Oct. 1, 1963

E. LAVIN ETAL

3,105,775

COMBINATION COATINGS

Filed April 3, 1961

FIG. 1

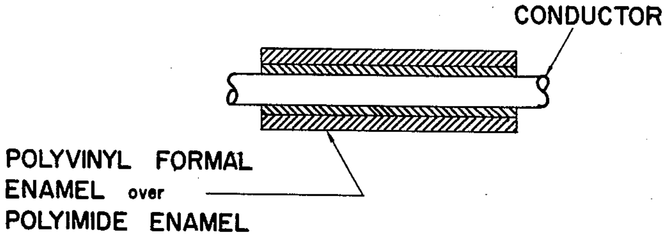


FIG. 2

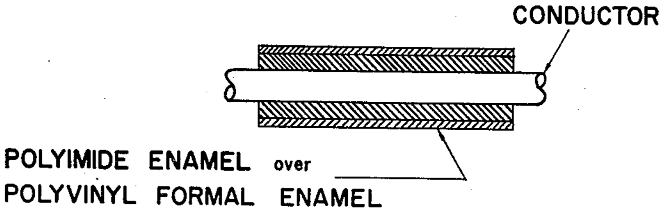
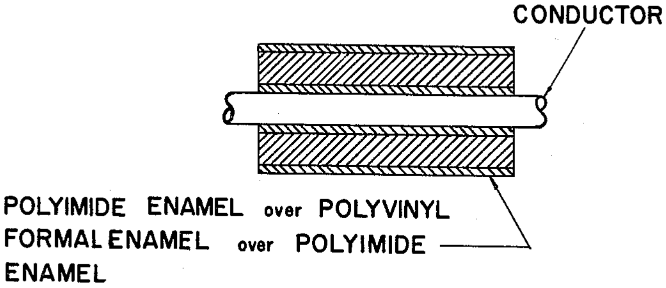


FIG. 3



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COMBINATION COATINGS

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This invention relates to enameled wires; more particularly, it relates to wires coated with multiple layers of cured polyvinyl acetal resin compositions and polyimide resin compositions.

Magnet wires coated with compositions based on polyvinyl formal are well known. They are generally used at operating temperatures not exceeding 105° C. and, for this reason, are considered to be "class A" wires, in accord with the prevailing electrical insulation code. The delicate balance of excellent mechanical, chemical and electrical properties possessed by these wires and their relatively low cost are certainly important factors contributing to the wide use of these polyvinyl formal wires in the electrical industry.

It is well established, on the other hand, that the output of motors and generators is increased considerably when the density of the current in the magnet wire of these machines is raised. Unfortunately greater current density creates higher operating temperatures, and that shortens the life of "class A" wire. Yet, if one keeps in mind the well balanced physical properties of polyvinyl acetal coated wire, its low cost, its general acceptance, the large investment of the wire coating industry in equipment designed to produce it, and the shortcomings of other classes of wires that have been proposed as substitutes, the desirability of upgrading "class A" polyvinyl acetal magnet wire to higher classifications while maintaining its other present acceptable properties, becomes evident.

A method commonly used to upgrade the thermal life of polyvinyl acetal coatings consists in impregnating the ready to use wire winding with special varnishes. However, because of differences in chemical composition, solubility and viscosity between varnishes and enamels, the varnishes do not achieve the improvement sought by this invention and, moreover, suffer from the inconvenience that they must be applied after motor and generator coils are wound.

It is therefore an object of this invention to upgrade the thermal life of polyvinyl acetal magnet wire so that it will perform efficiently at operating temperatures up to 130° C. ("class B") and up to 155° C. ("class F"). Another object is to produce organic "class B" and "class F" wire coatings which can resist hydrolysis, are not bulky and possess good abrasion resistance for machine winding.

These and other objects are attained by applying a thin layer of certain aromatic polyamide enamels over and/or under a coat of polyvinyl acetal or modified polyvinyl acetal enamel.

The following examples will serve to illustrate but not to limit this invention. For instance, although it has been found practical and convenient to effect all the polyvinyl acetal coatings with well known standard preparations or mixtures of components available commercially, it must not be concluded that the invention is thus circumscribed.

