United States Patent

[11] 3,632,440

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[73] Assignee **Essex International, Inc.**

[54] **RESINOUS COMPOSITION FOR COATING ELECTRIC CONDUCTORS**
3 Claims, No Drawings

[52] **U.S. Cl.** ..... **117/218,** 117/128.4, 117/161 ZA, 117/232, 260/824 R, 260/824 EP

[51] **Int. Cl.** **B44d 1/42,** H01b 3/46, H01b 3/42

[50] **Field of Search** ..... 117/128.4, 218, 232, 161 ZA; 260/824, 826, 827

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ABSTRACT: A magnet wire characterized by an insulating resinous coating composition used as base coat and/or topcoat over a different base coating, said coatings having a low coefficient of friction. These coatings retain the ability to be overcoated with other coatings such as wire varnishes and enamel. The coatings, such as the reaction product of a polytrimellitamideimide film-forming resin and methyl tetradecyl polysiloxane, are applied in single or multiple coats from solutions over the wire or a base-coated wire, each coat being cured in an oven to cause the polymers to react or interact to produce smooth, hard, slippery surfaces.

RESINOUS COMPOSITION FOR COATING ELECTRIC CONDUCTORS

This invention relates to an improved magnet wire having a resinous insulating coating characterized by a low coefficient of friction, and to the method of making the coating.

It is an object of the present invention to provide magnet wire which requires no oil for winding, that is, the coefficient of friction of the coating is so low that it can be wound at high speeds without pretreatment of any kind. The wire of this invention has a slippery, dry surface which makes high-speed winding possible, but the slick nature of the surface does not prevent overcoating or adhesion of other coatings. The coating provides a significantly superior dry lubricity with an oil-free surface, resulting in significant advantages: cleaner winding and therefore cleaner shop and material storage areas because dust and dirt will not collect as readily as where ordinary mineral oils are used; no oil can be thrown from the wire or burned due to heat developed from friction; reduction in contamination of wound units with foreign material, improving product reliability; obviating problems resulting from inconsistent lubrication due to the excess or lack of oil application; and improved space and wire utilization results from winding units with reduced mean turn lengths because the slippery wire coils slide into tight, closely-abutting relation during winding to eliminate unnecessary spaces therebetween.

The wire of the invention also allows winding machines to operate at the maximum winding speeds; therefore, better efficiencies are obtained. More compact windings allow improvement in balance of rotating parts and reduced loading of bearings and bushings. Additional insulations such as slot wedges can be more easily placed in units because of the improved space factors.

Work hardening of metal conductors is a problem in winding magnet wire, and wire made in accordance with my invention reduces this problem because high-winding tensions are not needed. Forming operations are facilitated and forming procedures on conductors are equalized because the wires slide past one another when formed. Coil windings made from wire coated according to this invention require less effort to seat and insert by various winding and forming devices.

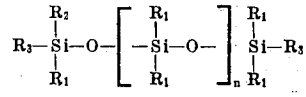
Taping of coils wound with wire made from this invention is more readily accomplished, tapes will stick to the wire and no oil removal procedures are necessitated. Better varnish coverage, spray and/or dipping techniques, are accomplished since no oil is present to interfere with the wetability of the varnish or other coatings. Many current encapsulants of wound units are plagued by entrapped air and/or oil left on wire by conventional wire operations. Encapsulation, thus, is improved because no trapped oil is present in units made from this invention.

Nylon insulations have long been recognized by the magnet wire industry as the most windable films available, due to their slick surfaces and consequent ability to nest into allotted winding spaces. The new resin coatings of my invention consistently outperform the nylon types based on comparative tests on high-speed automatic winding equipment and in laboratory-controlled coefficient of friction tests.

Wire coatings of the invention exhibit a 20 percent coefficient of friction improvement over nylon and up to 90 percent over other common films. In these tests, optimum windability is predicted by the lowest coefficient of friction value. The coefficient of friction obtained on any insulation is primarily due to the material used for the outer coating and can be affected to a limited degree through the use of spooling oils or other topical lubricants. For nylon over-coated insulations, the coefficient of friction is 0.17; with other commonly used films it ranges up to 0.33. For insulation of the invention, it consistently measures 0.14 or below.

