Hiraoka et al.

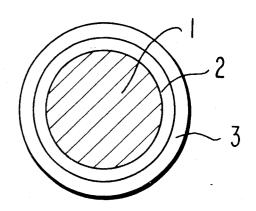
[45] **Sept. 16, 1975**

[54]	INSULAT	ED WIRE	2,787,561	4/1957	Sanders 117/232		
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[21]	Appl. No.:	394,611	Attorney, Agent, or Firm—Sughrue, Rothwell, I Zinn & Macpeak				
[30]	_	Application Priority Data 2 Japan 47-103340	[57]		ABSTRACT		
[52]		428/383; 260/29.6 T; 204/181; 427/118	baked laye	er of a spe	uitable as a magnet wire having a scific polyacryl resin as an under-		
[51] [58]		H01B 3/44 arch	for producing the insulated wire are disclosed. The in				
[56]	UNIT	References Cited ED STATES PATENTS					
2,191,	581 2/194	0 Nowak et al 117/218 X		26 Clain	s 2 Drawing Figures		

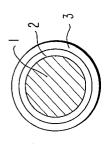
3,112,223	11/1963	Logemann et al 117/232
3,220,882	11/1965	Lavin et al 117/218
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3,406,045	10/1968	Sattler 117/218
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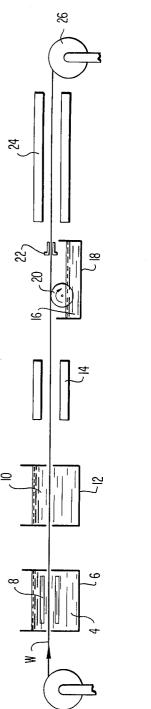
ACT

26 Claims, 2 Drawing Figures









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thermosetting polyester resin on the above polyacryl resin layer and to a process for producing such an insulated wire.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an insulated wire useful as a magnet wire for use in electric equipment such as motors, transformers and the like, and to a process for producing the insulated wire.

2. Description of the Prior Art

Most of the conventional magnet wires insulated with an insulating varnish heretofore in use generally do not satisfy all the critical properties recently required, except for magnet wires coated with recently developed heat resistant resins, such as the polyamideimides, and 15 techniques for multiple coating of the conductor with two or more different insulating materials have been proposed as disclosed in U.S. Pat. No. 3,022,200 and U.S. Pat. No. 3,702,813, etc.

Generally speaking, the multiple coating insulating 20 layer exhibits some advantages, i.e., the excellent properties possessed by specific layers included in the layers of multiple coatings compensate for the defects of the other layers. On the other hand, the excellent properties possessed by the layers sometimes can be masked 25 by the presence of other layers and, in some cases, the presence of other layers adversely affects the properties. For example, the difficulty of operations for uncovering the tip of the wire coated with a polyamideimide resin due to an excessively strong chemical resistance of the resin to a remover can be solved by providing a polyester layer under the polyamide-imide layer, but, due to the presence of the polyester layer the abrasion resistance, the heat resistance, etc., of the polyester-polyamide-imide dual coated wire are inferior to 35 those of a wire coated with the polyamide-imide alone. The thermoplastic polyester layer of the insulated wire wherein the thermoplastic polyester layer is coated on a baked thermosetting polyester layer functions to improve the heat-shock resistance and the abrasion resis- 40 tance properties of the baked polyester layer, but it lowers the cut through temperature of the insulated

As a result of extensive studies, it was surprisingly found that a dual insulating coating comprising a specific polyacryl resin layer having coated thereon a specific polyester resin layer exhibits excellent heat resistance properties over a coating of each of the above described resins and further it possesses well-balanced overall properties required for a coating of magnet wires. The present invention has been completed by a further investigation of the above unexpected finding.

SUMMARY OF THE INVENTION

A primary object of this invention is to provide an insulated wire having excellent heat resistance and wellbalanced overall properties required for magnet wires.

Another object of this invention is to provide a process for improving the heat resistance of the magnet wires

A further object of this invention is to provide a process for producing a magnet wire having excellent heat resistance and well-balanced overall properties for magnet wires.

More specifically, the present invention comprises an insulated wire having a baked layer of a specific polyacryl resin on a conductor and a baked layer of a specific

BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWINGS

FIG. 1 is an enlarged schematic sectional view of the dual coated wire prepared according to an embodiment of this invention.

FIG. 2 illustrates an example of the processing line for producing the dual coated wire according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Referring now to FIG. 1, the dual coated wire having an excellent heat resistance and well-balanced overall properties can be obtained by providing a baked insulating layer 2 of the polyacryl resin as hereinafter specified on a conductor 1, and further by providing a baked insulating layer 3 of the polyester resin as hereinafter specified on the layer 2.

The polyacryl resin which can be used in the present invention is a copolymer of (a) at least one compound (hereinafter, designated the a-component for brevity) represented by the formula (I):

$$\begin{array}{c|cccc}
H & R_1 \\
 & | & | \\
C = C \\
 & | & | \\
H & R_2
\end{array}$$
(I)

and (b) at least one compound (hereinafter, the b-component) of the formula (II):

$$\begin{array}{c|c}
H & R_3 \\
 & | & | \\
C = C \\
H & R
\end{array}$$
(II)

and (c) an unsaturated organic acid (hereinafter, the c-component) having 3 to about 30 carbon atoms and at least one double bond which is reactable with the double bond of the a-component or b-component.

In the formula (I) or (II), R_1 represents hydrogen atom and an alkyl group having 1 to about 30 carbon atoms, such as methyl, ethyl, propyl, butyl and the like, R₂ represents a cyano group, an aldehyde group and a carboxyalkyl ester group having 2 to about 30 carbon atoms, such as carboxymethyl ester, carboxyethyl ester, carboxypropyl ester, carboxybutyl ester and the like, R₃ and R₄ each represents a hydrogen atom, an amide group, a glycidyl ester group, glycidyl ether group and an organic group having 1 to about 30 carbon atoms selected from the group consisting of an alkyl group, such as methyl, ethyl, propyl, butyl and the like, an N-alkylamide group, such as N-methylamide, N-ethylamide, N-propylamide and the like, and an alkylol group, such as methylol, ethylol, propylol and the like, except that both R₃ and R₄ are not simultaneously a hydrogen atom or an alkyl group. When the number of carbon atoms of the above c-component and the R₁, R₂, R₃, or R₄ organic groups exceed about 30, the heat resistance of the resulting polyacryl resin tends to decrease and, therefore, the maximum number of carbon atoms of the c-component and the above R_1 , R_2 , R_3 , or R4 organic groups preferably does not exceed about 20.

Examples of the c-component are monobasic unsaturated acids, such as acrylic, crotonic, vinylacetic acid, methacrylic, tiglic, α -ethylacrylic, β -methylcrotonic, 2-pentenoic, 2-hexenoic, 2-heptenoic, 2-octenoic, 10undecenoic, 9-octadecenoic, cinnamic, atropic, α-ben- 5 zylacrylic, methyl atropic, 2,4-pentadienoic, 2,4hexadienoic, 2,4-dodecadienoic acid. 9.12octadecadienoic acid; dibasic unsaturated acids, such as maleic, fumaric, itaconic, citraconic, mesaconic, glutaconic, dihydromuconic, muconic; and tribasic un- 10 als in an amount greater than that described above resaturated acids, such as 1,2,4-tricarboxylic butene and

The polyacryl resin used in the present invention can be prepared by the well-known polymerization procedures such as an emulsion polymerization, a solution 15 polymerization, a suspension polymerization and the like as described, for example, in U.S. Pat. Nos. 2,787,561 and 3,509,033, and in "Acryl Resin" by Kou Asami, published by Nikkan Kogyo Shinbun, Tokyo, 1970, p. 25 to p. 27, using about 1 to 20 moles, prefera- 20 bly about 2 to 10 moles, or most preferably about 4 to 6 moles, of the a-component per one mole of the bcomponent and about 0.01 to 0.2 mole, preferably about 0.03 to 0.1 mole of the c-component per one mole of the a- and b- components, i.e., per mole of the 25 sum of the moles of the a-component and the bcomponent.