In the accompanying drawing, longitudinal sectional views of wires (conductors) insulated in the manner of this invention are shown. FIGURE 1 illustrates a wire coated with two layers of polyimide enamel and four layers of polyvinyl formal enamel; the polyimide layers are next to the metal. In this and subsequent figures, the thickness of the insulation coatings is scaled to show approximately the number of layers of each type of coating. In FIGURE 2, the order of superposition of enamels has been reversed so that the polyvinyl formal enamel is now next to the metal. In FIGURE 3, the conductor is covered with four layers of polyvinyl formal sandwiched between two layers of polyimide.

EXAMPLES 1–7

Four enamels containing a polyvinyl acetal resin have been employed along with one laboratory synthesized polyamide enamel and a commercially available enamel chemically similar in nature. The compositions of the polyvinyl acetal enamels are shown, in parts by weight, in Table I. The polyamide enamels will be described subsequently.

Table I

Components	Enamels			
	A	B	C	D
Polyvinyl formal resin	100	100	100	100
Phenolic resin	50	40	10	40
Polyurethane	------	10	60	45
Melamine formaldehyde resin	------	------	7.5	7.5
Cresylic acid	250	250	250	227
Hydrocarbon solvent	500	500	500	518

Both these components and enamels are well known to the trade.

The polyvinyl formal resin employed contains 10.5% acetate groups calculated as polyvinyl acetate, 6% hydroxyl groups calculated as polyvinyl alcohol, and 83.5% formal groups calculated by difference as polyvinyl formal. The phenolic resin is a soluble, fusible, heat-hardenable reaction product of 100 parts cresol, 60 parts formalin, and 3.2 parts ethanolamine, dissolved in commercial cresylic acid. The polyurethane is the phenol blocked reaction product of one mol trimethylol propane with three mols of a mixture containing about 80% 2,4- and about 20% 2,6-tolylene diisocyanates. The melamine-formaldehyde resin is a relatively low molecular weight, butylated, internally plasticized condensation product of 1 mol melamine with 3.5 mols formaldehyde and 0.5 mol para-toluene sulfonamide. Finally, the last two components employed in the preparation of these enamels are commercial cresylic acid and naphtha. Little need be said about enamels A to D themselves; they will be easily recognized by workers in the field.

One of the polyamides employed in the examples, enamel E, is the condensation product of pyromellitic dianhydride with 4,4'-oxydianiline. The oxyaniline was recrystallized from ethyl alcohol-dimethyl acetamide, and technical pyromellitic dianhydride (86.7%) was purified by heating at 250° C. for two hours at 80 mm. pressure. The resulting pyromellitic dianhydride, 14.8 g., was slurried in 71 ml. dry dimethyl-acetamide in a 3-neck, round-bottom flask fitted with a thermometer and an air condenser, protected with a calcium chloride drying tube. A solution of 13.4 g. oxydianiline in 71 ml. dry N-methylpyrrolidone was added. The reaction mixture was held at 50° C. with stirring for two hours. The polyamide solution thus obtained was applied on wire. Suffice it to mention at this stage that the polyamide, after it has been applied to the wire, is converted in situ to a polyamide structure during the subsequent processing of the wire.

The other polyamide enamel used in the examples (F) is a commercial product marketed under the brand name "ML"; it consists essentially of a polyamide chemically similar to that in enamel E, dissolved as a 15% by weight solution in a 1:1 mixture of N-methylpyrrolidone and dimethylacetamide and having a viscosity of about 4800 cps. at 25° C.

The enamels were applied to number 18 (0.0403 inch) copper wire by conventional wire coating means, each layer of enamel being cured by passing the dipped wire through a vertical oven 12 feet high with a set cure temperature of 350° C. at a constant rate of speed selected from the range of 12 to 19 feet of wire per minute. A split applicator was employed so that the desired number of different coats could be put on in one continuous operation.

Control wires were prepared with each enamel by applying six successive coats of the enamels to the bare wire. Since each coat has a thickness of approximately 0.25 mil, the resulting wires were thus given a heavy build, the insulated wires having a diameter approximately 3.0 mils larger than that of the bare original wires. In the case of enamels E and F, the polyamides, a two coat control wire was also prepared, having a build of approximately 1 mil.

The testing of the enameled wires was done by standard procedures. Although numerous chemical, physical and electrical properties of the control wires and of the new insulated wires were tested, the descriptions of the testing procedures will be limited to those measuring the properties in which significant changes were observed, namely one-kilovolt life, abrasion resistance and resistance to hydrolysis.