Most products produced from magnet wire must be further coated with bonding varnish, or where no varnish, enamel or paint is used to over coat a magnet wire, electrical tapes of various types may be needed to hold the magnet wire shapes in position. These tapes likewise must adhere to these slippery coatings. The resin coatings of the invention possess tape and varnish adhesiveness which is responsible in large part for the success of the invention.

The foregoing objects and advantages of my invention may be accomplished by coating wire with a conventional coating resin, e.g. polyamides, polyester, polytrimellitamide-imide, alkyd, epoxy and the like, modified by the addition of from 0.01 to 25.0 percent by weight of a two-dimensional linear organo polysiloxane based upon the weight of the resin. The polysiloxane may have the following formula:



Where R_1 is an alkyl or aryl radical, R_2 is an alkyl radical or unsaturated organic material or side chain having from one to 20 carbon atoms or more, R_3 is an alkyl radical and/or —H, —OH, and —COOH or unsaturated side chain, and n equals 2–10 or more.

The operable polysiloxanes have a molecular weight ranging from 600–8,000, with 2,500 as a median, and a viscosity of from 1–200,000 centistokes at 77° F. with a median of 1,500. These compounds are known to the art and may be prepared by the hydrolysis of di-organo di-halogen silanes, such as methyl phenyl di-chlorosilane or methyl ethyl di-chlorosilane, followed by the partial condensation of the hydrolysis product and further reacted or copolymerized with an unsaturated organic material.

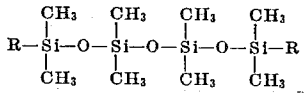
The nature of the polysiloxane polymers is critical in the practice of the invention. Polymers such as dimethyl polysiloxane of various molecular weights provide a surface having a low coefficient of friction when incorporated with various resins. However, most paints, enamels, varnishes and tapes will not adhere to such a surface. On the other hand, monomeric silicones or three-dimensional resinous silicones have varnish adhesiveness, but are not suitable since they do not impart the desired slipperiness. It is necessary to use linear dimethyl polysiloxane polymers having a pendant radical attached to a silicon atom directly or through CH_2 groups, or as an end group, that will accept a bond with a resinous coating. The silicone polymers may have a variety of organic side groups along the basic polymer chain (Si—OSi). These may be methyl, ethyl, propyl, butyl, phenyl, carboxyalkyl, methyl alkyl, hydroxyalkyl, cyanoalkyl, or aminoalkyl. Of these, methyls and phenyls are used most extensively.

The coatings of the invention are prepared by mixing the aforesaid polysiloxanes with a solution of certain film-forming resins and/or elastomers commonly used as wire coatings, preferably in a quantity from 0.10 to 5 percent based on the weight of the resin. The polysiloxane polymers interact and react at elevated temperatures to combine with the conventional coating resin to form a hard, dry, slippery surface. Among the conventional coating resins which may be modified in accordance with the invention are polyesters, polyamides, polytrimellitamide-imide, polyvinyl butyral, polyvinyl formal, polyvinyl formal-phenolic, polyvinyl formal-isocyanate, polyurethane, epoxy, acrylic, alkyd, polycarbonate, polypropylene, polyhydantoin, and compatible mixtures thereof.

The probable mechanism by which the polysiloxane is cured is by oxidation. This may be triggered by heat when an oxidation threshold is reached and free radicals are formed. A catalyst may or may not be used to help trigger this reaction. In oxidation breakdown, oxygen reacts with the organic groups of the molecules gradually increasing the viscosity of the polysiloxanes until gelation occurs. The reaction is dependent upon temperature and the supply of oxygen present. Some of the operable polysiloxane polymers have pendant or terminal hydroxy groups in low quantity that can be activated at room temperature by means of a catalyst or at elevated temperature. These may tend to keep the silicones in stable solution or dispersion with the resin components being modified.

