

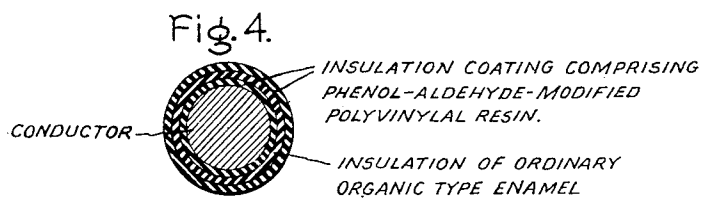
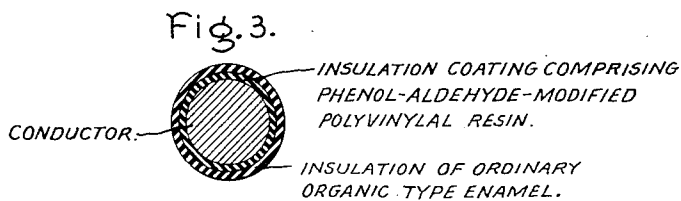
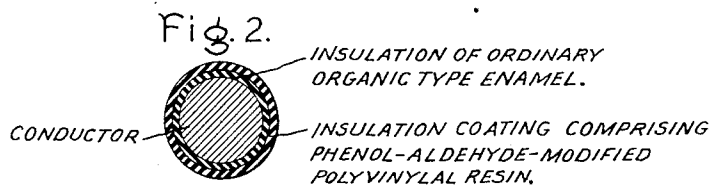
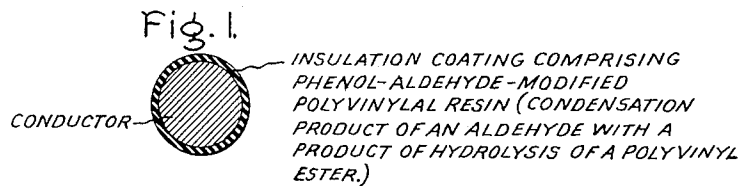
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2,307,588

INSULATED ELECTRICAL CONDUCTOR

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UNITED STATES PATENT OFFICE

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INSULATED ELECTRICAL CONDUCTOR

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3 Claims. (Cl. 174-125)

This invention relates to insulated electrical conductors and more particularly is concerned with the manufacture of insulated electrical conductors having insulation of the organic enamel type thereon.

As pointed out in Patnode and Flynn Patent No. 2,085,995, which is assigned to the same assignee as the present invention, insulated conductors wherein the insulation is a resinous composition produced by condensing an aldehyde with a product of hydrolysis of a polyvinyl ester have distinct advantages over conductors insulated with conventional oil-type enamels. However, such resinous compositions are as yet relatively expensive. Further, comparatively high-priced solvents are required to form suitable wire enamels therefrom. As a result conductors insulated with the above resin have been limited in their application.

We have discovered a resinous composition which is soluble in relatively inexpensive solvents or solvent mixtures and from which can be made insulated wires having properties practically the same, and in certain respects even better, than wires produced as described in the above Patnode et al. patent, and at a substantially lower cost than heretofore has been possible.

In accordance with our invention metallic conductors are insulated with a composition produced by suitably combining a resinous condensation product of an aldehyde and a partially or completely hydrolyzed polymerized vinyl ester with a suitable phenol-aldehyde resin which is compatible therewith, as will be described more fully hereafter. The insulation on the conductor is hard, tough, flexible, remarkably abrasion- and moisture-resistant and resistant to attack by such agencies as oil, varnish, and the like. It also has a high dielectric strength and a low power factor.

The novel features of our invention are set forth in the appended claims. The invention itself, however, will be understood most readily from the following description when considered in connection with the accompanying drawing in which

Fig. 1 is a cross-sectional view of an electrical conductor provided with insulation in accordance with our invention;

Fig. 2 is also a cross-sectional view showing the conductor provided with a coating of insulation of ordinary organic type enamel and a superimposed coating of the new insulating material hereinafter described;

Fig. 3 is another cross-sectional view illustrat-

ing a further modification of the invention; and Fig. 4 is also a cross-sectional view showing a still further modification of the invention.