1 kilovolt-life test.—The 1 kv.-life test was made in accordance with the provisions of the American Institute of Electrical Engineers specifications No. 57, dated October 1955. The test is a measure of the period for which a coating can be exposed at the particular temperature indicated before it will fail as electrical insulation upon the application of 1000 volts for one second to the sample. Ten samples are used in each test.

The scrape abrasion test.—This test consists essentially in scraping repeatedly the insulated wire sample with a steel needle loaded with a set weight which is varied according to the build of the wire. The tester records the number of strokes and shuts off when contact is made between the needle and the bared wire. Insulation which withstands an average of 30 strokes in six different places is considered standard provided that no one place wears down with less than 15 strokes.

The hydrolysis resistance test.—In this test, entwined wire pairs are heated at 150° C. in sealed glass tubes containing 0.5 ml. water. At definite intervals, a pair is taken out and is tested under increasing electrical potential until the insulation breaks down. Results are reported as the period, in hours, of exposure to the conditions of the test, that the wire can withstand before it breaks down under a potential of one-kilovolt applied for one second.

Table II shows the significant properties of the control wires covered with standard enamels at optimum cure. These values will serve as a basis for evaluation of the new insulations of the later examples.

Table II

Enamel	Build (mils)	Abrasion (strokes)	1 kv.-life (hrs.)					Hydrolysis Resistance (hours)
			180° C.	200° C.	225° C.	250° C.	300° C.	
A	3	43	218	125	25	10	4	>144
B	3	63	152	113	28	12	3.5	>144
C	3	63	439	158	34	13	3	>144
D	3	78	435	180	40	15	3.5	>144
E	1	2	$2,000^{6}$	$2,000^{6}$	390	41	28	<16
F	1	1	$2,000^{7}$	$2,000^{6}$	544	50	27	<16
F	3	8	$2,000^{10}$	$2,000^{10}$	$2,000^{10}$	$1,600^{10}$	658	<16

(The values accompanied by a superscript are not final in that at the time indicated by the figures, e.g. 2000 hours for enamel F at 200° C. a number of samples represented by the superscript were still resisting the conditions of the test. It will later become clear that these incomplete values do not detract from the understanding of the invention.) The results, as they are, certainly demonstrate the excellent abrasion and hydrolysis resistance of polyvinyl formal enamels (A to D) and the excellent thermal stability of the polyimide insulations (E and F).

EXAMPLES 8–13

Wires were then prepared with insulation consisting of four coats of polyvinyl formal resin over two coats of polyimide enamel as illustrated by FIGURE 1. The significant properties of these new coatings are summarized in the following table.

Table III

Enamel	Build (mils)	Abrasion (strokes)	1 kv.-life (hours)					Hydrolysis resistance (hours)
			180° C.	200° C.	225° C.	250° C.	300° C.	
A on E	2+1	31	$2,000^{10}$	$2,000^{10}$	$2,000^{2}$	620	112	>144
C on E	2+1	40	$2,000^{10}$	$2,000^{10}$	$2,000^{8}$	880	124	>144
A on F	2+1	34	$2,000^{8}$	$2,000^{10}$	$1,650^{2}$	547	145	>144
B on F	2+1	38	$2,000^{8}$	$2,000^{10}$	$1,900^{3}$	715	117	>144
C on F	2+1	56	$2,000^{10}$	$2,000^{9}$	$2,000^{9}$	961	152	>144
D on F	2+1	70	$2,000^{10}$	$2,000^{10}$	$2,000^{6}$	669	117	>144

A comparison of these results with those of the control wires of Table II will quickly indicate that, although the regular six coat (3 mil build) polyimide wire has a thermal life superior to any of the above combination enamels, two coats of enamels E or F placed under four coats of polyvinyl formal enamel will form insulation that is far superior than that provided by two coats of enamel F alone. A comparison of the thermal life of combination coatings with that of the one mil polyimide coatings at temperature 225° C. and above shows that the improvement in the polyvinyl formal enamel thermal life is not due merely to the presence of the polyimide in the combination coatings, since at those temperatures, the thermal lives of the combination coatings are longer than those of either the polyvinyl formal coating and the one mil polyimide coatings alone. It should also be noted that in abrasion resistance and in hydrolysis resistance, the superiority of the combination coatings extends also to the 3 mil (six coat) polyimide enamel.