Among the above described a-, b-, c-components, more preferred examples are those components in which the total number of carbon atoms is less than 15 30 from the standpoint of the heat resistance of the polyacryl resin obtained. More preferred examples of the a-component are acrylonitrile, methacrylonitrile, methylacrylate, ethylacrylate, propylacrylate, butylaethylmethacrylate, methylmethacrylate, propylmethacrylate, and acrolein. More preferred examples of the b-component are glycidylacrylate, glycidylmethacrylate, allylglycidylether, acrylamide, methacrylic acid, α-ethylacrylic acid, crotonic acid, maleic acid, and fumaric acid.

The polyacryl resin employed in the present invention may also be those modified with one or more of styrene and its derivatives or diolefins. As the derivatives of styrene, there are employed those compounds in which the phenyl group of styrene is substituted with at least one group selected from the group consisting of a cyano group, a nitro group, a hydroxy group, an amine group, a vinyl group, a phenyl group, a halogen atom such as chlorine, bromine, etc., an organic group having 1 to 20 carbon atoms, such as an alkyl group, an aralkyl group, an N-alkylamine group. Examples of the above alkyl groups are methyl, ethyl, propyl, butyl, 55 etc., and examples of the above aralkyl groups are benzyl, α - or β -phenylethyl, etc., and examples of the above N-alkylamine groups are N-methylamine, Nethylamine, N-propylamine, etc. Among the styrene derivatives, those which have 1 to 3 substituent groups are preferable because of their ready reactivity with the a- to c-components. Preferable examples are methyl styrenes, ethyl styrenes, divinyl benzenes, chlorostyrenes. As the diolefins used as a modifying agent, those compounds are used whose total number of carbon 65 atoms is 3 to about 20, preferably 4 to about 10. Examples of the above diolefins are the butadienes, pentadienes, methyl-butadienes and the like.

Polyacryl resins modified with those modifying agents can be prepared using well-known polymerization methods previously described using a starting material mixture containing one or more of the above modifying materials in addition to a-, b-, and ccomponents. However, the amount of styrene and its derivatives or diolefins should be restricted to about 2 moles or one mole or less, respectively, per one mole of the a-component, since use of the modifying materisults in the formation of a polyacryl resin poor in flexibility in the case of styrenes, and in the formation of polyacryl resin poor in the cut through temperature in the case of the diolefins.

In the present invention, a polyacryl resin (including the modified resin) having a degree of polymerization of approximately about 10,000 to about 1,000,000 is used, since a polyacryl resin having too low a degree of polymerization is lacking in toughness, and, in turn a polyacryl resin having too high a degree of polymerization tends to result in a somewhat uneven coating surface due to a poor fluidity of the resin in the uncured state. Therefore, more preferable polyacryl resins are those having a degree of polymerization of about 100,000 to about 500,000.

The polyacryl resin employable in this invention prepared by any one of the prior art processes can be coated on a conductor in the form of a dispersion or a solution in water or in an appropriate organic solvent such as N-methyl-2-pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide and the like using a polymer concentration of about 5 to about 50, preferably about 10 to about 30% by weight and subsequently the coating can be baked at a temper-35 ature ranging from about 100°C to about 600°C, preferably about 200°C to 500°C, whereby a tough insulating film can be formed on the conductor by crosslinking.

The polyester resin used in the present invention is a ferred examples of the c-component are acrylic acid, 40 copolymer of (d) at least one terephthalic acid compound and its derivatives, generally represented by the Formula (III);

$$R_5$$
 OC \longrightarrow \bigcirc \bigcirc COR₆ (III)

and (e) a mixture of polyols represented by the Formula (IV);

$$R_7$$
— $(OH)_n$ (IV)

the mixture comprising at least one diol (that is, n in the Formula (IV) is 2) and at least one compound of tri- and/or tetraol (that is, n in the Formula (IV) is 3 or 4), and containing the diol(s) in an amount of about 40 to 97% equivalents in this polyol mixture.

In the polymerization between a compound represented by Formula (III) and a mixture of polyols represented by Formula (IV), the same polyester resin is obtained whether terephthalic acid or a derivative thereof is used as the compound of Formula (III), in other words, in spite of wide variation in R₅ and/or R₆ of the same formula. As a result, a broad range of R5 and R6 components can be used in that R₅ and R₆ are removed as condensation by-products in the course of the polymerization. Therefore, in the present invention, as R₅ and R₆ of Formula (III), various kinds of groups well-known to those in the art can be employed and are suitable. Examples of R₅ and R₆ groups are hydroxyl groups, amino groups, halogen atoms, such as chlorine, bromine, etc., alkoxy groups, such as methoxy, ethoxy, propoxy, butoxy, etc., N-alkylamino groups, such as N-methylamino, N-ethylamino, etc., aryloxy groups such 10 as phenoxy groups. However, from the standpoint of reactivity of the terephthalic acid derivatives with the polyol mixture, R₅ and R₆ groups having a total number of carbon atoms less than about 10, especially less than about 5, are preferred.

In the Formula (IV), n is a positive integer of 2 to 4, and R_7 represents saturated or unsaturated hydrocarbon group having 1 to 10 carbon atoms. When the above n in the Formula (IV) is 2, 3, or 4, the valency of R_7 becomes divalent, trivalent, or tetravalent, respectively.

Examples of divalent R₇ groups are alkylene, alkenylene, alkylidene or alkenylidene groups alkylene or alkenylene groups of which one or two hydrogen atoms on one or both end carbon atoms can be replaced by one or two alkyl groups or alkenyl groups, alkylidene or alkenylidene groups of which one hydrogen atom of the end carbon atom having two free valencies can be substituted with one alkyl group or alkenyl group, and the like.

Examples of trivalent R₇ groups are alkane-yl-ylidene groups or alkane-yl-ylidene groups, the above groups of which one hydrogen atom of the end carbon atom having two free valencies can be replaced by one alkyl group or alkenyl group, or of which one or two hydro- 35 gen atoms of another end carbon atom can be replaced by one or two alkyl or alkenyl groups, alkylene or alkenylene groups of which a hydrogen atom of one end carbon atom is replaced by one alkylene, alkenylene, alkylidene, or alkenylidene group, or of which a hydrogen atom of both end carbon atoms are replaced by one alkyl or alkenyl group and one alkylidene or alkenylidene group, alkylene or alkenylene group of which an inner carbon atom between both end carbon atoms is substituted with one alkylene or alkenylene group and 45 one alkyl or alkenyl group and the like.

Examples of tetravalent R7 groups are alkenedivlidene groups or alkene-divlidene groups, the above groups of which one hydrogen atom of one or both end carbon atoms is replaced by one alkyl group or alkenyl group, alkane-yl-ylidene or alkene-yl-ylidene groups of which a hydrogen atom of one end carbon atom are replaced by one alkylene, alkenylene, alkylidene or alkenylidene group, alkylene or alkenylene groups of which a hydrogen atom of an end carbon atom and another end carbon atom, are substituted with one alkylene, alkenylene, alkylidene or alkenylidene group, or of which an inner carbon atom between the both end carbon atom is substituted with two alkylene or alkenylene groups, and the like. The above hydrocarbon group may contain in its carbon chain a hetero atom such as oxygen, nitrogen and the like or at least one, preferably 1 to 5, four to eight membered heterocyclic ring, such as a pyrazine ring, a pyrazole ring, a triazine ring, etc., or 1 to 5 benzene type rings, such as phenylene, phenylene ether, and may also be substituted with at least 1, preferably 1 to 5, phenyl groups and/or aralkyl groups having about 7 to 10 carbon atoms such as benzyl groups.