The resinous hydrolyzed polymerized vinyl ester-aldehyde condensation products referred to above are described, generally, in Reissue Patent No. 20,430, Morrison et al., and, as pointed out in said patent, may be produced from various aldehydes and various polyvinyl esters. In the following description of the invention and in the appended claims, this class of resins is designated, generally, as "polyvinylal resins." A polyvinylal resin may be prepared, for instance, as follows:

One hundred parts of a polymerized vinyl acetate is dissolved in 185 parts of glacial acetic acid. To this is added 83 parts of an aqueous solution of formaldehyde, containing 37½ per cent of formaldehyde, and a suitable amount of mineral acid, for example 6.8 parts of concentrated sulfuric acid. All proportions herein given are by weight. Hydrolysis is carried out at about 70° C. in an enameled vessel. Samples of the reaction mixture are removed at suitable intervals of time and analyzed for their formaldehyde content. The results of analyses indicate the extent to which the polyvinyl ester has been converted into polyvinyl formal. When the desired degree of conversion has been effected, a suitable amount of a neutralizing agent, for example 13 parts of concentrated ammonia, is added to the reaction vessel. The neutralized mass is poured as a thin stream into water, whereupon the reaction product is precipitated in the form of threads. The thread-like material is washed with water and dried in a current of warm (60° C.) air. The dried threads are white, or nearly so.

Aldehydes other than formaldehyde may be used in making polyvinylal resins, for example, acetaldehyde, propionic aldehyde, butyric aldehyde, benzaldehyde and the like. Likewise polyvinyl esters other than polyvinyl acetate may be employed, for instance polyvinyl propionate, polyvinyl butyrate and the like. The properties of polyvinylal resins may be varied through a wide range by varying the viscosity and the extent of the hydrolysis of the polyvinyl ester, the amount and the character of the aldehyde reacted with the hydrolyzed polymerized vinyl ester, and the character and the amount of the acid catalyst used.

In order that those skilled in the art better may understand how this invention may be carried into effect, the following illustrative examples of the preparation of the phenolic modifying resin are given, together with a more complete

description of how such resin preferably is incorporated with polyvinylal resins in making the new resinous compositions and wire enamels:

EXAMPLE 1

PREPARATION OF MODIFYING RESIN

	Parts by weight
Cresol	750
Aqueous solution of formaldehyde (approximately 37.2% HCHO)	448.4
Triethanolamine (commercial grade)	23.9

The cresol preferably is meta-para cresol, water white, and containing approximately 50 to 55 per cent meta-cresol, the remainder para-cresol and xlenols. It will be noted that in the foregoing formula the cresol and formaldehyde are in the ratio of 1 mole cresol to approximately 0.8 mole dry formaldehyde.

The materials are charged into a suitable reaction vessel or kettle provided with a reflux condenser, and are stirred and reacted at atmospheric pressure at the boiling point (approximately 94° to 98° C.). The reaction is allowed to proceed until incipient precipitation of the resin occurs as indicated by the cloudiness of the solution. Ordinarily this point will be reached in about 2 hours. The mass is cooled to about 30° C., after which it is dehydrated, preferably under reduced pressure with the external application of heat. The maximum temperature attained during dehydration is not permitted to exceed substantially 80° C. After dehydrating, a clear, amber, very viscous liquid (at 80° C.) results. It is semi-solid at room temperature.

A sample (15 grams) of a resin prepared as above described was heated in a 30 cc. crucible for 2 hours at 105° C. At the end of this time the mass was a stiff gel when hot. When similarly heated for a total of 8 hours, the resin sample cured to an amber, transparent, tough, substantially infusible mass which was hard even when hot.

The dehydrated resin is dissolved or dispersed in a suitable volatile solvent. Preferably cresol is added to the hot (80° C.) liquid resin in the reaction vessel in an amount such that the resulting solution contains approximately 50 per cent cresol-formaldehyde resin and 50 per cent cresol as solvent. It is convenient to use as solvent meta-para-cresol such as is employed in the manufacture of the resin. The mixture is well stirred, cooled to room temperature and removed from the reaction vessel for subsequent use in making wire enamels.