EXAMPLES 14–15

In these examples, the order of application of the enamels to the wires was reversed so that the insulation on the wires now consisted of two coats of polyimide enamel over four coats of polyvinyl formal enamel, as illustrated by FIGURE 2. The following results were noted:

Table IV

Enamels	Build (mils)	Abrasion (strokes)	1 kv.-life (hours)				
			180° C.	200° C.	225° C.	250° C.	300° C.
F on C	1+2	11	$2,000^{10}$	$2,000^{10}$	$2,000^{10}$	$1,600^{10}$	338
F on D	1+2	22	$2,000^{10}$	$2,000^{9}$	$2,000^{10}$	$1,600^{10}$	250

An even greater advance in thermal life of polyvinyl formal enamel is thus obtained by coating the polyimide over the enamels C and D rather than under them.

EXAMPLES 16–17

The combination effect obtained by overcoating enamel F is so great in fact that only one coat of it over five coats of a polyvinyl formal enamel is considerably superior to two coat enamel F insulation alone, as will become evident when the results in the next table are compared with the appropriate ones in Table II.

Table V

Enamel	Build (mils)	Abrasion (strokes)		1 kv.-life (hours)				
				180° C.	200° C.	225° C.	250° C.	300° C.
F on C	0.5+	2.5	28	$2,000^{6}$	$1,800^{8}$	$1,900^{6}$	792	80
C on F	2.5+	0.5	23	$1,100^{1}$	508	265	------	29

It is also obvious from these results that a single enamel F undercoat with five polyvinyl formal resin coats is not as desirable as a single enamel F overcoat.

However, when a sandwich type of insulation was put on a wire, with four coats of polyvinyl formal enamel placed between two non-contiguous coats of polyimide as shown in FIGURE 3, a thermal life was obtained which has been shown to be intermediate between two contiguous enamel F undercoats and two contiguous enamel F overcoats.

In summary then, it is shown conclusively in the examples that the thermal life of polyvinyl acetal resin insulations is sensibly lengthened when they are used in conjunction with thinner layers of a polyimide enamel, the excellent abrasion and hydrolysis resistance of the former enamels being retained in the process.

It is evident, of course, that many widely different embodiments of this invention other than those provided in the examples may be made by persons skilled in the art without departing from the scope and the spirit thereof.

For instance, the polyvinyl acetals that may be used in this invention are obtained by the acetalization of polyvinyl esters, partially hydrolyzed polyvinyl esters, and fully hydrolyzed polyvinyl esters, according to methods well known in the art, such as those found in U.S. Reissue No. 20,430 to Morrison et al. Polyvinyl acetals normally contain a certain number of hydroxyl groups and may contain a certain number of ester groups depending upon the extent of the hydrolysis and the acetalization reactions; the preferred resins will be those containing on a weight basis from about 1 to about 35% ester groups calculated as polyvinyl ester, from about 3 to about 15% hydroxyl groups calculated as polyvinyl alcohol, the balance being substantially aldehyde acetal. In the commercial polyvinyl formals which were used in the examples, the ester groups were acetate groups. While formaldehyde is preferred as an acetalizing agent because of its greater reactivity, the process may be carried out with acetaldehyde, propionaldehyde, butyraldehyde and mixtures thereof. Higher aliphatic aldehydes, as well as aromatic aldehydes, may also be employed.

The phenol aldehyde resins used in these compositions are soluble, heat-hardenable condensates of a phenol and an aldehyde, as revealed in U.S.P. 2,307,588. They are generally prepared by reacting 1 mol of a phenol with from 0.7 to 2 mols of a lower aldehyde under alkaline conditions. Acetaldehyde, propionaldehyde and butyraldehyde may be used as well as others, but formaldehyde is usually preferred because of its greater reactivity. A variety of phenols may be used including monohydric phenols such as phenol, cresols, xylenols, ethylphenol, p-t-butyl phenol, other alkyl phenols etc. or mixtures thereof.

Usable polyurethanes are polyisocyanates blocked with organic compounds containing at least one reactive hydrogen atom. These blocking agents must split off at enamel cure temperatures in order to provide free isocyanate groups to crosslink the resinous compositions of the enamel.

