United States Patent Office

2,801,672

Patented Aug. 6, 1957

1

2,801,672

RESINOUS COMPOSITIONS AND FIRE-RESISTANT LAMINATES PREPARED THEREFROM

David E. Baldwin, Hampton, S. C., and Robert H. Runk, Pittsburgh, Pa., assignors to Westinghouse Electric Corporation, East Pittsburgh, Pa., a corporation of Pennsylvania

No Drawing. Application July 15, 1954, Serial No. 443,720

9 Claims. (Cl. 154—2.6)

The object of this invention is to prepare novel impregnating resinous varnish compositions to be employed in preparing fire-resistant thermostat laminates therefrom, and the products so produced.

It has been desirable to have available, particularly in the electrical industry, resinous laminates that are highly fire resistant while possessing good electrical resistance properties, both dry and when subjected to humidification, as well as high strength and other physical properties. Resinous laminates of this type in the forms of plates, tubes, channels, angles and other forms are particularly desirable for use in switchgear, switchboards, tap changers and similar electrical apparatus that may be subjected to electrical arcs due to opening of electrical contacts. The art has produced a considerable number of laminates wherein expedients, such as incorporation of fireproofing agents, have been made use of. In most cases, however, these added fireproofing agents, such for example as chlorinated materials, have reduced the strength of the laminates or the electrical resistance properties, and consequently, satisfactory results have not been obtained. Certain fire-resistant resins, such as melamine formaldehyde resins, are not only substantially more expensive than phenolic resins, but when applied to cellulosic fibrous materials, their moisture resistance is poor. The dielectric strength of melamines is not as high as that of other cheaper laminates, and thick sections, that is over one-quarter of an inch, tend to crack badly on aging, particularly at temperatures of 100° C. For example, a melamine formaldehyde laminate 1½ inches thick when heated to 100° C. had cracked badly in one day.

In testing the fire resistance of laminates, we have employed a test that is a slight modification, as advocated by Gale, Stewart and Alfers, in the ASTM Bulletin, page 23, December 1944, of Method 2023.1 of Federal Specification L-P-406b. The test equipment comprises a ventilated box approximately 18 inches square in cross section and about 3 feet high with an opening at the top in which there is disposed a constant speed exhaust fan to withdraw gases from the box. At the bottom of the box is located a four-jawed chuck adapted to hold in a vertical position laminate specimens having dimensions of ½ inch by ½ inch by 5 inches in length. A heating coil composed of nickel-chromium alloy wound on a 1 inch diameter of a length of 2 inches is located with its center about the specimen held in the chuck. Above the top turn of this heating coil are disposed two automobile spark plugs with their ignition electrode tips approximately ¹⁄₁₀ of an inch away from two opposite sides of the laminate sample to be tested.

In testing a sample of the laminate, a rod of the sample machined to dimensions of ½ inch by ½ inch by 5 inches in length is inserted in the chuck, and the heating coil is energized with 55 amperes of electrical current and the spark plugs are energized with electrical current so that an electrical arc plays across the ignition electrodes continuously. The "ignition time" is the

2

elapsed time from the start of energization of the coil and the arcing of the spark plugs until a flame settles upon the sample. Once a flame appears about the sample, the flow of electrical current to the spark plugs is terminated, but the heating coil is energized for 30 seconds longer at which time electrical current to the coil is also turned off and timing is begun from the moment that current to the coil is terminated until the flame extinguishes, this latter time period being designated as the "burning time" of the sample. It will be apparent that both the "ignition time" and "burning time" are factors of considerable value in selecting fire resistant laminates.

The object of this invention is to provide for thermosettable resinous reaction products comprising phenol, dicyandiamide and formaldehyde, which when applied to fibrous sheet material and cured under heat and pressure result in resinous laminates that are highly fire resistant.

A further object of the invention is to provide thermoset laminates comprising a fibrous sheet material and a thermoset reaction product of phenol, dicyandiamide and formaldehyde, which laminate has a high fire resistance, good electrical insulating properties and high physical strength.

