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INSULATING ENAMEL FOR ELECTRIC CONDUCTORS

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Fig. 1.

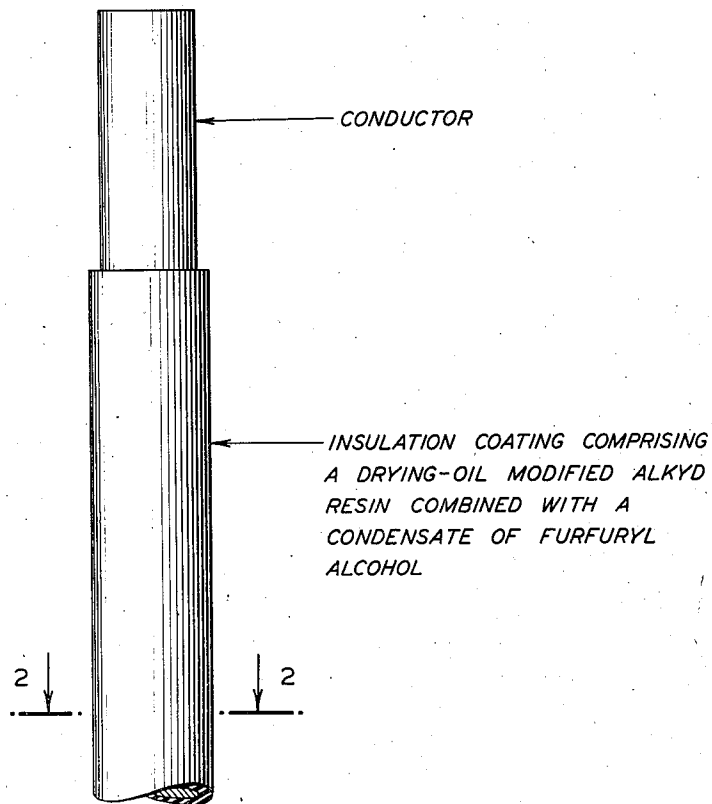
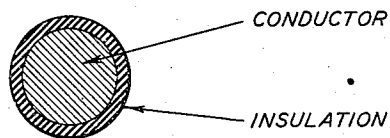


Fig. 2.



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INSULATING ENAMEL FOR ELECTRIC CONDUCTORS

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6 Claims. (Cl. 174—125)

This invention relates to insulating enamels for coating electrical conductors and other articles; to the method of making and applying the enamel; and to the article produced; and has for an object the provision of improvements in this art. In particular, the invention provides an insulating enamel which has good electrical properties, including high dielectric strength; which has good adhesion; which has high heat resistance; which is very tough and hard; which has good flexibility; which is unusually resistant to solvents; which is low in cost, and which can be applied at a much higher speed than enamels now available, or can be baked at much lower temperatures.

An illustrative embodiment of the invention selected merely for descriptive purposes is shown in the accompanying drawing, in which:

Figure 1 is a side elevation of an enamel insulated conductor, the insulation coating being cut back so as to disclose the conductor; and

Figure 2 is a cross section on the line 2—2 of Figure 1.

The legends appearing on the drawing are for illustrative purposes only and are not by way of limitation.

In the conventional or commonly practiced method of enameling wires, a film of varnish is applied to the wire and then subjected to a temperature of from 300° C. to 500° C. in order to bake the varnish film; the temperature and time being regulated to secure the desired properties. The most widely used materials for forming enamels are the oleo-resinous varnishes consisting of drying oils such as China-wood, perilla, linseed, soy bean, etc., combined with such gums as kauri, manila, congo copal, etc., and thinned with suitable solvents. During recent years, certain synthetic resins have in some cases replaced all or part of the natural gums used. The oil-soluble, modified phenol-aldehyde resins and the drying-oil-modified alkyd resins are examples of such synthetic substitutes. However, all of these materials require the high temperature treatment of the natural materials since these modified enamels are essentially oleo-resinous varnishes.