Suitable reactive hydrogen compounds include phenols, such as phenol, cresol, xylenols, etc., secondary aromatic amines, mono- and polyfunctional alcohols, amines, lactams, enols, and mixtures thereof. The preferred blocking agents are compounds in which an hydroxyl group is attached to an aromatic ring.

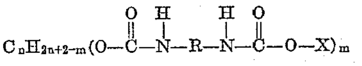
The simplest class of useful polyisocyanates can be represented by the following formula:

$$R(—N{=}C{=}O)_n$$

where R represents a member of the class consisting of aliphatic hydrocarbons containing up to 8 carbon atoms, aromatic hydrocarbons containing up to 13 carbon atoms, alicyclic hydrocarbons containing up to 6 carbon atoms, and alkyl-aryl substitutes thereof, and *n* is an integer from 2 to 4. Suitable polyisocyanates include compounds such as phenylene diisocyanates, diphenylene diisocyanates, tolylene diisocyanates, naphthylene diisocyanates, diphenylmethane diisocyanates, cyclohexane diisocyanates, ethylene diisocyanates, tetramethylene diisocyanates, hexamethylene diisocyanates, polyaryl polyisocyanates, trimers of polyisocyanates, polyisocyanates which are the reaction products of diisocyanates or triisocyanates with polyhydric alcohols and the like, and mixtures, trimers and isomers thereof.

The preferred polyurethanes are produced from monomers or trimers of aromatic diisocyanates which are fully blocked in order to advantageously avoid premature curing and yet obtain the rapid, uniform and complete curing required for good solvent resistance, heat stability and the numerous other properties needed for satisfactory electrical insulation.

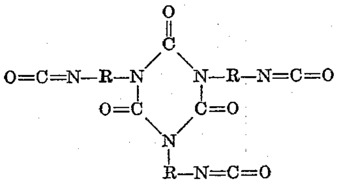
This preferred class of polyurethanes is made of the blocked reaction products of a polyhydric alcohol with an arylene diisocyanate. The polyhydric alcohols are in general limited to compounds containing not more than 16 carbon atoms and when used in wire enamels should preferably contain not more than 10 carbon atoms. Examples of these polyhydric alcohols are ethylene glycol, propylene glycol, glycerol, trimethylol propane, pentaerythritol, hexane-triols, etc. The class of polyurethanes is illustrated by the general formula



$$C_nH_{2n+2-m}(O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-X)_m$$

where R represents a member of the class consisting of the phenylene, methyl phenylene, naphthylene and methyl naphthylene groups, X represents a member of the class consisting of the phenyl and alkylphenyl groups, said alkyl groups containing 1–6 carbon atoms; *m* is an integer greater than 1 but not greater than *n* and *n* is an integer from 2 to 10. The polyurethane of the examples belongs to this class.

Another class of useful polyurethanes consists of blocked trimers of aromatic isocyanates and is illustrated by the general formula



where R is an aromatic hydrocarbon radical containing up to 13 carbon atoms, or an alkyl substitute thereof. The isocyanate groups are blocked with a reactive hydrogen containing compound such as phenol.

The melamine resins which can be used in the present wire enamel compositions can be selected from the general class of resinous aldehyde condensation products of melamine which are soluble in the organic liquids employed as solvents for the resinous components of the enamel. The useful melamine compounds include such derivatives of melamine as melam and melem. The aldehyde condensation products are well known and may be formed by reacting from 1–6 mols of the aldehyde with 1 mol of melamine. The solubility of the aldehyde-melamine condensation product is generally obtained by further reacting the condensation product with an alcohol or by co-condensing the melamine and aldehyde in the presence of an alcohol.

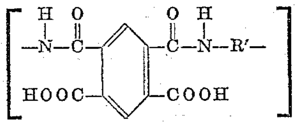
The usable aldehydes are aliphatic, aromatic cyclic and heterocyclic aldehydes including formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, valeraldehyde, octaldehyde, benzaldehyde, cinnamaldehyde, cyclohexanone, furfural, etc.