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

We have discovered that highly fire-resistant thermoset resinous laminates may be prepared from a resinous product derived by reacting phenol, dicyanidiamide and formaldehyde in the proportions of 1 mole of the phenol, from 0.8 to 2 moles of dicyandiamide and from 0.9 to 1.5 moles of formaldehyde per mole of the phenol and dicyandiamide. Water is present, being usually furnished as a part of aqueous formaldehyde solution (37% to 40%), and amounting to at least 10% of the weight of the reactants, and ordinarily should not exceed the weight of the reactants. The mixture is reacted under alkaline conditions for at least ½ hour, and preferably by refluxing from 1 to 2 hours, and then is vacuum dehydrated at a temperature not exceeding 100° C. until substantially all of the water is removed and then a volatile solvent is applied to produce an impregnating varnish. The varnish may include a small proportion of the order of 2% to 10% by weight of finely divided solids such as silica, aluminum oxide, antimony oxide and the like refractory solids to impart better flame resistance.

The impregnating varnish is applied to fibrous sheet materials and particularly cellulosic fibrous materials, such as kraft paper, alpha paper and cotton cloth. Exceptional flame resistant properties and high strengths are obtained using such cellulosic materials. However, other fibrous materials may be used, such as glass cloth, glass mat, asbestos cloth, nylon cloth and other synthetic resinous fabrics or mixture of two or more fibrous materials, such for example as a cloth woven from the mixture of nylon and cotton. The fibrous sheet material is dipped in the varnish one or more times until it has picked up resin solids in an amount of from 0.7 to 2 times the weight of the dry fibrous material and the varnish impregnated fibrous material is passed through an oven or other dryer after each dip to remove the volatile solvent. During drying, it is desirable to heat the fibrous material treated with the varnish composition at a temperature of from 110° C. to 150° C. in order to remove the solvent therefrom promptly and to advance the cure of the resin well into the "B" stage. The heat treatment of the applied phenol-dicyandiamide-formaldehyde resin at this stage is conducted so that the resulting treated fabric has a "greenness" of from 0.5 to 10%. The greenness is determined by placing a small piece of the resin treated sheet material in a hot press at a temperature of 175° C. and a pressure of 1,000 pounds per square inch for 5 minutes, and then measuring the amount of resin that is forced out of the sample, that is, the resin that extends beyond the fibrous sheet material proper, and determining the proportion of this exuded resin to all of the resin in the sample. A greenness of 10% is relatively high and is desirable for the making of certain products, such as tubes which require a considerable flow of resin between laminations in order that the laminations bond adequately. A greenness of about 0.5% on the other hand is relatively low but is essential for the purpose of making thick flat laminates, for example, ½ inch thickness and greater. For preparing laminates of thicknesses of ⅛ inch, a greenness of from 1% to 3% is adequate.

The sheet fibrous material, with the applied "B" stage phenol-dicyandiamide-formaldehyde resinous reaction product thereon, may be molded into laminates, tubes and other members by superimposing a plurality of layers of the treated sheet material and compressing it at pressures of from 150 to 5,000 pounds per square inch at temperatures of from 135° C. to 165° C. It will be appreciated that the fibrous sheet material may be chopped or macerated, or otherwise treated, and members molded from such comminuted fibrous material. Of course, the highest strength products are secured with laminates made from superimposed layers of the impregnated fibrous sheet material.

In preparing the varnish impregnating composition from the resinous reaction product, we have secured particularly good results by using as a solvent a mixture of ethanol and water wherein the ethanol comprised from 20% to 80% by weight of the mixture. However, acetone may be employed alone or in admixture with the alcohol, or water and alcohol. Other solvents and solvent mixtures may be employed, as desired. We have obtained exceptionally well impregnated cellulosic sheet fibrous material by employing water-alcohol mixtures as the solvent. By employing mixtures containing 50% or more by weight of water, the balance being ethanol, we have secured particularly thorough impregnation of paper and cotton fabrics.

The following examples are illustrative of the practice of the invention.

EXAMPLE I

Into a steam heated reaction kettle there were introduced the following:

	Parts by weight
Phenol	2750
Dicyandiamide	2100
Formaldehyde (37%)	4620
Ammonia (28%)	166

The ammonia and the formaldehyde were admixed before being introduced into the kettle with the remainder of the ingredients, the mixture having a pH of approximately 8.5. The mixture was slowly heated, and at 80° C. an exothermic reaction took place that carried the temperature to approximately 95° C. Additional heat was then supplied in order to cause the reaction mixture to reflux. The mixture was refluxed for 90 minutes and then dehydrated under a vacuum of 28 inches of mercury, and the temperature gradually increased to approximately 75° C. during dehydration. Substantially all the water had been removed. To the hot reaction product there was added 2000 parts by weight of 95% ethanol, and the resulting thick varnish was cooled to room temperature. The resinous reaction product was then further diluted with a mixture comprising 50% by weight of ethanol and 50% by weight of water to produce a solution comprising approximately 53% by weight of resin solids. The viscosity of the composition is approximately 250 centipoises.