The conventional enamels described have certain definite limitations which have not been removed or greatly expanded by the efforts of manufacturers to improve these products. From the standpoint of plant operation, the relatively long time and high temperature required to bake these enamels to a suitably hard condition, are limitations which greatly affect the economical pro-

duction of enameled wires. The maintenance of enamel ovens at the high temperatures required results in high heat loss and this loss cannot be compensated by greatly increased production speeds because the conventional materials, even in their highest state of development, require a relatively long time for their conversion to the solid non-tacky condition. Also, the conventional materials have limitations which prevent the attainment of the ultimate properties sought in the enamel film.

As is well known by users of enameled wire, it is particularly desirable that the insulating film be very hard, tough and abrasion resistant and more especially that these properties are retained when the enameled wire is subjected to the action of solvents such as those found in the varnishes, lacquers and other coil treating compounds used during manufacture, as well as any solvents which may be encountered later during the normal operation or use of the wire. Conventional enamels are definitely weak in this respect because the hardness, toughness and abrasion resistance of these materials are much below the desired standards and especially because these properties are almost completely lost when the films are subjected to the action of solvents.

A few examples will illustrate some of the superiorities of the products of this invention over conventional materials:

1. DRYING AND BAKING SPEED

At 100° C. the time required to dry one of the faster drying conventional enamels in a film 0.0005" thick to a tack-free condition was found to be 60 minutes.

At 100° C. the time required to dry the enamel of this invention in a film 0.0005" thick to a tack-free condition was found to be 2 minutes.

In a short tube, similar to, but smaller than a commercial enamel oven, at 310° C. satisfactory conversion of a fast-baking, conventional enamel could be made at a maximum speed of 1 ft. per minute. Under identical baking conditions in the same tube the enamel of this invention was satisfactorily converted at a speed of 35 ft. per minute.

2. SOLVENT RESISTANCE

An idea of the comparative merits of conventional enamels and the enamel of this invention with respect to solvent resistance can be obtained from the following tests in which three different well-baked and aged samples of con-

ventional enameled wires were immersed in various solvents, together with samples of wire finished with the new enamel and the film properties after immersion determined by scraping the films with a standard scrape test fixture having a 10 oz. load on the knife edge. In the table, C indicates that the film was removed completely to the copper and N indicates that the film was not in any way affected by the scrape test.

The time of immersion is shown.

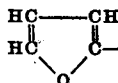
	Conven- tional A	Conven- tional B	Conven- tional C	New enamel
	Minutes (C)	Minutes (C)	Minutes (C)	Hours (N)
Acetone.....	5	5	3	72
Ethyl acetate.....	5	5	5	72
Benzol.....	5	5	5	72
Toluol.....	7	5	5	72
Chloroform.....	3	3	2	72

Such improvements in manufacturing economy and in wire quality have been earnestly sought by the industry for a long time. The present invention provides materials which have the desired properties and the methods which produce the desired results. Furan derivatives are employed, furfuryl alcohol being preferred.

The furan nucleus group and furan derivatives, including furan $C_4H_3O.H$, furfural $C_4H_3O.CHO$, and furfuryl alcohol



which contain the furan nucleus or furan residue C_4H_3O , that is, diagrammatically,



have properties which suggest the possibility of their use as a low temperature baking enamel.

As shown in the structural formula above, the furan derivatives contain a conjugated diene system in a hetero cyclic group. This particular structure makes it active in regard to both polymerization and oxidation. Its easy polymerization and the rapidity of a further conversion to insoluble, infusible forms when the partially condensed material is heated in air at low temperatures, constitute the basis of the present attack on the problem of providing a quick setting, low temperature baking enamel.

The fact that heating of the furan derivatives induces condensation and finally resinification suggests that if furfuryl alcohol, for example, were simply applied as a coating on an object and then heated, there should be formed on the object a film of the resinified furfuryl alcohol. However, if an attempt is made to coat a wire and bake at once at even a reasonably low temperature, say 170-180° C. for furfuryl alcohol, the coating material will all be evaporated. This is true because furfuryl alcohol boils at 170.2° C. and has a relatively high vapor pressure even below its boiling point, and resinification or polymerization by heating requires a much longer time than is required for the complete volatilization of any film of ordinary furfuryl alcohol on a wire where a large surface is exposed for evaporation.