The alcohols which may be used include aliphatic, cycloaliphatic, aromatic, nitro and amino alcohols such as methanol, ethanol, propanol, isopropanol, butanol, isobutanol, pentanols, octanols, lauryl alcohol, cetyl alcohol, stearyl alcohol, cyclohexanol, benzyl alcohol, cinnamyl alcohol, allyl alcohol, 2-nitro-1-butanol, 2-nitro-2-methyl-1-propanol, 2-nitro-2-methyl-1,3-propane diol, 2-nitro-2-ethyl-1,3-propane diol, tris(hydroxymethyl)nitromethane, 2-amino-1-butanol, 2-amino-2-methyl-1-propanol, 2-amino-2-methyl-1,3-propane diol, 2-amino-2-ethyl-1,3-propane diol, tris(hydroxymethyl)aminomethane etc. Mixtures of two or more alcohols may be used if desired. The amounts of alcohol reacted are generally equal to or in excess of the formaldehyde on a molar ratio.

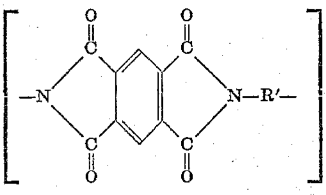
The preferred melamine resins are the further reaction products of the melamine aldehyde and alcohol reactants with an aryl sulfonamide. These products are also well known and may be obtained by co-condensation of all the reactants named, as taught in U.S. 2,508,875, which is hereby incorporated by reference. The useful aryl sulfonamides include benzene sulfonamide and the ring-substituted derivatives thereof such as toluene sulfonamides, chlorobenzene sulfonamides, nitrobenzene sulfonamides, etc.

For reasons of economy and availability, it is preferred to use the co-condensation products of melamine, toluene sulfonamide, formaldehyde and butanol. The proportions of reactants may be varied between the limits of 1 mol of melamine to from 0.1 to 1.0 of toluene sulfonamide and from 1 to 6 or more mols of formaldehyde. An excess of the formaldehyde may be used. The toluene sulfonamide may be any of the isomeric ortho, meta or para derivatives or it may be a mixture of two or more of the isomers.

The polyamides useful in this invention are the condensation products of tetracarboxylic aromatic acids with diamines and may be illustrated by the recurring structural unit



These polymers are soluble, and can be converted in situ, as mentioned earlier, by further heating into polyimide structures that are extremely resistant to solvents:



The pyromellitic acid residue incorporated in these formulae can be replaced of course with two ring tetracarboxylic acids, provided that the carboxyl groups of the latter compounds are arranged in two o-phthalic configurations. Meeting these requirements are, for example, the tetracarboxylic acids corresponding to naphthalene, diphenyl methane, 2,2′-diphenyl propane, diphenyl ether, diphenyl sulfide and diphenyl sulfone. The R′ of the formulae stands for a bivalent radical of either benzene, naphthalene, biphenyl, diphenyl ether, ditolyl ether, diphenyl sulfide, diphenyl sulfone, diphenyl methane, 2,2′-diphenyl propane, benzophenone, or from a low molecular weight saturated aliphatic hydrocarbon containing not more than six carbon atoms.

The preferred class of polyamides is limited to the condensation products of pyromellitic dianhydride with a diamine characterized by a lack of aliphatic hydrogen atoms and by the possession of a flexible linkage such as the ether group of 4,4′-oxydianiline. These polyamides should preferably be such that they show a viscosity ranging from about 1300 centipoises to 5000 centipoises for a 15% by weight solution in 1:1 dimethylacetamide and N-methylpyrrolidone at 25° C.

Some of the resinous coatings that may be used in this invention are the solid reaction products, cured at 250 to 450° C. of 100 parts by weight of a polyvinyl acetal resin, 2.5 to 100 parts of a phenol aldehyde resin, and when desired, 10 to 200 parts of a polyurethane with or without 0.5 to 20 parts of a melamine resin. Alternately the phenol-aldehyde resin may be excluded altogether from such compositions. The preferred balance of the properties required for insulated wire is obtained by the application of polyvinyl acetal resins containing, for each 100 parts of polyvinyl acetal, 5 to 80 parts of a phenol aldehyde resin, 5 to 80 parts of a polyurethane and 0.5 to 20 parts of a melamine resin, and of a polyamide resin made from pyromellitic dianhydride and 4,4′-oxydianiline. The actual compositions formulated for each wire can vary within these ranges and are dependent upon the number and type of component resins used and upon the ultimate properties desired.