The resulting varnish of this Example I was employed to impregnate the following sheet fibrous materials:

(1) 10 mil thick alpha paper, the impregnated paper containing 101% of its weight of the resin solids at a greenness of 0.5%.

(2) 5 mil thick kraft paper, the treated paper containing 98% of its weight of resin solids, the greenness being 0.8%.

(3) 6½ ounce bleached cambric, the resin solids being equal to the weight of the cambric, the greenness being 0.5%.

Laminates were prepared from each of these three impregnated materials by superimposing a sufficient number of laminations to produce consolidated members of various thicknesses of up to ½ inch. The superimposed layers were consolidated at 1,000 pounds per square inch with the temperature of the press platens slowly rising to a final temperature of 165° C. The following table sets forth the ignition time and burning time in seconds of the laminates, and includes a standard XXX-grade phenolic laminate prepared from alpha cellulose paper for comparison purposes.

TABLE I

Fire-resistances of laminates

Laminate	Ignition time, sec.	Burning time, sec.
Alpha paper-based	199	79
Kraft paper-based	245	95
Cambric cloth-based	154	137
XXX Phenolic	145	437

It will be apparent that the first three laminates are considerably superior in ignition time and very much better in burning time to the standard XXX phenolic.

The dielectric properties of the laminates used in Table I were then determined, both in the as-received condition and after humidification and water immersion, and these data are set forth in Table II.

TABLE II

Dielectric properties

Laminate	Test Conditions[1]	100 Tan δ			Dielectric Constant		
		60 cy	1 Kcy	1 Mcy	60 cy	1 Kcy	1 Mcy
Alpha-base	A	1.09	1.44	2.19	4.89	4.78	4.51
	C—96/23/96	4.55	4.12	4.28	6.22	5.86	4.90
	D—24/23	4.60	3.60	3.14	5.67	5.59	5.15
Kraft-base	A	1.18	1.44	2.17	4.79	4.68	4.34
	C—96/23/96	6.47	4.43	4.60	6.48	6.02	4.93
	D—24/23	8.30	4.37	4.26	6.14	5.89	5.15
Cambric-base	A	1.93	1.75	2.57	4.97	4.81	4.49
	C—96/23/96	14.6	6.19	5.23	6.45	5.63	4.64
	D—24/23	17.0	6.53	4.22	6.59	5.65	4.75
XXX Phenolic	A	1.35	1.15	3.31	5.27	5.16	4.67
	D—24/23	14.3	6.7	5.18	6.80	5.80	4.82

[1] Condition "A"—Tested as received.
Condition "C—96/23/96"—After 96 hours at 23° C. and 96% relative humidity.
Condition "D—24/23"—Tested after 24 hours immersion in distilled water at 23° C.

The physical properties of the laminates were also determined, and these data are set forth in Table III.

TABLE III

Mechanical properties (ASTM)

Laminate	Bond Strength, lbs.	Tensile Strength, p. s. i.	Flexural Strength, p. s. i.	Compressive Strength, p. s. i.
Alpha-based	785	14,483	25,613	61,253
Kraft-based	1,200	19,174	33,618	54,577
Cambric-based	1,105	16,684	32,658	51,682
XXX Phenolic	1,042	11,000	13,000	36,000

Laminates made from kraft paper treated with the resin of Example I to a 120% resin content, exhibited tensile strengths of 22,800 p. s. i., flexural strength of 28,050 p. s. i., compressive strength of 51,320 p. s. i., and izod impact of 2.2 ft. lbs. per inch width flatwise (XXX grade phenolic having an izod impact of 1.4 ft. lbs. per inch width flatwise).

EXAMPLE II

The procedure of Example I was employed in reacting the following:

Phenol	pounds	560
Dicyandiamide	do	500
Formaldehyde (37%)	do	1160
Ammonia (28%)	gallons	3

The mixture was dehydrated under a vacuum of 27 inches of mercury and a final temperature of 70° C. The resulting reaction product was then dissolved in a solvent mixture comprising 90 gallons of 95% ethanol and 35 gallons of water. The resulting varnish had a viscosity of approximately 250 centipoises and between 52% and 55% by weight of recoverable resin solids. The set time of the varnish was approximately 16 minutes at 153° C.