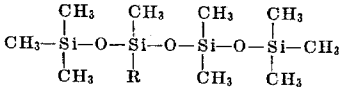
When the wire is passed through a resin-polysiloxane coating solution and then through a vertical tower or other suitable oven maintained at a temperature of from 200°–500° C., the desired coating is formed. The silicone in the cured coating does not bleed to the surface and is effective in reducing the coefficient of friction of from 20–50 **percent compared with the same coating from which the polysiloxane has been omitted, depending upon the particular resin solution to which it is added. Additionally, the presence of the polysiloxane may improve the resistance of the coating to ozone, moisture, and heat.**

Several types of polysiloxanes are useful as modifiers in this invention. One is a dimethylpolysiloxane with copolymeric terminal groups R such as:



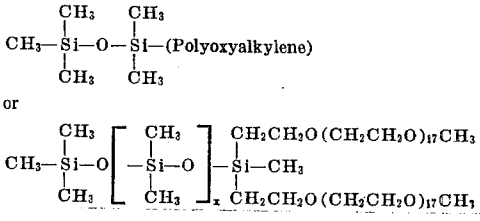
in which R is a partially unsaturated hydrocarbon group of from one to 20 carbon atoms or more, e.g., octene, butene, ethyl phenylene, or tetradecene.

Another type may be a conventionally blocked polydimethyl siloxane with an alkyl olefinic pendant group such as:



wherein R is an alkyl radical of from one to 20 carbon atoms or more. The copolymeric pendants account for the varnish adhesiveness of the silicone containing coatings.

A third type may be the so-called copolymers of dimethylpolysiloxane and a polyoxyalkylene ether such as:

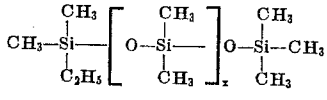


where the organic portion of the copolymer gives the varnish and/or resin compatibility and the silicone portion is responsible for the lubricity of the film. A portion of the organic radical may be reacted with the coating resin upon heating.

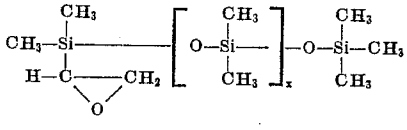
Alkyl/aryl silane diols, e.g., diphenyl silane diol are also useful modifying silicones, particularly when reacted with the reactants used in producing the polyester type resins.

The following is a partial illustrative list of specific silicones found usable in this invention.

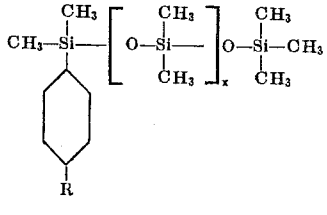
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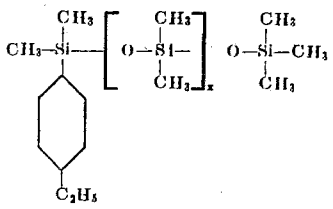
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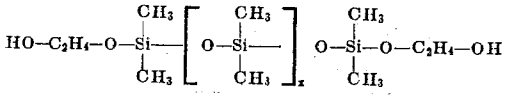


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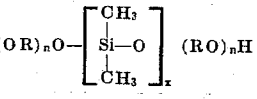
Where x in number 1, 2, 3 and 4 equal 2–10 or more.

No. 5



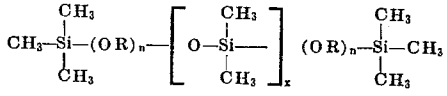
Where x is equal to 2 to 20 or more as a copolymer.

No. 6



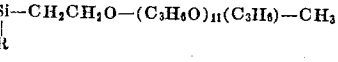
Where x is equal to 2 to 10 or more and n is 1 or more.

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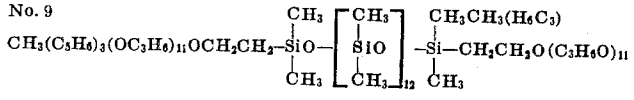


Where x is equal to 2 to 20 or more and n is 2 or more.