The preferred number of coats of resins are four and two for the acetal resins and the polyamide resin respectively for heavy build magnet wire. This invention is not bound by these optimal figures, however. Under certain circumstances, wires with satisfactory properties can be made with an insulation cover of any thickness between 0.1 to 4 mils, this up to a point being a function of the wire diameter and the viscosity of the enamels, applied in 2 to 14 layers. As to the particular number of coats of a particular enamel, no restriction is intended to the four and two arrangement. Combinations of five coats of polyvinyl acetal resin and one coat of polyamide, for instance, have shown quite acceptable properties. As to the order of application of the resins, the examples have shown that while an outside covering of polyamide gives the best thermal results, the use of the polyamide as an undercoat to the polyvinyl acetal resin also achieves a great improvement in the significant wire properties.

These combinations of enamels may be used on any size of wire, on a variety of metals, and on other materials. Other non-electrical uses of this coating process are indicated where chemical resistance, temperature stability, smoothness, toughness, adherence to metal, resistance to abrasion or resistance to solvents is required of the finished coating.

Various other materials such as fillers, plasticizers, coloring agents, etc., as well as minor amounts of other resins such as polyesters and epoxies, may be incorporated in these enamels as is conventional in the art.

Other applications will readily suggest themselves to the many skilled in the art.

What we claim is:

1. A metal conductor coated with multiple layers of a cured polyvinyl acetal resin composition and of a polyimide composition comprising the condensation product of an aromatic tetracarboxylic acid with a diamino compound selected from the group consisting of aromatic diamines containing from 6 to 16 carbon atoms and saturated aliphatic diamines containing up to 6 carbon atoms.

2. A metal conductor coated with insulation of a thickness of 0.1 to 4.0 mils consisting of 2 to 14 layers of the resins of claim 1.

3. An insulated conductor comprising a metallic element coated with multiple layers of

(A) a resinous composition comprising, in parts by weight,

(1) 100 parts of the polyvinyl acetal of a saturated aliphatic aldehyde and

(2) 5 to 80 parts of a soluble, heat-hardenable alkylphenol-formaldehyde resin

(B) and of another resinous composition comprising the condensation product of an aromatic tetracarboxylic acid with a diamino compound selected from the group consisting of aromatic diamines containing from 6 to 16 carbon atoms and saturated aliphatic diamines containing up to 6 carbon atoms.

4. The conductor of claim 3 wherein the polyvinyl acetal is polyvinyl formal.

5. The conductor of claim 3 wherein the polyvinyl acetal composition is modified by the inclusion of 10 to 80 parts of a blocked organic polyisocyanate.

6. The conductor of claim 5 wherein the blocked polyisocyanate is the phenolic adduct of the reaction product of about one mol trimethylol propane with about three mols tolylene diisocyanate.

7. The conductor of claim 5 wherein the polyvinyl acetal composition is further modified by the inclusion of 0.5 to 20 parts of a melamine formaldehyde resin.

8. A process for producing a wire coated with 0.1 to 4.0 mil thick covering consisting of about 2 to 14 layers of insoluble and infusible resins, separately dried and cured at 250° to 450° C., originally applied by passing the wire through two liquid compositions comprising essentially, in parts by weight,

(A) in one of the compositions,

(1) 100 parts of a polyvinyl acetal resin obtained by the partial acetalization of polyvinyl alcohol with a member of the group consisting of formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde and mixtures thereof.

(2) 5 to 80 parts of a soluble, heat-hardenable phenol aldehyde resin obtained by condensing one mol of a phenol selected from the group consisting of phenol, cresol, xylenol, and mixtures thereof, with from 0.75 to 2.0 mols of formaldehyde, under alkaline conditions,

(3) 10 to 80 parts of a blocked organic polyisocyanate adduct of the general formula

$$C_nH_{2n+2-m}(—O—CO—NH—R—NH—CO—OX)_m$$

where R is a member of the class consisting of phenylene, methyl phenylene, dimethyl phenylene, naphthylene and methyl naphthylene groups, where X represents a member of the class consisting of phenyl and alkyl phenyl groups, said alkyl groups containing 1 to 6 carbon atoms, where *m* is an integer greater than 1 but not greater than *n*, and where *n* is an integer from 2 to 10;

(4) 0.5 to 20 parts of the co-condensation products of one mol melamine with from 0.1 to 1.0 mol of a toluene sulfonamide and from 1 to 6 or more mols formaldehyde, in the presence of butanol;

(B) and in the other composition, the polyamide condensation product of pyromellitic dianhydride with a diamino compound selected from the group consisting of aromatic diamines containing from 6 to 16 carbon atoms and saturated aliphatic diamines containing up to 6 carbon atoms.