PREPARATION OF WIRE ENAMEL

Materials

Polyvinylal resin produced by reacting formaldehyde with a product of hydrolysis of polyvinyl acetate, specifically a polyvinylal resin known in the trade as "Formvar No. 15-95."

Cresol solution of cresol-formaldehyde resin made as described above.

Solvents.—Meta-para-cresol such as used for dissolving the cresol-formaldehyde resin, and solvent naphtha such, for example, as a crude coal-tar naphtha designated in the trade as "No. 100 heavy naphtha" and commonly known as "wire enamel naphtha." Such naphtha usually has a distillation range of 155° to 290° C., with 75 to 85 per cent distilling off at 200° C.

Formula

Resins, 16% composed of:

Per cent
by weight

5	Cresol-formaldehyde resin	5.33
	Polyvinylal resin	10.67
	Solvents, 84% composed of:	
	Cresol ¹	25.20
	Naphtha	58.80

¹NOTE.—A part of this cresol is added to the dehydrated resin in the reaction vessel.

The proper amounts of naphtha and cresol are weighed into a mixing tank and agitated, the 50—50 cresol solution of cresol-formaldehyde resin is added, and the whole is well mixed. The solid polyvinylal resin is added slowly, and the mixture stirred until the polyvinylal resin is completely dissolved. The resulting enamel is clear and viscous. It may be dyed, if desired, by adding a small amount of a suitable dye and stirring until the dye is dissolved. Preferably the enamel is filtered through a pressure filter prior to use for enameling wire.

The following examples are illustrative of other formulas for preparing the modifying resin:

EXAMPLE 2

Same formula and general procedure as described under Example 1, with the exception that in lieu of triethanolamine 23.9 parts by weight of morpholine is used as catalyst. The dehydrated resinous mass is a clear, amber, viscous liquid.

A sample (15 grams) of a resin so prepared was heated in a 30 cc. crucible for 9 hours at 105° C. The resulting mass was a stiff gel when hot. When similarly heated for a total of 100 hours, the resin cured to a transparent, amber-colored, infusible somewhat brittle resin.

A wire enamel is made of the dehydrated resin in essentially the same manner as described under Example 1.

EXAMPLE 3

	Parts by weight
Phenol	750
Aqueous solution of formaldehyde (approximately 37.2% HCHO)	643.3
Triethanolamine (commercial grade)	25.8

Essentially the same process is followed in making the resin as described under Example 1. The dehydrated resin is a clear, amber solid.

A sample (15 grams) of a resin so prepared was heated in a 30 cc. crucible for 1¾ hours at 105° C. The resulting mass was a stiff gel when hot. When similarly heated for a total of 7 hours the resin cured to a hard, tough, substantially infusible mass which was amber-colored and transparent.

A wire enamel is made of the dehydrated resin in essentially the same manner as described under Example 1.

It is to be noted that in the formula of this example the phenol and formaldehyde are reacted in approximately equimolecular proportions.

The properties of the modifying resin, and therefore the properties of the phenol-aldehyde-polyvinylal resinous composition, may be varied by varying the ratios of the phenolic body and the aldehyde. This is shown in the following table wherein is set forth the properties of res-

inous condensation products obtained by reacting different mole ratios of meta-para-cresol and an aqueous solution of formaldehyde, using the same percentage of triethanolamine (2.54%) and essentially the same procedure as described under Example 1.

per cent, the other 80 to 60 per cent being either benzene or toluene. A more specific example is 25 per cent ethyl alcohol and 75 per cent toluene. With the above alcohols, xylene or any of the higher boiling aromatic hydrocarbons cannot be substituted for the benzene or toluene in the

Table

Meta-para cresol	HCHO	Appearance of dehydrated resin	Time sample (15 g. in 30 cc. crucible) was heated at 105° C.		Appearance of hard (cured) in- fusible, insoluble resin
			To form a stiff gel (hot)	To form a hard resin (hot)	
<i>Mole</i> 1	<i>Mole</i> 2	Clear, amber solid.	<i>Hours</i> ¼	<i>Hours</i> 2	Amber, transpar- ent, tough. Do. Do. Do.
1	1	Clear, amber semi- solid.	1¼	4½	
1	0.9	-----do-----	1½	5½	
1	0.7	Clear, amber vis- cous.	3¼	16	
1	0.6	-----do-----	6¼	Did not harden beyond a very stiff gel even after two weeks' heating.	
1	0.5	-----do-----	Surface formed a very tough skin after a short time but the resin itself never hardened beyond a viscous solution (hot) even after two weeks' heating.		