Examples of the above polyols which can be used in the preparation of the polyesters are aliphatic diols such as ethylene glycol, propylene glycol, butane diol and the like, aromatic ring-containing diols such as 2,2bis(p-hydroxyethoxyphenyl)propane and the like, triols such as glycerine, 1,1,1-trimethylolethane, 1,1,1trimethylolpropane, tris-2-hydroxyalkyl isocyanurate and the like, and tetraols such as pentaerythritol and the like. When the amount of the diol in the polyol mixture is greater than about 97% equivalents, the cut through temperature of the resulting polyester resin tends to decrease, and, on the other hand, when the amount of the diol is lower than about 40%, a reduction in flexibility of the polyester resin tends to result. Thus, the polyol mixture preferably contains about 45 to 90% equivalents of the diols. The polyester resins can be prepared using well-known polymerization techniques, e.g., a solution polymerization as described in U.S. Pat. No. 3,296,024. In the polymerization of terephthalic acid or its derivatives with the polyol mixture, isophthalic acid or its derivatives in an amount less than about 60 moles per 100 moles of terephthalic acid of the Formula (III) may be added in the polymerization reaction. As derivatives of isophthalic acid, those corresponding to the derivatives of terephthalic acid described above can be employed. Particularly preferred polyester resins are those obtained by reacting about 25 to 56 % equivalents of terephthalic acid or a derivative thereof with about 15 to 46% equivalents of ethylene glycol and about 7 to 22% equivalents of glycerine and about 7 to 22% equivalents of tris-2-hydroxyethyl isocyanurate. In the above reaction, the proportion of glycerine and tris-2-hydroxyethyl isocyanurate can be varied as long as the sum of equivalents of glycerine plus tris-2-hydroxyethyl isocyanurate is about 14 to 44%.

The polyester resins which can be used in the present invention can be a modified polyester resin containing not greater than 70 imide groups or the sum of the amide groups plus the imide groups per 100 ester linkages in the resin. Modified polyester resins can be prepared by using an imide- or amide-imide-containing substance in the reaction between terephthalic acid or a derivative thereof and a polyol mixture. Alternatively, the modified polyester resins can also be prepared by reacting an imide- or amide-imide-containing substance with a polymerization product having a low degree of polymerization of about 1 to about 10 between terephthalic acid or a derivative thereof and the polyol mixture. Such an imide- or amide-imidecontaining substance can be obtained, for example, by reacting a polybasic acid or its anhydride higher than tribasic acid as disclosed in U.S. Pat. Nos. 3,489,696, 3,471,444 and 3,485,796 such as trimellitic anhydride, pyromellitic dianhydride, butane tetracarboxylic dianhydride, with a diamine as disclosed in U.S. Pat. No. 3,480,588 such as 4,4'-diaminodiphenyl methane, 4,4'diaminodiphenyl ether, hexamethylenediamine, and/or a diisocyanate as disclosed in U.S. Pat. No. 3,489,696 such as 4,4'-diisocyanate-diphenyl methane, 4,4'diisocyanate-diphenyl ether, hexamethylene diisocyanate. Preferred imide- or amide-imide-containing substances are those having a low degree of polymerization, containing imide groups or the sum of amide and imide groups of 1 to 2, to a degree of polymeri-

zation about 10. Substances having such a degree of polymerization can easily be prepared by adjusting the molar ratio of starting materials and polymerization conditions such as temperature and period of polymerization. An alternative procedure of introducing the 5 imide groups or amide and imide groups into the polyester resin comprises dissolving the above described imide- or amide-imide-containing substance, a polyamide-imide resin, or a polyamic acid resin which is a precursor of the polyimide together with the polyester 10 resin in a suitable solvent, such as phenol, cresol, xylenol, N-methyl-2-pyrollidone, N,N-dimethylacetamide and the like, applying the resulting varnish on a conductor, and baking the varnish. In this case, the polyester resin reacts with the above additive upon baking 15 whereby the imide groups or amide-imide groups are introduced into the polyester resin.

In the present invention, a polyester resin (including the modified resins) having a degree of polymerization of approximately about 2 to 200 is used, since a polyester resin having too low a degree of polymerization lacks toughness, and a polyester resin having too high a degree of polymerization tends to gel in the preparation of a varnish thereof. Therefore, more preferable polyester resins are those having a degree of polymerization ranging from about 10 to 50.

The polyester resin used in the present invention forms a tough insulating layer by crosslinking when a dispersion or solution thereof in a solvent such as water, phenol, cresol, xylenol, N-methyl-2-pyrollidone, ³⁰ N,N-dimethylacetamide and the like in a polymer concentration of about 5 to about 50%, preferably about 15 to about 45% by weight is applied to a conductor and baked at a temperature ranging from about 100°C to about 600°C, preferably about 200°C to about ³⁵ 500°C.

In the present invention, the layer thickness of both the under-layer and the upper-layer can be varied freely, but the layer thickness of the under-layer is preferably from about 1 to 300 μ , particularly, from about 5 to 100 μ and the thickness of upper-layer is preferably from about 0.3 to 100 μ , particularly, from about 2 to 50 μ . The particularly preferred heat resistance and the well-balanced overall properties as an insulated wire for coils can be obtained when the thickness ratio of the under-layer to the upper-layer is within the range of from about 0.1 to 30, preferably from about 7 to 15.

In producing an insulated wire according to the present invention, the layer of the polyacryl resin and the layer of the polyester resin can be formed on a conductor using any conventional procedure such as, for example, by a well-known coating method such as dipcoating, spray-coating, brush-coating or using electrodeposition coating as described in Wire World, vol. 13, May/June, page 69, 1971, and Wire, vol. 40, No. 6, page 832, 1965, followed by baking according to a conventional baking procedures. The polyester resin varnish can be applied onto an uncured or cured polyacryl resin layer, and baked together with the uncured or already cured polyacryl resin layer. In using either a separate or a simultaneous baking of the polyacryl resin layer and polyester resin layer, the baking can generally be carried out at a temperature ranging from about 200°C to 600°C. It is preferred to dry the coated wire 65 at a temperature below about 200°C prior to the baking since the tendency of blistering of the coating layers which is frequently observed in baking without previ8

ous drying, can effectively be prevented. The above described drying prior to the baking is desirable when the insulated wire is produced at a rate higher than about 50 m per minute.

However, in a preferred embodiment for advantageously, especially economically, producing an insulated wire of high quality, the polyacryl resin is first electrodeposited on a conductor, and then the polyester resin film is formed thereon using electrodeposition coating or the dip-coating of a polyester resin varnish.

The process for producing the insulated wire according to the present invention is hereinafter described in greater detail by reference to FIG. 2 in a preferred embodiment comprising coating a conductor with a polyacryl resin by electrodeposition coating and then applying a polyester varnish by dip-coating to the polyacryl resin film.

Referring to FIG. 2, a conductor W such as copper, aluminum and the like which is connected to the positive terminal of a D.C. power supply (not shown) is passed through an electrodeposition bath 6 filled with a polyacryl resin varnish 4 in the form of an aqueous solution or an aqueous dispersion. A cylindrical cathode 8 is mounted in the electro-deposition bath 6, and the polyacryl resin particles from the varnish are deposited uniformly on the conductor W by electro-phoresis due to the potential difference between the conductor, as the anode, and the cathode while the conductor passes through the cathode. As a polyacryl resin varnish used in the electrodeposition coating, suitable varnishes may be used, such as the emulsified product per se of a polyacryl resin prepared by the emulsion polymerization process described in U.S. Pat. Nos. 2,787,561 and 3,509,033, an aqueous solution of a polyacryl resin together with, if necessary, an amine disclosed in U.S. Pat. No. 3,230,162, and a water dispersion of a polyacryl resin having particle size of about 0.01μ to about 1.0μ in diameter with a well-known surface active agent.