In order to overcome this difficulty the present invention, first of all, provides for the partial condensation, polymerization or resinification of the substance before it is applied to the wire or other object on which it is to be baked. The partial condensation converts the substance from

a thin, mobile liquid of low boiling point and high vapor pressure to a very viscous oil or semi-solid material of high boiling point and very low vapor pressure. This material can now be applied and baked with practically no loss by evaporation to leave a resinous film which is permanently stable at ordinary temperatures.

Most of the furan derivatives may be polymerized by the use of suitable catalysts as well as by heating. Furfuryl alcohol has been found to have the additional characteristic of being self-condensing with the elimination of water as a by-product and this is particularly advantageous for present purposes because when this autogenous condensation is effected there are formed long chain molecules which impart toughness to the product.

Partial condensation of the furfuryl alcohol has been shown to be one of the important features of the invention. This preliminary partial condensation can be carried out in several ways as will be shown presently. The preliminary condensates formed by any of the following processes can be combined with modifying materials as will be shown later:

1. CONDENSATION BY USE OF HEAT ALONE

It has been found that furfuryl alcohol can be condensed to form the desirable initial condensates of this invention by heat alone without the addition of any foreign materials as catalysts. Because this method does not introduce any catalyst which could cause instability in the finished enamel or in the enameled wires, it is not necessary to give the products of this process any special treatment in order to guard against such deteriorating influences. An example of the practice of this process follows:

Example #1

Furfuryl alcohol is charged into a pressure kettle and heated until the temperature reaches 190-210° C. The pressure gradually builds up even when the temperature is held constant, due to the production of water as a by-product of the reaction. The vapor in the kettle is allowed to leak slowly into a condenser during the heating and the pressure can be maintained at any desired level by adjusting the rate of leaking of the vapor. The distillate issuing from the condenser consists essentially of a mixture of water and furfuryl alcohol. The latter can be recovered from the mixture and used again. The viscosity of the liquid in the kettle increases progressively as the condensation reaction proceeds. After about twelve hours of heating, the evolution of water diminishes sharply. The condensation product at this stage is a very viscous oily material or a soft semi-solid which dries rapidly when spread in a thin film and exposed to air. The time and temperature of the reaction can be varied but the products formed are essentially the same in all cases. The product can be dissolved in acetone, ethyl acetate, benzol, toluol and other common solvents.

2. CONDENSATION BY USE OF VOLATILE CATALYSTS

The initial condensation of the furfuryl alcohol can be conveniently accomplished by using volatile catalysts such as the low molecular weight organic acids like formic and acetic acids. These materials are not the most active catalysts and unless used in excessive amounts will not eliminate the necessity of heating the furfuryl alcohol-catalyst mixture somewhat. The advantage in their use lies in the fact that because they are

generally of sufficiently low activity, when not used in excessive amounts, they may be left in the partial condensation products without seriously affecting the stability of solutions made therefrom, particularly when a solvent is used, and because they do not remain in the baked film but are volatilized along with the solvents during baking. The catalyst can be added directly to the furfuryl alcohol or to a solution of the furfuryl alcohol in solvents. From the standpoint of controlling the reaction the latter is preferable. An example of this procedure follows:

Example #2

Parts by weight

Furfuryl alcohol.....	98
Formic acid.....	46
Ethyl acetate (solvent).....	150

The mixture is heated under a reflux condenser for about one hour at 110° C. The heating is then discontinued and the liquid filtered to produce a clean solution of the initial condensates. When the solvent is evaporated from this solution a soft, solid, brownish colored residue or film is left. This film rapidly converts to the insoluble and infusible condition when heated; complete conversion of thin films taking place in 30 seconds at 120° C.

3. CONDENSATION BY USE OF NON-VOLATILE, NON-RESINOUS CATALYSTS

The preliminary condensation of furfuryl alcohol can be effectively accomplished by the use of very active non-volatile catalysts such as sulphuric acid, phosphoric acid, ferric chloride, zinc chloride and similar dehydrating agents, but these materials continue to act after the initial condensation is completed with resulting instability of solutions and poor aging properties of films made from such products. It has been found that removal or inactivation of the catalyst after the preliminary partial condensation eliminates these undesirable features and allows the production of stable solutions which do not gel on storing and which give films which do not quickly become brittle. Because of their easy inactivation and removal, the mineral acid catalysts are preferred, especially sulphuric acid. Condensation in the presence of solvents is preferred. An example of a process using sulphuric acid and removing it after the initial condensation is given below:

Example #3

Parts by weight

Furfuryl alcohol.....	2000
Acetone (solvent).....	2000
Sulphuric acid (sp. gr. 1.84).....	30
CaO (for acid removal).....	200

The concentrated sulphuric acid is first dissolved in the acetone and this acetone solution is then mixed with the furfuryl alcohol. The solution is held at room temperature, by cooling if necessary, for eight hours. After this treatment, samples will dry to tacky solid films in a few seconds at room temperature. The solution is then treated with an excess of dry calcium oxide or calcium hydroxide and stirred for a few minutes. The lime does not dissolve in the solution but reacts with the sulphuric acid, forming inactive, insoluble calcium sulphate. The solution is filtered and for best results, is again treated with lime and refiltered. Other neutralizing bases such as ammonium hydroxide, organic amines, alkali hydroxides, etc., may be used but

the use of lime is preferred. The proportion of catalyst used can be varied over a wide range as can the proportion of solvent. Increasing the proportion of catalyst causes quicker reaction and more spontaneous heating. Increasing the proportion of solvent has the opposite effect. The filtered solutions are stable and suitable for use in the preparation of the new wire enamels.

4. CONDENSATION WITH NON-VOLATILE, RESINOUS CATALYSTS

Of the few materials which have been found to be compatible with furfuryl alcohol condensates and which produce improvements in film properties, the alkyd resins, particularly the fatty acid modified alkyd resins, are outstanding. Their use in conjunction with the initial condensates prepared by any of the foregoing methods will be shown later. It has also been found that these materials themselves exert a catalytic effect on the condensation of the furfuryl alcohol at elevated temperatures and therefore can be made to serve the double purpose of catalyzing the initial condensation and at the same time improving the flexibility, heat-resistance, durability and toughness of the films. As an example of the practice of this process the following is given:

Example #4

Parts by weight

Furfuryl alcohol.....	671
Modified alkyd resin.....	671

The modified alkyd resin is dissolved in the furfuryl alcohol with the aid of gentle heating. The solution formed is then heated in a kettle fitted with a collecting condenser. At about 155 deg. C. an exothermic reaction sets in and continues for a while without the application of external heat. A light liquid consisting essentially of water and furfuryl alcohol distills during the reaction. The temperature is maintained at 155-165° C. until distillation is completed. This requires about 2 hours. The last traces of water can be removed by adding some toluene to the contents of the kettle and distilling this out by further heating. The resulting material is a viscous, semi-solid mass having pronounced drying properties and being easily soluble in acetone, benzol and other solvents. Such solutions, after filtering represent typical examples of the alkyd-modified furfuryl resin enamels of this invention.

The initial condensation products formed in Examples 1, 2 and 3 can be dissolved in any suitable solvent such as acetone, ethyl acetate, benzol, toluol, etc., and mixed with solutions of modified alkyd resins to form the most desirable modifications for use as wire enamel. The product of Example 4 is already modified by the alkyd resin during its manufacture and needs no further additions. The products of Example 1 are preferred for use where further modification by alkyd resins is to be made after the initial condensation of the furfuryl alcohol. A typical wire enamel formulation is shown here.

Example #5

Parts by weight

70 Furfuryl condensates (of Ex- ample 1).....	100	1-4 P. B. W.
Acetone.....	100	
Modified alkyd resin.....	100	4-1 P. B. W.
75 Acetone.....	100	

The two solutions shown are simply mixed together. The concentration of each solution and the ratio of the two solutions used can be varied over wide limits.

The alkyd resins used are preferably the oxidizing type in which drying oil fatty acids are used to modify the glyceryl-phthalate.

Specific examples are:

Example #6

	Parts by weight
Glycerol	92
Phthalic anhydride	194
Linseed fatty acids	110

Example #7

	Parts by weight
Glycerol	92
Phthalic anhydride	185
Linseed fatty acids	70
Chinawood fatty acids	70

Other resins of the same general type in which ethylene glycol, diethylene glycol, and other polyhydric alcohols are used to partially or entirely replace glycerol and in which maleic anhydride, sebacic acid, pimelic acid, succinic acid, "Petrex"—3 isopropyl 6, methyl 3,6, endo-ethylene Δ^4 tetrahydro phthalic anhydride, or other dibasic acids are used in place of phthalic anhydride are also suitable. The fatty acids used for modifying these materials may be obtained from many oils such as linseed, soy bean, perilla, Chinawood, etc.