As shown in the table, resins containing 0.7 or more moles formaldehyde will convert to a substantially infusible, insoluble state when heated at elevated temperatures, whereas those containing 0.5 or 0.6 mole formaldehyde are thermoplastic. While for certain applications such thermoplastic resins may be used as modifying agents of the polyvinylal resins, in general we prefer to use in the preparation of wire enamels those phenolic resins which are produced by reacting 1 mole phenolic body with from 0.7 to 2.0 moles of an active methylene-containing body such as formaldehyde or other suitable aldehyde. No particular advantage is gained by using more than 2 moles formaldehyde to 1 mole of the phenolic body, since the excess formaldehyde is volatilized during the cooking of the resin.

Enameled wires are produced by drawing the clean wire, for example clean copper wire, through a bath of wire enamel made by incorporating the modifying phenolic resin with a polyvinylal resin and solvent as more particularly set forth under Example 1. The proportions of phenolic and polyvinylal resins may be varied, for example from, by weight, about 5 to 50 parts phenolic resin to from about 95 to 50 parts polyvinylal resin. The total resin to solvent proportions also may be varied, for instance, from about 5 to 25 parts resin to about 95 to 75 parts solvent. We prefer to use a phenolic resin-polyvinylal resin ratio and a total resin-solvent ratio such as described under Example 1, since the particular combination of ingredients there described has been found to produce a wire enamel which is most readily and effectively applied to wire, and to yield an insulated wire having the most desirable combination of properties.

The solvent may be a mixture of a suitable hydrocarbon, such as benzene or toluene, and an hydroxy compound compatible therewith, for example a compatible aromatic alcohol such as benzyl alcohol or a compatible monatomic saturated alcohol as, for example, methyl, ethyl, n-propyl, n-butyl, n-amyl, hexyl (2-ethylbutanol), octyl (2-ethylhexanol), etc. Or, the solvent may comprise an aromatic or other suitable hydrocarbon and a mixture of two or more alcohols or other hydroxy compounds compatible with the hydrocarbon used. The percentage by weight of alcohol in the solvent mixture may vary, for instance, from approximately 20 to 40

solvent mixture. However, when the hydroxy compound is a phenolic body such as cresol, xyenols, etc., then benzene, toluene, xylene, or any of the high flash or other solvent naphthas commonly used in making wire enamels may be used. As a more specific example, we mention as being suitable a solvent mixture formed of 30 per cent by weight of meta-para-cresol and 70 per cent by weight of crude, heavy solvent naphtha such as described more fully under Example 1.

Having passed the wire through a bath of wire enamel made as above described, the coated wire is subjected to heat, for instance by introducing it into a suitable oven or chamber wherein the enamel coating is baked at a suitable temperature, for example at an oven temperature of about 250° to 500° C. The coating is baked simultaneously with the annealing of the copper. Usually it is necessary to run the wire successively through the enamel bath and baking oven several times in order to provide adequate insulation thereon. Baking advances the phenol-aldehyde component of the mixed or combined resin film to the insoluble infusible state, and likewise improves the properties of the polyvinylal resin component. Specifically, the hardness, abrasion resistance and resistance of the resin film to attack by oils, solvents, varnishes and various chemicals are improved by such treatment.

The following data show the properties of wire insulated with polyvinylal resin modified with phenolaldehyde resin (specifically with a cresol-formaldehyde resin of the kind and in the amount described under Example 1) as compared with unmodified polyvinylal resin and with conventional oil-type organic enamel. For sake of brevity, these compositions are designed as "Enamel A," "Enamel B" and "Enamel C," respectively.

FLEXIBILITY AT 25° C.

This test is made by stretching the wire to a known degree and winding on a mandrel of definite diameter, from which the actual flexibility of the film is calculated.