The electrodeposition coating using the above described polyacryl resin in the present invention can be carried out under the conditions well-established in the art as described in U.S. Pat. No. 3,378,477. That is, the polyacryl resin varnish containing from about 5 to 50% by weight of a polyacryl resin can be used with a load voltage of from about 10 to 200 V for the aqueous solution varnish and from about 1 to 50 V for the aqueous dispersion varnish. In the electrodeposition coating, an A.C. current can be superposed on the D.C. current. The conductor W having coated thereon the electrodeposited coating of the polyacryl resin can then be dried and baked, or can be directly subjected to the overcoating of the polyester resin varnish. However, it is preferred, in particular, when the polyacryl resin varnish is in the form of an aqueous dispersion, that the polyacryl resin coated conductor be passed through an organic solvent bath 12 filled with an organic solvent 10 which is capable of dissolving water to an extent of at least about 1% by weight, preferably at least about 10% by weight and which is capable of at least swelling, preferably, dissolving the polyacryl resin deposited on the conductor prior to the heat-drying or the crosslinking of the resin. In this manner, the water contained in the polyacryl resin deposited on the conductor is eluted into the organic solvent and, at the same time, a portion of the organic solvent penetrates into the deposited polyacryl resin layer during the passage of the conductor

through the organic solvent bath, whereby the penetrated solvent retained in the resin layer serves to render the film more uniform with less pinholes by swelling or dissolving the resin until it is removed in a subsequent evaporation step. The treatment with the organic solvent should preferably be accomplished while the polyacryl resin deposited on the conductor remains wet by a medium for the polyacryl resin varnish (in this embodiment, water), or a poor result will be obtained if the treatment is carried out after the deposited polyacryl resin is dried.

Also, since the treatment with the organic solvent is not effective on the semi-cured or completely cured polyacryl resin, it is necessary that the organic solvent used be capable of at least swelling the polyacryl resin 15 before the semi-cured stage. Examples of such organic solvents both dissolving water and swelling and/or dissolving the resin are monohydride or polyhydric alcohols such as methanol, ethanol, propanol, ethylene glycol, glycerine and the like, cellosolves such as ethylene 20 glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol isopropyl ether, ethylene glycol monobutyl ether, ethylene glycol diethyl ether, ethylene glycol dibutyl ether, ethylene glycol monophenyl ether and the like, nitrogen-containing organic solvents 25 such as N,N-dimethylformamide. N.Ndimethylacetamide, N-2-methylpyrrolidone and the like, sulfur-containing organic solvents such as dimethylsulfoxide, etc. In particular, N,N-dimethylformamide. N,N-dimethylacetamide, N-2-methylpyrrolidone and 30 dimethylsulfoxide are preferred.

In a preferred and particularly, advantageous embodiment of this invention, a D.C. voltage of from about 30 to 500 V with or without an A.C. voltage superposed thereupon lower than the D.C. voltage is applied between a cathode (not shown) mounted in the bath 12 and the conductor W passing through the cathode. In this manner, the water in the deposited layer can be removed uniformly and effectively so as to give an insulated wire having more stable qualities.

As an alternative procedure for treatment of the deposited resin layer with an organic solvent, the deposited resin layer can be exposed to an organic solvent vapor or the organic solvent can be sprayed on the deposited resin layer, etc. as described in British Pat. No. 1,169,447.

It is preferred to continuously remove any excess of the bath liquid 4 and the bath liquid 10 adhering to the resin layer by providing a wiping means such as an airwiper, roll-wiper and the like at the outlet of the electrodeposition bath 4 and the organic solvent bath 12. The adhering liquid sometimes prevents a high speed operation of the electrodeposition coating of the polyacryl resin, because of blistering of the adhering liquid in the baking process and such a wiping means eliminates the liquid so as to permit a conductor line speed of greater than about 50 m per minute.

The conductor from the organic solvent bath 12 is then introduced into a drying means 14 where the conductor is heated and the organic solvent from the bath 12 and water remaining in the resin layer in those methods retaining water are removed by evaporation. The drying temperature in the drying means 14 varies somewhat depending upon the type of the organic solvent, but generally ranges from about 60° to 200°C, preferably from about 100° to 200°C. In the drying means 14, an elevated temperature (for example, about 200°C to

600°C) can be used for promoting the removal of liquids and at the same time for curing or semi-curing the polyacryl resin deposited on the conductor. Alternatively, the last portion of the drying means 14 can be maintained at the temperature required for curing the polyacryl resin or a baking means can be provided separately at the end of the drying means, whereby the polyacryl resin layer is first dried at a relatively low temperature, i.e., about 100°C and then cured or semicured at a high temperature. The above-described procedure where the drying and baking are conducted separately is particularly preferred for prevention of blistering due to the rapid evaporation of the liquid from the polyacryl resin layer. The conductor from the drying means 14 is then passed on the bath 18 filled with a polyester resin varnish 16 while contacting a roll 20 which is mounted in the bath 18 and rotates freely. While passing on the roll 20, the polyacryl resin layer on the conductor is over-coated with a polyester resin varnish 16 by the roll 20, and an excess of the varnish 16 is wiped by a metering device 22 such as a metal die which is fixedly mounted downstream of the roll 20. The conductor W which has been dual coated with the polyacryl resin and the polyester resin is sent to a baking oven 24 and both layers (or the polyester layer alone when the polyacryl resin layer has already been baked) are baked and cured. The baking temperature of the baking oven 24 can be approximately the same whether both polyacryl and polyester layers are baked simultaneously or only the polyester resin layer is baked and generally is in the range of from about 200° to 600°C. The conductor from the baking oven can be immediately wound on a reel 26 or, if necessary, the conductor may be repeatedly passed several times through the polyester resin bath 18 and the baking oven 24 in order to obtain a desired layer thickness of the polyester resin layer.

In place of the application of the polyester resin as described above, the polyester resin can be coated on the polyacryl resin layer using electrodeposition coating under conditions and procedures similar to those described for the electrodeposition of the polyacryl resin layer using an electrodeposition varnish of the polyester resin in the form of an aqueous dispersion or an aqueous solution containing about 5 to 50% by weight of the polyester resin.

The following examples illustrate in greater detail the insulated wires of the present invention and their excellent properties as well as the process for the production of the insulated wires, but they are not to be construed as limiting the scope of this invention.

The coating materials containing polyacryl resins or polyester resins were prepared according to the following procedures. Of these coating materials, "Acryl-A" to "Acryl-L" and "Polyester-A" to "Polyester-I" are polyacryl resins and polyester resin coating materials, respectively, suitable for the present invention, and "Acryl-M" and "Polyester-J" were prepared for the purpose of comparison.

[Polyacryl-A]

A monomer mixture consisting of 5 moles of acrylonitrile, 1 mole of acrylic acid, 0.3 mole of glycidylmethacrylate, 760 g of deionized water, 7.5 g of sodium lauryl sulfate, and 0.13 g of sodium persulfate were charged into a flask, and stirred under a nitrogen stream at room temperature for 15 to 30 minutes.

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Thereafter the mixture was reacted at a temperature of 50° to 60°C for a period of 4 hours to obtain an acryl varnish as an aqueous dispersion.

[Polyacryl-B]

The acryl varnish was prepared in the same manner as described in the preparation of Polyacryl-A but using a monomer mixture consisting of 5 moles of acrolein, 1 mole of methacrylic acid and 0.3 mole of acrylic amide in place of the monomer mixture of Polyacryl-A. 10

[Polyacryl-C]

The acryl varnish was prepared in the same manner as described in the preparation of Polyacryl-A but using a monomer mixture consisting of 5 moles of ethylacrylate, 1 mole of acrylic acid, 0.3 mole of methylol acrylamide, 1200 g of deionized water, 12 g of sodium lauryl sulfate and 0.2 g of sodium persulfate.

[Polyacryl-D]

The acryl varnish was prepared in the same manner as described in the preparation of Polyacryl-A but using 5 moles of acrylonitrile, 1 mole of maleic acid, 0.3 mole of glycidyl methacrylate, 840 g of deionized water, 8 g of sodium lauryl sulfate and 0.15 g of sodium persulfate.

[Polyacryl-E]

The acryl varnish was prepared in the same manner 30 as described in the preparation of Polyacryl-A but using 5 moles of ethylacrylate, 1 mole of maleic acid, 0.3 mole of glycidyl acrylate, 1300 g of deionized water, 13 g of sodium lauryl sulfate and 0.2 g of sodium persulfate.

[Polyacryl-F]

The acryl varnish was prepared in the same manner as described in the preparation of Polyacryl-A but using a monomer mixture consisting of 5 moles of 40 methacrylonitrile, 1 mole of methacrylic acid, 0.3 mole of methylol acrylamide, 900 g of deionized water, 9 g of sodium lauryl sulfate and 0.2 g of sodium persulfate.