The product of Example 4, that is, a coating solution formed by the reaction or condensation of furfuryl alcohol and a modified resin, dissolved in acetone, dried in 2 minutes at 100 degrees C. to form a hard, tough insoluble enamel which when heated at 110° C. for more than 160 hours was tougher and more adherent than before.

Even better results may be obtained by partially oxidizing the viscous partial condensation product by air-blowing it before dissolving it in acetone. Air blowing may also be usefully employed with the other partial condensation products.

Any of the partial condensation products may have added to them prior to baking, one of the volatile catalysts which is inactive in the solution at normal temperatures but which acts as a catalyst at baking temperatures and is driven off as a vapor when the reaction is completed so as to prevent further action to cause deterioration upon aging.

The drawing discloses in Figures 1 and 2 an insulated conductor construction in which the conductor has applied thereto an insulation coating comprising a drying-oil modified alkyd resin combined with a condensate of furfuryl alcohol.

Wires enameled with furfuryl resins according to the present process have several advantages over the materials now used. They are equivalent to enameled wires of common manufacture in electrical properties and are much superior in regard to solvent resistance. The enamel will stand almost indefinitely at ordinary temperatures without deteriorating. The wire enameling process itself can be carried out along the same general lines as the present process except that the improved process permits lower temperatures and higher speeds to be used.

After the wire has been run through the bak-

ing oven at high speed the enamel is sufficiently cured for spooling and handling. It has been found, however, that the product is greatly improved in aging properties and adhesion by heating the spooled wire for a long period at a relatively low temperature, say for 16 hours at 110° C. This after-curing has been used to some extent for ordinary enamels to give a slight improvement; but with the present material the improvement is very much more pronounced. The extent of improvement by after-baking varies with the ratio of furfuryl resins to alkyd resins, being greater as the ratio of furfuryl resins increases.

It is thus seen that the preliminary treatment and the after treatment both contribute to the speeding up of the baking operation which heretofore has required the most time, equipment and cost. And the present materials, which have produced such outstanding enamels, could not be used at all in practice except for the preliminary partial condensation operation.

With prior processes requiring high baking temperatures the enamel is spoiled if the wire travel is halted even for a short time. With the present process permitting low baking temperatures the enamel is not injured even if the wire travel is stopped for a considerable time. Scrap loss from this cause is practically eliminated. Another beneficial effect is that the wire may be stopped for inspection whenever desired.

To reduce the expense it is possible in any of the examples to use a less expensive furan derivative with the furfuryl alcohol.

The alkyd resins used may also be of the phenol-aldehyde modified type or may be added together with heat-convertible phenol aldehyde resins. Such modifications produce somewhat harder films which are less liable to mechanical injury when the hot, freshly baked wire is passed over sheaves.

It is to be understood that the invention may be variously modified within the limits of the prior art and the scope of the subjoined claims. I claim:

1. The method of producing an enamel for electrical conductors which comprises partially condensing furfuryl alcohol and adding to the partially condensed product a drying-oil modified alkyd resin and a solvent.

2. The method of claim 1 further characterized by this: that the resin is added to the alcohol at a preliminary stage in the process so as to assist in the condensation of the alcohol.

3. The method of claim 1 further characterized by this: that in the condensation step a compound containing the aldehyde of furane, may be substituted for a part of the alcohol.

4. A baked coating on wires comprising the combination of a drying-oil modified alkyd resin, with a resin produced by the partial condensation of furfuryl alcohol.

5. A flexible, tough insulating enamel for electrical conductors comprising a drying-oil modified alkyd resin combined with a furfuryl alcohol condensate, said enamel being hard and having high resistance to abrasion and solvents.

6. A flexible, tough insulating enamel for electrical conductors comprising a drying-oil modified alkyd resin combined with a condensate of furfuryl alcohol and the aldehyde of furane, said enamel being hard and having a high resistance to abrasion and solvents.

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