9. A process for producing a wire coated with 0.1 to 4 mil thick covering consisting of about 2 to 14 layers of insoluble and infusible resins, separately dried and cured at 250–450° C., originally applied by passing the wire through two liquid compositions consisting essentially of, in parts by weight,

(A) for one of the compositions

(1) 100 parts of polyvinyl formal containing about 10.5% acetate groups calculated as polyvinyl acetate, about 6% hydroxyl groups calculated as polyvinyl alcohol, and about 83.5% formal groups calculated by difference as polyvinyl formal,

(2) 5 to 45 parts of a soluble, fusible, heat-hardenable reaction product of about 100 parts cresol, about 60 parts formalin and about 3.2 parts ethanolamine;

(3) 40 to 65 parts of the phenolic adduct of the reaction product of about one mol trimethylol propane with about three mols tolylene diisocyanate;

(4) 2.5 to 12.5 parts of the butylated internally plasticized condensation product of about one mol melamine with about 3.5 mols formaldehyde and about 0.5 mol para-toluene sulfonamide;

(5) 200 to 750 parts of cresylic acid

(6) 0 to 600 parts of naphtha

(B) and for the other composition, the polyamide condensation product of pyromellitic dianhydride with 4,4'-oxydianiline dissolved in equal volumes of dimethyl acetamide and N-methylpyrrolidone.

10. A metal conductor coated with insulation of a thickness of about 3 mils consisting of

(A) four layers of a resinous composition comprising, in parts by weight,

(1) 100 parts of a polyvinyl acetal resin obtained by the partial acetalization of polyvinyl alco-

hol with a member of the consisting of formaldehyde, propionaldehyde, butyraldehyde and mixtures thereof,

(2) 5 to 80 parts of a soluble, heat-hardenable phenol aldehyde resin obtained by condensing one mol of a phenol selected from the group consisting of phenol, cresol, xylenol, and mixtures, thereof, with from 0.75 to 2.0 mols of formaldehyde under alkaline conditions,

(3) 10 to 80 parts of a blocked organic polyisocyanate adduct of the general formula

$$C_nH_{2n+2-m}(\text{—O—CO—NH—R—NH—CO—OX})_m$$

where R is a member of the class consisting of phenylene, methyl phenylene, dimethyl phenylene, naphthylene and methyl naphthylene groups, where X represents a member of the class consisting of phenyl and alkyl phenyl groups, said alkyl groups containing 1 to 6 carbon atoms, where *m* is an integer greater than 1 but not greater than *n*, and where *n* is an integer from 2 to 10,

(4) 0.5 to 20 parts of the co-condensation products of one mol melamine with from 0.1 to 1.0 mol of a toluene sulfonamide and from 1 to 6 or more mols formaldehyde, in the presence of butanol, and

(B) two layers of the polyimide condensation product of pyromellitic dianhydride with a diamino compound selected from the group consisting of aromatic diamines containing from 6 to 16 carbon atoms and saturated aliphatic diamines containing up to 6 carbon atoms.

11. A metal conductor coated with insulation of a thickness of about 3 mils consisting of

(A) four layers of a resinous composition comprising, in parts by weight,

(1) 100 parts of a polyvinyl formal containing about 10.5% acetate groups calculated as polyvinyl acetate, about 6% hydroxyl groups calculated as polyvinyl alcohol, and about 83.5% formal groups calculated by difference as polyvinyl formal,

(2) 5 to 45 parts of a soluble, fusible, heat-hardenable reaction product of about 100 parts cresol, about 60 parts formalin and about 3.2 parts ethanolamine;

(3) 40 to 65 parts of the phenolic adduct of the reaction product of about one mol trimethylol propane with about three mols to tolylene diisocyanate;

(4) 2.5 to 12.5 parts of the butylated internally plasticized condensation product of about one mol melamine with about 3.5 mols formaldehyde and about 0.5 mol para-toluene sulfonamide; and

(B) two layers of the polyimide condensation product of pyromellitic dianhydride with 4,4′-oxydianiline.

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