[Polyacryl-G]

The acryl varnish was prepared in the same manner as described in the preparation of Polyacryl-A but using 5 moles of methacrylonitrile, 1 mole of maleic acid, 0.3 mole of allyl glycidyl ether, 970 g of deionized water, 10 g of sodium lauryl sulfate and 0.15 g of sodium persulfate.

[Polyacryl-H]

The acryl varnish was prepared in the same manner as described in the preparation of Polyacryl-A but using 3 moles of acrylonitrile, 2 moles of ethylacrylate, 0.5 mole of acrylic acid, 0.5 mole of methacrylic acid, 0.2 mole of glycidyl methacrylate, 0.1 mole of acrylamide, 950 g of deionized water, 9.5 g of sodium lauryl sulfate and 0.16 g of sodium persulfate.

[Polyacryl-I]

The acryl varnish was prepared in the same manner as described in the preparation of Polyacryl-A but using 5 moles of methylmethacrylate, 0.5 mole of acrylic acid, 0.5 mole of methacrylic acid, 0.2 mole of glycidyl methacrylate, 0.1 mole of acrylamide, 1200 g

of deionized water, 12 g of sodium lauryl sulfate and 0.2 g of sodium persulfate.

[Polyacryl-J]

the acryl varnish was prepared in the same manner as described in the preparation of Polyacryl-A but using 5 moles of butyl acrylate, 0.5 mole of acrylic acid, 0.5 mole of methacrylic acid, 0.2 mole of glycidyl methacrylate, 0.1 mole of acrylamide, 1500 g of deionized water, 15 g of sodium lauryl sulfate and 0.25 g of sodium persulfate.

[Polyacryl-K]

The acryl varnish was prepared in the same manner as described in the preparation of Polyacryl-A but using 5 moles of acrylonitrile, 1 mole of acrylic acid, 0.3 mole of glycidyl methacrylate, 2 moles of styrene, 1200 g of deionized water, 12 g of sodium lauryl sulfate and 0.2 g of sodium persulfate.

[Polyacryl-L]

The acryl varnish was prepared in the same manner as described in the preparation of Polyacryl-A but 25 using 3 moles of acrylonitrile, 2 moles of ethyl acrylate, 0.5 mole of acrylic acid, 0.5 mole of methacrylic acid, 0.2 mole of glycidyl methacrylate, 0.1 mole of acrylamide, 1 mole of 1,3-butadiene, 1100 g of deionized water, 11 g of sodium lauryl sulfate and 0.18 g of sodium persulfate.

[Polyacryl-M]

The acryl varnish was prepared in the same manner as described in the preparation of Polyacryl-A but using 2 moles of styrene, 5 moles of ethyl acrylate, 1400 g of deionized water, 14 g of sodium lauryl sulfate and 0.2 g of sodium persulfate.

The concentration of a polyacryl resin in each of the above Polyacryl-A to Polyacryl-M varnishes was about 30% by weight.

[Polyester-A]

The polyester resin was prepared from the following composition:

Dimethyl Terephthalate 223.1 g (46% equivalents) Ethylene Glycol 48.1 g (31% equivalents) Glycerin 35.2 g (23% equivalents)

A mixture of the above composition and 50 g of xylol was charged into a four-necked flask equipped with a thermometer, a stirrer and a Liebig condenser. The flask was then heated to a temperature of about 130°C over 30 minutes while introducing nitrogen gas through an additional inlet, with the methyl alcohol formed in the course of the reaction being removed continuously from the flask as an azeotropic mixture with the xylol. At this point, lead acetate was added to the reaction mixture in an amount equivalent to about 0.03% by weight based on the weight of dimethyl terephthalate, and the heating was continued for additional 3.5 hours at the end of which time the temperature of reaction mixture reached 240°C. To the resulting hot resin was then added cresol in an amount sufficient to obtain a resin solution having a solids content of 44.8% by weight.

[Polyester-B]

52.4 g of 4,4'-diisocyanate-dicyclohexylmethane, 57.6 g of trimellitic anhydride and 250 g of cresol were heated in a flask at a temperature of 70° to 75°C for a 5 period of 5 hours while stirring. To the resulting solution was then added an excess of acetone to precipitate a resin.

388 g (39.8% equivalents) of dimethyl terephthalate, 137 g (35.8% equivalents) of propylene glycol, 75 g 10 (24.4% equivalents) of glycerin, 337 g of the above resin precipitate and xylene were then charged into a flask, and lead acetate was added to the mixture in an amount of 0.05% by weight based on the amount of dimethyl terephthalate. The mixture was then heated at 15 a temperature of 150°C under a nitrogen stream for 10 hours to obtain a polyesteramide-imide resin. The resin was diluted with cresol to a solids content of 40% and zinc octoate was added in an amount sufficient to adjust to a zince content of 0.2% by weight to obtain the 20 desired varnish.

[Polyester-C]

The polyester varnish was prepared in the same manner as described in the preparation of Polyester-A but 25 using 43.5 g (10% equivalents) of tris-2-hydroxyethyl isocyanurate and 19.9 g (13% equivalents) of glycerin in place of 35.2 g (23% equivalents) of glycerin to obtain a varnish having a solids content of 40% by weight.

[Polyester-D]

The polyester varnish was prepared in the same manner as described in the preparation of Polyester-B but using 33.6 g of hexamethylene diisocyanate in place of 52.4 g of 4,4'-di-isocyanate-dicyclohexylmethane and 51.6 g of butane tricarboxylic anhydride in place of 57.6 g of trimellitic anhydride.

[Polyester-E]

The polyester varnish was prepared in the same manner as described in the preparation of Polyester-A but using 223.1 g (46% equivalents) of dimethyl terephthalate, 31.0 g (20% equivalents) of ethylene glycol, 20.9 g (11% equivalents) of propylene glycol, 19.9 g (13% equivalents) of glycerin and 22.3 g (10% equivalents) of 1,1,1-trimethylolpropane to obtain a varnish having a solids content of 30% by weight.

[Polyester-F]

150 g of trimellitic anhydride was dissolved in 500 g of cresol at a temperature of 150°C and, after the anhydride was completely dissolved, 60 g of 4,4′-diaminediphenylmethane was added to the resulting solution. The mixture was then stirred for 6 hours at a temperature of 140°C and allowed to cool to obtain a pale yellow precipitate. The precipitate was filtered and washed several times with ethanol and ether to obtain an imide-group containing substance.

Separately, 388 g (39.8% equivalents) of dimethyl terephthalate, 163 g (36.0% equivalents) of 1,4-butanediol and 75 g (24.2% equivalents) of glycerin were reacted in the same manner as described in the preparation of Polyester-A to obtain a polyester resin.

137 g of the above imide-group containing substance was then added to the polyester resin, and the mixture was heated at a temperature in the range of from 180° to 215°C until a homogeneous mixture where the

imide-group containing substance was completely integrated with the polyester resin was obtained. Then, 1.8 g of cadmium acetate was added to the mixture and the resulting mixture was heated at a temperature of 215°C for 3 hours in vacuo. 450 g of cresol and 27 g of a cresol solution containing 9 g of butyl titanate were added followed by cresol to obtain a varnish having a solids content of 37% by weight.

[Polyester-G]

The polyester varnish was prepared in the same manner as described in the preparation of Polyester-F but using 70 g (22.5% equivalents) of ethylene glycol and 51 g (13.3% equivalents) of propylene glycol in place of 163 g (36.0% equivalents) of 1,4-butanediol and 45 g (14.6% equivalents) of glycerin and 85 g (9.8% equivalents) of tris-2-hydroxyethylisocyanurate in place of 75 g (24.2% equivalents) of glycerin to obtain a varnish having a solids content of 37% by weight.