In order to prepare laminates for use in electrical insulating applications from phenolic and similar resins, it has been regarded as necessary to employ a purified cotton fabric. Such purified cotton fabric is prepared from what is known in the trade as "grey-goods." The grey goods are treated with solvents and the like to remove naturally present waxes and the like. However, we have employed 3 ounce grey cotton fabric which has not been treated to remove waxes and other naturally present impurities, and impregnated the fabric with the varnish composition of this Example II to provide thereon an amount of resin solids equal to the weight of the cotton fabric. The greenness of the fabric varied from 1 to 3% for different batches thereof. Laminates of a thickness of 1/16 inch and 1/8 inch were molded from this treated cotton fabric employing, however, a top sheet of the same cotton fabric containing the resin in an amount equal to 150% of the weight of the fabric. Such laminates were consolidated in a hot press at 1,500 pounds per square inch at 155° C., and were tested for their electrical properties. The water absorption of the 1/16 inch laminate after immersion in water for 24 hours at 25° C. was 1.05%, while the 1/8 inch laminate absorbed only 0.677%. Bleached cotton fabric made into similar laminates absorbed 75% more water than did the grey-goods base laminate of this example. The dielectric strength of the grey goods laminates was 522 volts per mil thickness for the 1/16 inch laminate and 372 volts per mil thickness for the 1/8 inch laminate. These dielectric strength values are excellent and equal to those of the best phenolic laminates available in the trade.

It will be understood that the resinous compositions of this invention may be prepared by substituting cresol for a part or all of the phenol. Furthermore, the phenol, dicyandiamide and formaldehyde may be reacted with other alkali catalysts than ammonia, and in some cases, we have found that the reaction will occur without the extraneous addition of any catalysts whatever. Suitable alkali catalysts are sodium hydroxide, sodium carbonate, disodium phosphate, calcium oxide and barium oxide. The catalysts may be employed in an amount of up to 5% based on the weight of the phenol.

The laminates of this invention have been applied with considerable success to circuit interrupters. Thus, arc barriers, splitters, channels and tubes and insulating supports for conductors, as well as the covers, bases and other structural parts not necessarily subject to full voltage of the conductors, have been prepared from the laminates of this invention. The laminates withstood arcs between contacts of such circuit interrupters with no burning, or in exceptional cases, any flames extinguished themselves promptly on termination of the arc. Fuse tubes and other fuse elements may be advantageously made from the laminates. Switchboards and cubicles containing electrical members subject to considerable heating from red hot resistors and other over-heated conductors and occasional arcing, may be fabricated from the laminates of this invention to advantage. It will be apparent that we have produced laminated members that can be used to great advantage with successful flame retardation in the vicinity of hot electrical conductors and arcing members. Jackets for bus bars are other insulating applications for the insulating members of this invention. It will be appreciated that the resinous members may be employed for non-electrical uses, especially near flames or hot objects.

It will be understood that the above examples and description are illustrative and not in limitation of the invention.

We claim as our invention:

1. In the process of preparing fire-resistant thermoset resinous laminates, the steps comprising impregnating a sheet fibrous material with a solution of a thermosettable resinous product derived by reacting only one mole of a phenol, from 0.8 to 2.0 moles of dicyandiamide, and from 0.9 to 1.5 moles of formaldehyde per mole of the phenol and dicyandiamide in the presence of water and an alkali catalyst in an mount of up to 5% of the weight of the phenol, the mixture being refluxed for a least 1/2 hour and then vacuum dehydrated at a temperature not exceeding 100° C., the resulting reaction product being dissolved in a volatile solvent to provide the said impregnating solution, the resin impregnated sheet fibrous material being heated to drive off the solvent and to advance the cure of the resin to a condition where its greenness is less than 5%, the fibrous sheet carrying from 0.7 to 2 times its weight of the resin after drying, superimposing a plurality of layers of the resin treated fibrous sheet and molding the superimposed layers at a pressure of from 500 to 5,000 pounds per square inch at temperatures of from 135° C. to 165° C. to fully cure the applied resin and to produce a thermoset laminate.

2. The process of claim 1, wherein the resious product is derived from the mixture by including an alkaline catalyst.

3. The process of claim 1, wherein the volatile solvent comprises a mixture of ethanol and water in the proportions of from 20% to 80% by weight of ethanol.

4. The process of claim 1 wherein the sheet fibrous material comprises cellulose and the volatile solvent in a mixture of water and ethanol in the proportions of from 20% to 80% by weight of ethanol.