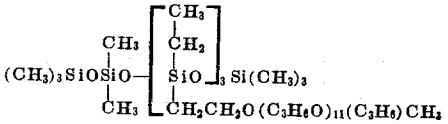
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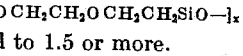
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No. 10

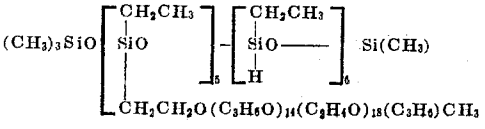


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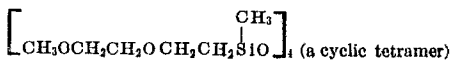


Where x is equal to 1.5 or more.

No. 12

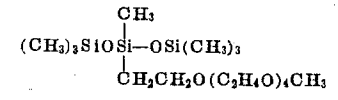


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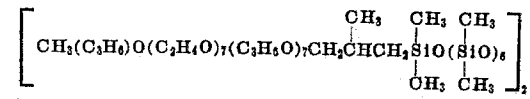


(a cyclic tetramer)

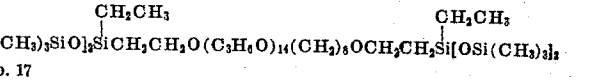
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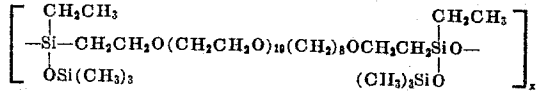
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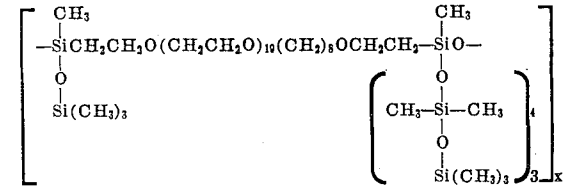
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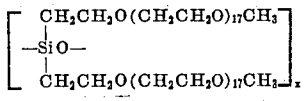
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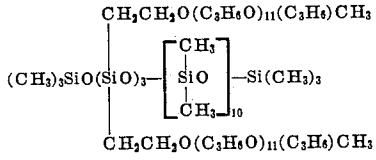
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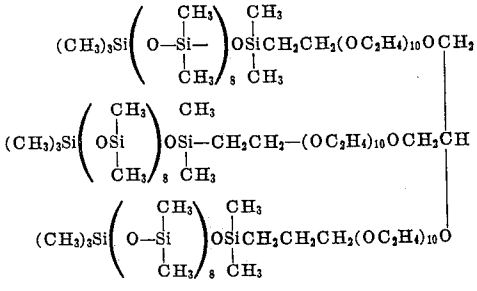
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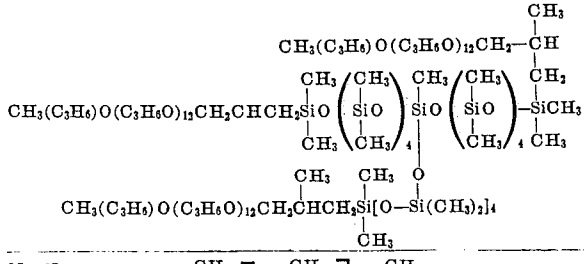
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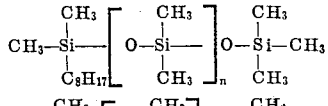
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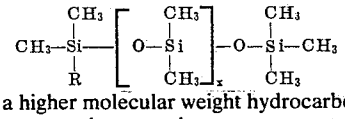
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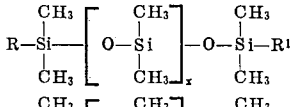


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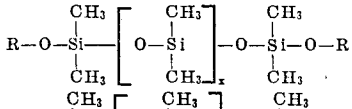


Where R is a higher molecular weight hydrocarbon side chain such as heptene, hexene, butene, propene, propylene, tetradecene, pentene, octene, or decene.