[Polyester-H]

The polyester varnish was prepared in the same manner as described in the preparation of Polyester-A but 25 using 195.0 g (40.2% equivalents) of dimethyl terephthalate, 28.1 g (5.8% equivalents) of dimethyl isophthalate, 31.0 g (20.0% equivalents) of ethylene glycol, 13.5 g (6.0% equivalents) of 1,4-butanediol and 42.9 g (28% equivalents) of glycerin to obtain a varnish having a solids content of 43% by weight.

[Polyester-I]

The polyester varnish was prepared in the same manner as described in the preparation of Polyester-A but using 223.1 g (46.0% equivalents) of dimethyl terephthalate, 38.8 g (25.0% equivalents) of ethylene glycol, 13.5 g (6.0% equivalents) of 1,4-butanediol, 30.7 g (20.0% equivalents) of glycerin, 5.1 g (3.0% equivalents) of pentaerythritol to obtain a varnish having a solids content of 30% by weight.

[Polyester-J]

98 g (23.8% equivalents) of maleic anhydride, 148 g (23.8% equivalents) of phthalic anhydride and 233 g (52.4% equivalents) of diethylene glycol were reacted in a manner similar to that described in the preparation of Polyester-A but using about 0.02 g of hydroquinone as a polymerization inhibitor and a sufficient amount of styrene to obtain a polyester resin solution having a solids content of 50% by weight.

EXAMPLE 1

A copper conductor having a diameter of 0.3 mm 55 was coated with Polyacryl-A by the conventional dipcoating procedure using a horizontal coating machine and a metal die, and the coated conductor was then baked at a line speed of 40 m/minute at a temperature of 400°C. The above procedure was repeated five times to form an insulating under-layer having a layer thickness of 22 μ on the copper conductor. Polyester-A was then coated on the insulating under-layer at a lined speed of 40 m/minute and the coated conductor was baked one time at a temperature of 450°C to form an insulating upper-layer having a layer thickness of 3 μ to obtain a dual coated wire having a total insulating coating thickness of 25 μ.

EXAMPLE 2

A copper conductor having a diameter of 0.3 mm as an anode was coated with Polyacryl-B by employing conventional electrodeposition coating using a hori- 5 zontal coating machine at a line speed of 40 m/minute under the following conditions:

Cathode: A copper cylindrical tube of 6 cm in diameter and 30 cm in length

Distance between Electrodes: 3 cm Electrodeposition Voltage: 5V D.C. Varnish Temperature: 30 ± 1 °C

The coated conductor was then passed through a chamber having a length of 1 m filled with a saturated a vapor of N,N-dimethylformamide on the acryl varnish resin layer deposited on the copper conductor, and the deposited layer thus treated with the vapor was dried at 200°C to from a smooth insulating under-layer having a layer thickness of 22 μ . Polyester-B was then coated one time on the above insulating under-layer at a line speed of 40 m/minute and a simultaneous baking of the insulating under-layer and the upper-layer was carried out at a temperature of 450°C to form an insulating upper-layer having a layer thickness of 3 μ whereby a dual coated wire having a total coating thickness of 25 μ was obtained.

EXAMPLE 3

A copper conductor having a diameter of 0.3 mm as an anode was coated with Polyacryl-C by employing conventional electrodeposition coating using a horizontal coating machine at a line speed of 60 m/minute under the following conditions:

Cathode: A copper cylindrical tube of 6 cm in diameter and 30 cm in length

Distance between Electrodes: 3 cm Electrodeposition Voltage: 7V D.C. Varnish Temperature: 30 ± 1°C

Any excess of the electrodeposition varnish remaining on the resulting deposited acryl resin layer was then removed using an air-wiper with a blowing nozzle angle and a slit width of the blowing nozzle of 45° and 0.1 mm, respectively, under an air supply pressure of 0.3 45 Kg/cm². And the thus coated conductor was passed through a cylindrical cathode tube described below which was set in a liquid bath filled with N,N-dimethylformamide, while a voltage was applied between the conductor as an anode and the cathode under the fol- 50 lowing conditions:

Cathode: A copper cylindrical tube of 6 cm in diameter and 30 cm in length

Distance between Electrodes: 3 cm

Voltage Applied: 200V D.C. Bath Temperature: $30 \pm 1^{\circ}$ C

Any excess of N,N-dimethylformamide remaining on the acryl resin layer leaving the bath was then removed by air-wipering as described above but using an airsupply pressure of 0.5 Kg/cm², and the resin layer was dried at a temperature of 200°C to form a smooth insulating under-layer having a layer thickness of 22 μ . Polyester-C was then coated one time on the above insulating under-layer at a line speed of 60 m/minute, and a simultaneous baking of the insulating under-layer and the upper-layer was carried out at a temperature of 550°C to form an insulating upper-layer having a layer

EXAMPLES 4 TO 12 AND COMPARATIVE

total coating thickness of 25 μ was obtained.

EXAMPLES 1 TO 5

Similar preparation methods for producing a dual coated wire as described in Example 3 were repeated in Examples 4 to 12, and in Comparative Examples 3 and 4, whereas similar preparation of Example 1 in 10 Comparative Examples 1, 2 and 5, were conducted but using the varnishes shown in Table 1 in place of the Polyacryl-B and Polyester-B, or Polyacryl-A and Polyester-A, respectively, employed in these examples.

The polyvinyl formal (PVF) varnish used in Comparvapor of N,N-dimethylformamide at 155°C to provide 15 ative Examples 4 and 5 is composed of 100 parts (by weight) of a polyvinyl formal resin (trade name: "BINI-REKKU-FL", manufactured by Chisso Co.), 70 parts of trimer of toluene diisocyanate stabilized with glycerin and phenol, 15 parts of a resole type phenolformaldehyde resin (trade name: "Plyophen 5030", manufactured by Japan Reichhold Chemicals Inc.), 5 parts of butylated melamine, 200 parts of m-cresol, and 300 parts of solvent naphtha.

> Each insulated wire prepared in Examples 1 to 12, 25 and Comparative Examples 1 to 5 was subjected to several tests including heat resistance as well as general test evaluations for determining the characteristics and properties of the insulated magnet wire.

The test results obtained are shown in Table 1, wherein heat resistance of each wire is shown as thermal life which corresponds to the period of time at the end of which wire, tested in accordance with IEEE No. 57, failed.

In order to compare the heat resistance of each dual 35 coated wire of the above Examples and Comparative Examples with those of corresponding single coated wires which are insulated only with the varnish used in the under or upper layer of corresponding dual coated wire, single coated wires prepared by the methods described hereinafter and were subjected to heat resistance test at 220°C and 260°C in accordance with IEEE No. 57.

The test result of each of single coated wire insulated with the under layer varnish of thhe corresponding dual coated wire is shown with thermal life in the row of Table 1 designated as "Single Coated Wires-a", whereas the test result of each wire insulated with the upper layer varnish of the corresponding dual coated wire in the row indicated as "Single Coated Wire-b", respectively.

Preparation of single coated wires

Using the above described polyacryl varnishes Polyacryl-A to Polyacryl-L, twelve kinds of polyacryl sin-55 gle coated wires were prepared by the method used in applying Polyacryl-C on a conductor as described in Example 3 except that the electrodeposition voltages was 8V instead of 7V, whereby a coating thickness after baking at 550°C became 25 μ . Insulated wires coated with Polyacryl-M or the PVF varnish were prepared using the method for applying Polyacryl-A on the conductor as described in Example 1 except that the coating and baking procedure was repeated six times instead of five times so that the film thickness became 65 25 μ after baking at 400°C. Also, using the above polyester varnishes, Polyester-A to Polyester-J, 10 kinds of polyester single coated wires were prepared, wherein a copper conductor, 0.3 mm in diameter, was coated with a polyester varnish aforementioned by the conventional dip-coating using a horizontal coating machine and a metal die, thenafter the coated conductor was introduced into an oven maintained at a temperature of 400° C in a line speed of 40 m/minute to bake the coating layer at that temperature. The above procedure was repeated six times to form a baked coating layer having a coating thickness of 25μ .

