oven and 2 hours in room air was repeated daily until the paper square were too weak and/or too brittle to give meaningful values.

EXAMPLE II

In the foregoing example, similar squares of electrical grade kraft paper were treated with each of the other above indicated solutions; namely, acetoguanamine, benzoguanamine, nicotinoguanamine, and succinoguanamine. The Mullen bursting strength results are those recorded in the table.

The degradation of untreated kraft paper is presumably caused by the formation of acid products and is especially deteriorated by acids formed by the oxidation of oil. In the oil test described above the oil upon heating becomes oxidized. The acid causes the cellulose molecules in the paper to break down and thereby reduces the strength of the paper. The effect of the additives is to retard the attack of the acid on the cellulose molecules. From the results shown in the table, it is apparent that the treated kraft paper has improved thermal stability at elevated temperatures of up to 150° C. when submerged in transformer oil.

The treatment of kraft paper and other cellulose materials in the s-triazine solutions without the use of water results in treated paper products that do not curl, warp or shrink, which disadvantages occur when treated.

Accordingly, the thermal stability of cellulosic insulation material such as kraft paper may be improved by impregnating the paper with an organic solution of 2,4-diamino-s-triazine prior to use. As a result of such treatment the life of the paper is increased more than threefold over the life of untreated paper so that the paper may be subjected to high temperatures including hot transformer oil for extended periods of time.

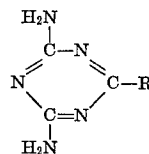
It will be understood that the above specification and drawing are merely exemplary and not in limitation of the invention.

What is claimed is:

1. Electrical apparatus comprising, in combination, an electrical winding developing heat during use of the appa-

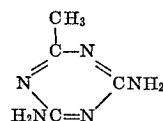
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ratus, cellulosic insulation being present in the apparatus in contact with the winding and subject to loss of physical strength with passage of time at the temperatures developed, a liquid dielectric consisting essentially of petroleum oil applied to the winding and in contact with the cellulosic insulation to dissipate the heat developed therein, and the cellulosic insulation containing from 0.1% to 10% by weight of at least one derivative of 2,4-diamino-s-triazine having the general formula:

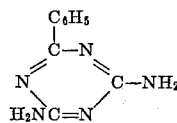


where R is selected from the group consisting of non acidic monovalent alkyl and monocyclic organic radicals having from 1 to about 11 carbon atoms.

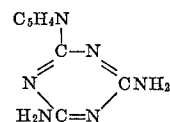
2. The apparatus of claim 1 in which the derivative of s-triazine has the general formula:



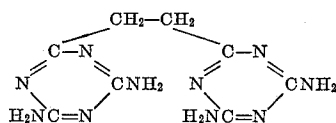
3. The apparatus of claim 1 in which the derivative of s-triazine has the general formula:



4. The apparatus of claim 1 in which the derivative of s-triazine has the general formula:



5. The apparatus of claim 1 in which the derivative of s-triazine has the general formula.



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