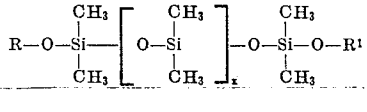
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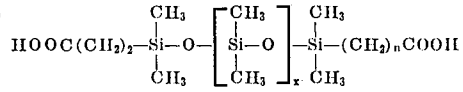


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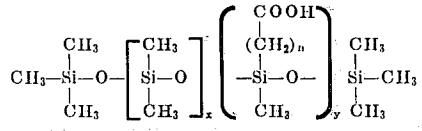


Wherein R and R¹ of examples **25, 26, 27** may be the same or different radicals or organic hydrocarbons having one to 20 or more carbon atoms, or may be —OH, —H, or —COOH, as the following:

No. 28



No. 29



Instead of curing a solution of resin and polysiloxane on the wire, the modified resin coatings of the invention may be prepared by reacting, in a suitable vessel, the polysiloxanes with a resin by graft copolymerization. Such a reaction can be accomplished by using a partially polymerized ester, such as an oil-free terephthalic acid-type resin, and carboxyalkyl polysiloxane, such as carboxy ethyl methyl poly disiloxane. Most reactable carboxy, hydroxy, or hydrogen terminated alkyl aryl, or di alkyl polysiloxanes may be successfully used under proper processing conditions. The polyester resin is heated to a proper esterification exchange temperature. The reactable polysiloxane is then added with an ester interchange catalyst such as litharge or a metal acetate. These are the so-called alcoholysis catalysts. Other examples of these catalysts are lead oxides, lead acetates, zinc oxides, cadmium acetates, cuprous acetates, and zinc acetate. The carboxy and/or hydroxy groups present on the polysiloxane chain react with the —COOR groups of the ester to form free radicals for a linkage or react as a poly basic acid with excess hydroxyls, or both. This results in a copolymer having a polyester backbone with pendant polysiloxanes dispersed along the chain. Solutions of resins such as these may be used per se or incorporated with conventional coating resins as wire insulating coatings having the desired slip and other physical properties. They have improved solution compatibility as either an overcoat enamel or as the sole enamel on the wire.

A third method of preparing coatings for satisfactory use in this invention comprises introducing the polysiloxane in a polymer backbone during the preparation of a conventional resin top coat. Such hybrid resins may be used as slippery top coats and/or as slippery base coats depending upon the type. Such a material is a polyester polysiloxane wherein terephthalic or isophthalic acids or their half esters are reacted with suitable polyols and an organosilicon in a conventional manner. A portion of the polyols or the acid is substituted for organosilicon compounds containing reactable H, OH, COOH. Examples of suitable organosilicons are diphenyl silanediol, carboxy alkyl polysiloxanes, carboxy-terminated alkyl aryl polysiloxane. Terephthalic acid, a glycol and the silicon compound are reacted together in suitable equipment to produce a resin. Resins of this type may be used alone or as additives to conventional wire topcoating resins to produce coatings having low coefficient of friction.

Another means of combining the polysiloxanes with conventional coating resins in accordance with this invention is by emulsifying the polysiloxane in an oil/water emulsion. Several magnet wire base coatings are applied from water, for example, acrylic and polyester resins. These base coats may be dispersions or emulsions. In order to gain a slippery surface, one or more coats of polysiloxane modified resin may be placed over the base coat applied from water. Better still, the polysiloxane of this invention (example 9) may be emulsified with the help of small quantities of surfactant and added to the water base coat resin used.

EXAMPLE 1

Copper wire having a base coating of Isonel 200E (Class H polyester wire enamel) was topcoated with the following composition:

Ingredients	Parts by Weight
Nylon type 6/6 (16% solution in a solvent mixture of phenol, cresylic acid and E.W. naphtha)	98
Methyl Alkyl polysiloxane	2
Iron Octoate (6%)	0.2

The nylon siloxane solution was applied in two layers over the base coat and each layer was cured in a wire tower at a temperature ranging from 275° at the bottom to 475° C. at the top. The coating after curing had a coefficient of friction of 0.095. Another example of the base-coated wire was topcoated in the same manner with the nylon solution, omitting the polysiloxane and the iron octoate. This wire had a coefficient of friction of 0.187.

Bobbins were wound at high speed on a winding machine with great ease using this coated wire. In spite of the slipperiness of the surface, electrical adhesive tapes and electrical varnishes such as a silicone, phenolic, and/or polyester varnish adhered to the wire without any pretreatment.