As seen in Table 1, all of the dual coated insulating wire of Examples 1 to 12 not only has a surpisingly superior thermal life (heat resistance) at both of the temperatures examined in comparison with the thermal life of the corresponding single coated wires as well as that of any of the dual coated insulating wires of the Comparative Examples, but also has well-balanced properties.

Table 1

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
112	Under Layer	Polyacryl	Polyacryl	Polyacryl	Polyacryl	Polyacryl	Polyacryl
Wire		-A	-B	-C	-D 1	-E	-F
Structure		Polyester	Polyester	Polyester	Polyester	Polyester	Polyester
C	Upper Layer	-A	-B	-C	-D	-E	-F
Continuity*							•
(number of		. 0	0	0	0 .	. 0	0
pinholes/5m)						-	ŭ
Mandrel Diameter*		good for	good for	good for	good for	good for	good for
		1X	1X	1X	1X	1X	1X
Breakdown Voltage* (KV)		9.0	8.8	9.0	9.5	9.0	8.5
Abrasion Resistance*		35	55	30	43	38	51
(strokes)		*				20	31 ,
Cut Through Tempera-		. 180	178	178	172	163	183
ture** (°C)						103	103
Heat Shock,		good for	good for	good for	good for	good for	good for
at 200°C × 1 hr		2X	1X	3X	1X	2X	
	Sulfuric			•	174	27	ix
Chemical and	Acid (S.G.	pass	pass	pass	pass		
Solvent	= 1.2)		Pull	pass	pass	pass	pass
Resistance*,	Sodium						
30°C × 24	Hydroxide	pass	pass	pass	m		
hrs	(1%)	Pass	Puss	pass	pass	pass	pass
	Benzene	pass	pass	*****			
Thermal Life***.	Donzono	2520	11840	pass 5830	pass	pass	pass
220°C (hrs)		2320	11040	2020	6510	1730	1820
Compared	Single coated	278	270	273	200		
Thermal	wire - a	2,70	270	213	280	278	303
Life***,							
220℃	Single coated	1380	4020	2.440			
(hrs)	wire - b	1300	4030	3420	2632	1221	1050
Thermal Life***	wire - 0	220			50.0		
260°C (hrs)		230	643	465	583	184	139
	C:11	1					
Compared Fhermal	Single coated	45	42	42	40	39	39
i nermai Life***,	wire - a						
	6.						
260°C	Single coated	153	344	338	268	154	- 81
hrs)	wire - b						

		Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
	Under Layer	Polyacryl	Polyacryl	D-1:1		·····	
Wire	Olider Eayer	-G		Polyacryl	Polyacryl	Polyacryl	Polyacryl
Structure			. н	-I	- J	-K	-L
Structure	t territoria	Polyester	Polyester	Polyester	Polyester:	Polyester	Polyester
Continuity*	Upper Layer	-G	-H	-I	-A	-C	-G
(number of		0					
pinholes/5 m)		0	0	0	0	0	. 0
Mandrel Diameter*			1.0				
Manarer Diameter		good for	good for	good for	good for	good for	good for
Breakdown Voltage* (KV)		1X	1X	1X	1X	1 X	1X
Abrasion Resistance*		9.0	9.0	8.8	9.4	9.2	9.0
(strokes)		52	34	40	36	40	49
Cut Through Tempera- ture** (°C)		185	170	169	163	180	177
Heat Shock,		good for	good for	good for	good for	good for	good for
at 200°C × 1 hr		1X	2X	3X	2X	3X	1X
61 · · · ·	Sulfuric				•		
Chemical and	Acid (S.G.	pass	pass	pass	pass	pass	pass
Solvent	= 1.2)					•	
Resistance*,	Sodium						
30°C × 24	Hydroxide	pass	pass	pass	pass	pass	pass
hrs	(1%)		•	•	F	Pubb	pass
	Benzene	pass	pass	pass	pass	pass	pass
Thermal Life***,		11400	i710	2030	1982	6321	11310
220℃ (hrs)	the second second second					002.	11310
Compared	Single coated	298	308	273	270	295	284
Thermal	wire - a				2.0	2,5	204
Life***,							
220℃	Single coated	5110	998	1032	1380	3420	5110
(hrs)	wire - b			1002	1560	3420	3110
Thermal Life***,		680	183	210	178	525	598
260°C (hrs)				210	170	343	270
Compared	Single coated	43	40	41	42	41	
Thermal	wire - a		70	71	44.	41	44
Life***,				1.00			
260°C	Single coated	473	126	127	1.53		
(hrs)	wire - b	4/3	120	137	153	338	473
	WIIC - D					_	

Table 1-Continued

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
	Under Layer	Polyacryl	Polyacryl	Polyacryl	Polyacryl	PVF
Wire		-M	-M	- A		15 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
Structure	11 PM	Polyester	Polyester	Polyester	PVF	Polyester
18 1 T	Upper Layer	÷J	-A	-J		-A
Continuity*						111
(number of		О	0	. 0	0	0
pinholes/ 5 m)				112		
Mandrel Diameter*		good for	good for	good for	good for	good for
		1X	1X	1X	1X	1 X
Breakdown Voltage*		8.1	8.4	9.1	9.4	9.9
Abrasion Resistance	·	3	5	17	44	65
(strokes)					1	
Cut Through Tempe	ra-	83	90	140	170	201
ture** (°C)						
Heat Shock,		good for	good for	good for	good for	good for
at 200°C × 1 hr	0.10	5X	4X	3X	1X	1X
	Sulfuric					
G	Acid (S.G.	pass	pass	pass	pass	pass
Chemical and	= 1.2)					the state of the s
Solvent	C 1'		4			
Resistance*,	Sodium		₹ :	* 4	* *	100
30°C × 24	Hydroxide	pass	pass	pass	pass	pass
hrs	(1%)	C '1	C 11	·		
771	Benzene	fail 100	fail 295	pass	pass	pass
Thermal Life***, 220°C (hrs)		100	295	195	185	290
Compared	Single coated	101	101	278	278	96
Thermal	wire - a	101	101	2/0	278	90
Life***,	wite - a				April 1	
220°C	Single coated	89 -	1380	. 89	96	1380
(hrs)	wire - b	07	1500	07		1360
Thermal Life***	WIIC - 0	19	49	29	33	43
260°C (hrs)		• • • • • • • • • • • • • • • • • • • •	11.7			73
Compared	Single coated	23	23	45	45	22
Thermal	wire - a					
Life***			1.10			
260℃	Single coated	13	153	13	22	153
(hrs)	wire - b	- 			to the least \widetilde{H}_{ij}^{T}	-55

*tested in accordance with JIS C 3210

**tested in accordance with MIL-W-583C 4,7,11,1.

***tested in accordance with IEEE No.57

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various 40 changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. An insulated wire comprising a conductor having thereon a coating of a baked insulating layer of a polyacryl resin and a baked layer of a polyester resin overcoated on said polyacryl resin layer,

said polyacryl resin comprising a copolymer of (a) at least one compound represented by the formula (I):

$$\begin{array}{c|cccc}
H & R_1 \\
 & | & | \\
C = C \\
 & | & | \\
H & R_2
\end{array}$$
(1)

(b) at least one compound represented by the formula (II)

and (c) at least one unsaturated organic acid, said acid having from 3 to about 30 carbon atoms and at least one double bond which is reactable with

the double bond of said compound of the formula (I) or (II), wherein R₁, represents a hydrogen atom or an alkyl group having 1 to about 30 carbon atoms, R2 represents a cyano group, an aldehyde group or a carboxyalkyl ester group having from 2 to about 30 carbon atoms, and R₃ and R₄ each represents a hydrogen atom, an organic group having 1 to about 30 carbon atoms selected from the group consisting of an alkyl group, an amide group, an N-alkylamide group, an alkylol group, a glycidylether group and a glycidylester group, except that both R₃ and R₄ are not simultaneously a hydrogen atom or an alkyl group and said polyester resin comprising a copolymer of (d) at least one compound selected from the group consisting of terephthalic acid and a derivative thereof, and (e) a mixture of polyols comprising at least one diol and at least one of a triol, a tetraol, or a mixture of a triol and a tetraol, and said polyol mixture containing about 40 to about 97% equivalents of said diol.