	Per cent
Enamel A.....	Above 150
Enamel B.....	Above 150
Enamel C.....	45 to 50

HEAT SHOCK RESISTANCE

A tapered helix of the insulated wire is heated for 15 minutes at 150° C. and the per cent of stretch of the film at which cracking occurs is recorded.

	Per cent
Enamel A.....	Above 150
Enamel B.....	Above 150
Enamel C.....	35 to 45

In another test of the resistance of the insulated wires to heat shock, the wires were wrapped on a mandrel three times their diameter and placed in an oven at 105° C. Both Enamels A and B were unaffected after 4000 hours' heating, whereas Enamel C cracked after heating for only 2 hours.

RESISTANCE TO AGEING UNDER HEAT

This test is made by placing wire unstretched and unbent in an oven maintained at a temperature of 105° C., after which it is removed and wrapped on a mandrel three times its diameter. The length of time it takes to cause general cracking of the film is taken as the end-point.

Enamel A.—No cracking at the end of 3000 hours

Enamel B.—No cracking at the end of 3000 hours

Enamel C.—Bad cracking of the film after heating for only 48 hours.

JERK ELONGATION

The samples of insulated wire were stretched 10, 15 and 20 per cent with a jerk testing machine at an elongation speed of 15 feet per second. The per cent elongation before cracking of the enamel film is recorded.

	Per cent
Enamel A.....	Above 20
Enamel B.....	10 to 20
Enamel C.....	Above 20

ABRASION RESISTANCE

Wires insulated with Enamel A consistently showed better abrasion resistance than wires insulated with Enamels B and C, both in laboratory tests and in production runs. The superior abrasion resistance of the phenolic resin modified polyvinylal resin makes it especially suitable for insulated wires to be wound on automatic coil-winding machines of the Kayser type.

SOLVENT RESISTANCE

Wires insulated with Enamels A and B were unaffected after prolonged immersion in naphtha at 25° C., whereas Enamel C began to soften after 48 hours' immersion therein. On a similar test in toluene, in xylene and in an insulating composition comprising a mixture of chlorinated diphenyl compounds (known under the trade name of "Pyranol") Enamel B was much more resistant to attack than Enamel C, and Enamel A was superior to Enamel B.

MOISTURE RESISTANCE

Wire insulated with Enamel A was found to be more resistant to water than wires insulated with Enamels B and C. Its dielectric strength in the presence of moisture therefore is better.

DIELECTRIC STRENGTH

The dielectric strength of films of Enamel A is comparable with that of similar films of Enamels B and C under all practical conditions of service use, being of the order of 1000 to 1400 volts per mil.

In general, it may be said that the phenol-aldehyde-modified polyvinylal resin is better than the straight polyvinylal resin in such properties as abrasion resistance, water resistance, and solvent resistance to toluol, xylol and chlorinated diphenyl compounds. It also appears to have less thermoplastic flow and better adhesion as indicated by the results of jerk elongation tests. In dielectric strength, flexibility and resistance to heat shock it shows about the same properties as the straight or unmodified polyvinylal resin. A particular advantage of the modified polyvinylal resin is that it provides a thicker coating on the wire during each pass of the wire through the enamel bath. This is because it is possible to use, with the same solvent, 16 to 20 per cent of modified polyvinylal resin in the enamel as compared with 11 to 13 per cent of straight polyvinylal resin, and yet obtain enamels of approximately the same viscosity and ease of application.

It is to be understood that this invention is not limited to the application of the new insulating composition directly upon the conductor, as shown in Fig. 1. For example, a coating of the new insulation may be applied over a coating of regular enamel, as shown in Fig. 2. The modified polyvinylal resin adheres tenaciously to the underlying enamel film, and protects the latter from abrasion and from embrittlement which otherwise results upon prolonged exposure to heat. Also, if desired, a conductor may be provided first with a coating of the phenolic resin modified polyvinylal resin, followed by one or more coatings of ordinary enamel, as shown in Fig. 3. In this way the adherence of the ordinary organic enamel is improved. Thereafter an outer coating or coatings of the modified polyvinylal resin may be put on, as shown in Fig. 4.