5. An impregnating varnish comprising in combination (*a*) from 30% to 60% by weight of a thermosettable resinous product derived by reacting only one mole of a phenol, from 0.8 to 2.0 moles of dicyandiamide, and from 0.9 to 1.5 moles of formaldehyde per mole of the phenol and dicyandiamide in the presence of water and an alkali catalyst in an amount of up to 5% of the weight of the phenol, the mixture being refluxed for at least 1/2 hour, and then vacuum dehydrated at a temperature not exceeding 100° C., and (*b*) from 70% to 40% by weight of a volatile solvent comprising a mixture of ethanol and water, the ethanol comprising from 20% to 80% by weight of the volatile solvent.

6. A fire-resistant thermoset laminate comprising a plurality of layers of sheet fibrous material and a thermoset resin impregnating each of the layers, the thermoset resin also uniting the layers, the thermoset resin comprising from 0.7 to 2 times the weight of the sheet fibrous material, the thermoset resin comprising the cured resinous product derived by reacting only one mole of a phenol, from 0.8 to 2.0 moles of dicyandiamide, and from 0.9 to 1.5 moles of formaldehyde per mole of the phenol and dicyandiamide in the presence of water and an alkali catalyst in an amount of up to 5% of the weight of the phenol, the mixture being refluxed for at least 1/2 hour, and then vacuum dehydrated at a temperature not exceeding 100° C.

7. A fire-resistant thermoset laminate comprising a

plurality of layers of cotton fabric and a thermoset resin uniting the layers, the thermoset resin comprising from 0.7 to 2 times the weight of the sheet fibrous material, the thermoset resin comprising the cured resinous product derived by reacting only one mole of a phenol, from 0.8 to 2.0 moles of dicyandiamide, and from 0.9 to 1.5 moles of formaldehyde per mole of the phenol and dicyandiamide in the presence of water and an alkali catalyst in an amount of up to 5% of the weight of the phenol, the mixture being refluxed for at least ½ hour, and then vacuum dehydrated at a temperature not exceeding 100° C., the resulting resinous reaction product being dissolved in a mixture of water and ethanol, the solution being applied to the cotton fabric and dried to evaporate the solvent and to advance the reaction product to the B stage.

8. In a circuit interrupter having an electrical conductor wherein arcing develops during operation of the circuit interrupter and subject to high temperatures, an insulating member comprising a fire-resistant thermoset laminate comprising a plurality of layers of sheet fibrous material and a thermoset resin uniting the layers, the thermoset resin uniting the layers, the thermoset resin comprising from 0.7 to 2 times the weight of the sheet fibrous material, the thermoset resin comprising the cured resinous product derived by reacting only one mole of a phenol, from 0.8 to 2.0 moles of dicyandiamide, and from 0.9 to 1.5 moles of formaldehyde per mole of the phenol and dicyandiamide in the presence of water and an alkali catalyst in an mount of up to 5% of the weight of the phenol, the mixture being refluxed for a least ½

hour, and then vacuum dehydrated at a temperature not exceeding 100° C., said member having a high resistance to ignition and rapid extinguishing of any flames.

9. In an electrical member having an electrical conductor subject to the development of high temperatures during operation, an insulating member comprising a fire-resistant themoset laminate comprising a plurality of layers of sheet fibrous material and a thermoset resin uniting the layers, the thermoset resin uniting the layers, the thermoset resin comprising from 0.7 to 2 times the weight of the sheet fibrous material, the thermoset resin comprising the cured resinous product derived by reacting only one mole of a phenol, from 0.8 to 2.0 moles of dicyandiamide, and from 0.9 to 1.5 moles of formaldehyde per mole of the phenol and dicyandiamide in the presence of water and an alkali catalyst in an amount of up to 5% of the weight of the phenol, the mixture being refluxed for at least ½ hour, and then vacuum dehydrated at a temperature not exceeding 100° C., said insulating member having a high resistance to ignition due to the high temperatures and being rapidly self-extinguishing.

References Cited in the file of this patent

UNITED STATES PATENTS

1,938,917	Loetscher	Dec. 12, 1933
2,314,701	Harvey	Mar. 23, 1943
2,315,400	D'Alelio	Mar. 30, 1943
2,328,825	McMahon	Sept. 7, 1943
2,606,885	Schmutzler	Aug. 12, 1952
2,660,215	Arone	Nov. 24, 1953