- 2. The insultated wire of claim 1, wherein said groups for R_1 , R_2 , R_3 and R_4 contain no more than about 20 carbon atoms.
- 3. The insulated wire of claim 1, wherein the total number of carbon atoms in each of said compound of the formula (I), said compound of the formula (II) and said unsaturated organic acid is less than about 15 carbon atoms.
- 4. The insulated wire of claim 1, wherein said polyacryl resin comprises from 1 to about 20 moles of said

compound of the formula (I) per mole of said compound of the forumula (II) and from about 0.01 to about 0.2 mole of said unsaturated organic acid per mole of the total moles said compound of the formula (I) and said compound of the formula (II).

5. The insulated wire of claim 1, wherein said compound of the formula (I) is acrylonitrile, methacrylonitrile, methylacrylate, ethylacrylate, propylacrylate, butylacrylate, methylmethacrylate, ethylmethacrylate, pound of the formula (II) is glycidylacrylate, glycidylmethacrylate, allylglycidylether, acrylamide, methlolacrylamide, or ethylacrylamide and wherein said unsaturated organic acid is acrylic acid, methacrylic acid, $\alpha\text{-ethylacrylic}$ acid, crotonic acid, maleic acid, or fu- 15 maric acid.

6. The insulated wire of claim 1, wherein said polyacryl resin is a copolymer of said components (a), (b), (c) and additionally styrene or a derivative thereof, said styrene or a derivative thereof being present at a level of no more than about 2 mole per mole of said component (a).

7. The insulated wire of claim 6, wherein said styrene derivative is styrene in which the phenyl group is substituted with at least one substituent, said substituent being an organic group having 1 to about 20 carbon atoms or a halogen atoms.

8. The insulated wire of claim 7, wherein said phenyl group is substituted with 1 to about 3 said substituents.

9. The insulated wire of claim 8, wherein said styrene derivative is methylstyrene, ethylstyrene, dimethylstyrene, benzylstyrene, dibenzylstyrene, divinylbenzene, chlorostyrene, or dichlorostyrene.

10. The insulated wire of claim 1, wherein said unsat- 35 is 2 said polyol is an aliphatic diol, or an aromatic diol. urated organic acid is a monobasic unsaturated acid, a dibasic unsaturated acid, a tribasic unsaturated acid or a mixture thereof.

11. The insultated wire of claim 9, wherein said unsaturated organic acid is acrylic acid, crotonic acid, 40 with vinylacetic acid, methacrylic acid, tiglic acid, α -ethylacrylic acid, β -methylcrotonic acid, 2-pentenoic acid, 2-hexenoic acid, 2-heptenoic acid, 2-octenoic acid, 10undecenoic acid, 9-octadecenoic acid, cinnamic acid, 2,4-pentadienoic acid, 9,12-octadecadienoic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, mesaconic acid, glutaconic acid, dihydromuconic acid, muconic acid, or 1,2,4-tricarboxybutene.

12. The insulated wire of claim 1, wherein said polyacryl resin is a copolymer of said components (a), (b), (c) and additionally a diolefin, said diolefin being present at a level of no more than about 1 mole per mole of said component (a).

13. The insulated wire of claim 12, wherein said diolefin has 3 to about 20 carbon atoms.

14. The insulated wire of claim 12, wherein said diolefin has about 4 to 10 carbon atoms.

15. The insulated wire of claim 14, wherein said diolefin is butadiene, pentadiene, or methyl-butadiene.

16. The insulated wire of claim 1, wherein said derivative of terephthalic acid is represented by the formula (III)

$$R_5 \text{ oc } - \text{COR}_6$$
 (III)

wherein R₅ and R₆ each represents a halogen atom, or 5 an organic group having 1 to about 5 carbon atoms selected from the group consisting of an amino group, an alkoxy group, an N-alkylamino group, or an aryloxy group.

17. The insulated wire of claim 1, wherein said polyol propylmethacrylate, or acrolein, wherein said com- 10 mixture comprises a mixture of polyols represented by the formula (IV)

$$R_7 - (OH)_n$$

(IV)

wherein R₇ represents a hydrocarbon group having 1 to about 10 carbon atoms and n is a positive integer of 2^n to 4.

18. The insulated wire of claim 17, wherein said hydrocarbon group is selected from the group consisting of a saturated hydrocarbon group and an unsaturated hydrocarbon group.

19. The insulated wire of claim 17, wherein said saturated hydrocarbon group contains at least one ring selected from the group consisting of a four to eight membered heterocyclic ring and a benzene type ring in the carbon chain thereof.

20. The insulated wire of claim 17, wherein said satu-30 rated hydrocarbon group is substituted with at least one group selected from the group consisting of a phenyl group and an aralkyl group having about 7 to about 10 carbon atoms.

21. The insulated wire of claim 17, wherein when n

22. The insulated wire of claim 17, wherein when nis 2 said diol is ethylene glycol, propylene glycol, budiol, or 2,2 -bis(p-hydroxyethoxyphenyl)propane, and wherein said polyol mixture is a mixture 1,1,1-1,1,1-trimethylolethane, glycerin. trimethylolpropane, tris-2-hydroxyalkyl isocyanurate or pentaerythritol.

23. The insulated wire of claim 1, wherein a portion of said terephthalic acid is replaced by isophthalic acid atropic acid, α -benzylacrylic acid, methyl atropic acid, 45 or a derivative thereof in an amount up to less than 60 moles of said isophthalic acid per 100 moles of said terephthalic acid.

24. The insulated wire of claim 1, wherein said polyester resin comprises the polymerization product of said terephthalic acid, said polyol mixture and additionally an imide- or amide-imide-containing substance comprising the reaction product of a tribasic or higher polybasic acid and a diamide, a diisocyanate or a mixtue of said diamine and said diisocvanate.

25. The insulated wire of claim 1, wherein the thickness of said polyacryl resin layer ranges from about 1 to 300 μ and the thickness of said polyester resin layer ranges from about 0.3 to 100 μ , and wherein the thickness ratio of said polyacryl resin layer to said polyester resin layer ranges from about 0.1 to 30.

26. The insulated wire of claim 1, wherein said resin layers are simultaneously baked.

UNITED STATES PATENT OFFICE Page 1 of 2 CERTIFICATE OF CORRECTION

Patent No. 3,906,139	Dated	April	15,	1975
Inventor(s) Yukio Hiraoka et al.				·

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, beginning at line 18 to line 60, delete the entire material from "bon group having . . . and the like." and insert therefor the following:

--bon group having 2 to 10 carbon atoms. When the above n in the Formula (IV) is 2, 3, or 4, the valency of R_7 becomes divalent, trivalent, or tetravalent, respectively.

Examples of divalent R₇ groups are alkylene or alkenylene groups of which one or two hydrogen atoms on one or two end carbon atoms can be replaced by one or two alkyl groups or alkenyl groups and the like.

Examples of trivalent R₇ groups are alkylene or alkenylene groups of which a hydrogen atom of one end carbon atom is replaced by one alkylene, or alkenylene group, or of which one hydrogen atom of both end carbon atoms is replaced by one alkyl or alkenyl group and one alkylene or alkenylene group or of which an inner carbon atom between both end carbon atoms is substituted with one alkylene or alkenylene group and one alkyl or alkenyl group.

UNITED STATES PATENT OFFICE Page 2 of 2 CERTIFICATE OF CORRECTION

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Patent No	3,906,139		Dated_	April 15, 197	5
Inventor(s)_	Yukio Hira	aoka et al.			
It is c and that sai	ertified that d Letters h	nat error appear Patent are hereb	s in the	above-identificted as shown be	ed patent low:
atom and alkylene atom betw	ne groups another or alken ween both	of tetravales of which a hy end carbon at ylene group, end carbon a ylene groups.	ydrogen om, are or of w toms is	atom of an esubsituted which an inner	end carbon with one r carbon
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[SEAL]			Twen	ty-fourth Day	of October 1978
		Attest:			
		RUTH C. MASON Attesting Officer	·	DONALD W Commissioner of Pate	