While we have described the preparation of the phenolic modifying resin which is incorporated with the polyvinylal resin with particular reference to phenol or cresol, it will be obvious to those skilled in the art that other phenolic bodies also may be used. For example, we may use xlenols; or mixtures of phenol and cresol; or mixtures of phenol or cresol, or phenol and cresol together with wood oil phenolic bodies of the kind described more fully in the copending application of Edmond F. Fiedler and Allan Shephardson, Serial No. 212,500, filed June 8, 1938, which has matured to Patent No. 2,221,511, dated Nov. 12, 1940, and assigned to the same assignee as the present invention; or petro-alkyl phenols of the kind described in the copending application of George Alexander, Serial No. 210,444, filed May 27, 1938, and also assigned to the same assignee as the present invention, which petro-alkyl phenols may be used as the sole phenolic body or in combination with coal-tar phenol, cresols and other phenolic substances. Likewise, active methylene-containing bodies other than formaldehyde may be used, either in solid or solution state. If desired, para-formaldehyde may be employed in place of an aqueous solution of formaldehyde and the reaction and dehydration may be carried out in an open vessel instead of as described under Example 1. While we prefer to use an organic alkaline catalyst such as ethanolamines, specifically triethanolamine, or morpholine, inorganic alkaline catalysts also may be employed, for example, the cyanides, hydroxides and carbonates of the alkali metals as, for instance, sodium or potassium hydroxide, carbonate or cyanide.

Although the phenolic resin modified polyvinylal resin herein described is particularly applicable to the manufacture of wire enamels and insulated conductors, it will be appreciated that its field of utility is not limited thereto. For example, it may be used as an adhesive for cementing together such materials as mica-flakes to form bonded mica sheet insulation as described more fully in the copending application of William Howard Miller, Serial No. 218,192, now Patent No. 2,195,254 dated March 26, 1940, filed concurrently herewith and assigned to the same assignee as the present invention. It also may be used as a cementing agent for bonding together fibrous materials in sheet, tape, felted, or other form. It also may be employed as a coil-impregnating varnish.

The phenolic resin modified polyvinylal resin may be made in the form of thin sheets or tapes and used alone, or adhesively bonded to, or otherwise in combination with other materials such as paper, cellulose esters, cellulose ethers, etc., as coil layer insulation, as described more fully in the copending application of Ralph V. Boyer, Serial No. 218,151, now Patent No. 2,195,233 dated March 26, 1940, filed concurrently herewith and assigned to the same assignee as the present invention. Such sheets or tapes also may be applied to a conductor, according to well-known strip-covering methods, as insulation therefor. They may be heat treated to improve their properties either before, during or after application. Varnishes made of the new resinous composition are particularly suitable for use in applying spun glass to wire as described in the copending application of Ralph W. Hall and Henry A. Smith, Serial No. 218,134, now Patent No.

2,243,560 dated May 27, 1941, filed concurrently herewith and assigned to the same assignee as the present invention.

The modified polyvinylal resin herein described, being a less costly product to prepare, has a wide field of practical application heretofore closed to straight or unmodified polyvinylal resins because of their high cost.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. An insulated electrical conductor in which the insulation comprises a heat-hardenable phenol-aldehyde-modified polyvinylal resin heat-treated in place to produce a hard, flexible, tough, abrasion-resistant insulation.

2. An electrical conductor provided with a hard, flexible, tough, abrasion-resistant coating of high dielectric strength, said coating being a heat-treated resinous composition comprising a polyvinylal resin having incorporated therewith not exceeding substantially 50 per cent by weight of the said composition of a compatible heat-hardenable phenol-formaldehyde resin.

3. An electrical cable comprising an electrical conductor having superposed directly thereon a hard, flexible, tough, abrasion-resistant coating of high dielectric strength, said coating being the heat-treated product of a mixture of a polyvinylal resin, obtained by condensing formaldehyde with a product of hydrolysis of polyvinyl acetate, and from 5 to 50 per cent by weight of the said mixture of a heat-hardenable resin obtained by condensing cresol with formaldehyde in the ratio of 1 mole cresol to at least 0.7 mole formaldehyde and in the presence of an alkaline catalyst.

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