The above coating was found to have superior resistance to continuously impressed voltage in addition to its slippery nature. Tested according to ASTM D-2307 procedure, the modified nylon top coated wire had an average life at 260° C. of 2,400 hours while the conventional nylon-coated wire tested 15.42 hours.

EXAMPLE 2

Copper wire treated as indicated in example 1, the base coating of Isonel 200E being topcoated with the following composition:

Ingredients	Parts by Weight
Polyethylene terephthalate (13% solution in orthochloro-phenol and orthocresol)	680
Methyl Butyl polysiloxane	15.6
Iron Octoate (6%)	8.0

This coating solution was applied as indicated in example 1, and the coefficient of friction was found to be 0.109. A second sample was prepared having a topcoating of the polyethylene terephthalate (Mylar) solution without the silicone or iron octoate. The coefficient of friction of this wire measured 0.183.

EXAMPLE 3

Copper wire having a four-layer base coating of Isonel 200E was topcoated with a resin having the following composition:

Ingredients	Parts by Weight
Polytrimellitamide-imide polymer* (18%) solution in cyclohexanone and N-methyl pyrrolidone)	100
Methyl tetradecyl polysiloxane	0.8.

This solution was applied in two layers, each of which was cured in a wire tower as indicated in example 1. Another sample of the same base-coated wire was top coated in the same manner with the same composition except that the siloxane was omitted. The composition with the siloxane had a coefficient of friction of 0.127 while the one without had a coefficient of friction of 0.192. The polytrimellitamide-imide polymer is reactive with the free radical produced in the polysiloxane above 170° C. and upon curing produces a smooth, hard resin without the necessity of added catalyst.

*Amoco Chemical Co. AI-10 resin or a condensation product of Trimellitic anhydride acid chloride and p,p'oxybis (aniline). See U.S. Pat. Nos. 3,347,828; 3,320,202 and 3,377,321.

EXAMPLE 4

Copper wire having a base coat of a commercial Class F polyester magnet wire resin was top coated as described in example 1, with the following composition:

Ingredients	Parts by Weights
Nylon 6/6 (16% solution in a solvent mixture of phenyl, cresylic acid and E.W. naphtha)	98
Phenyl ethyl polysiloxane	0.3
Cobalt Octoate (6%)	0.05

After curing, this topcoat composition had a coefficient of friction of 0.113. A second sample of the same wire was overcoated with the nylon solution from which the polysiloxane and catalyst were omitted. This wire had a coefficient of friction of 0.177.

EXAMPLE 5

Copper wire having a base coating of siloxane alkyd modified terephthalic acid type polyester was overcoated with the following composition:

Ingredients	Parts by Weight
Nylon 6/6 (16% solution in a solvent mixture of phenol, cresylic acid and E.W. naphtha)	100
Co-polymer of dimethylpolysiloxane and polyoxyalkylene ether	1.0
Catalyst	0.2

After curing as indicated in example 1, this wire had a coefficient of friction of 0.117 while wire coated with the base coat alone had a coefficient of friction of 0.131. While the silicone-modified polyester base coat has reduced the coefficient of friction, a topcoat is still advisable to protect the base coat from the rigors of thermal shock.

EXAMPLE 6

Bare copper wire was coated with the following composition:

Ingredients	Parts by Weight
Nylon 6/6 (16% solution in a solvent mixture of phenol, cresylic acid and E.W. naphtha)	100
Carboxyethyl methyl siloxane	3.5
Catalyst	0.3

This wire with multiple coats was cured as indicated in example 1 and the resulting coating had a coefficient of friction of 0.123. For improvement of other properties, a different base coat may be used with the nylon siloxane top coat.

EXAMPLE 7

Copper wire having a base coating of Isonel 200E (Class H polyester wire enamel) was overcoated with one coat of the following composition:

Ingredients	Parts by Weight
Commercial Class H polyester wire enamel	80
Alkyl-aryl siloxane	20.8

After curing, this topcoated composition had a coefficient of friction of 0.103. A second sample of the same wire was over-

coated with one coat of the above solution from which the polysiloxane was omitted and had a coefficient of friction of 0.177. The coating containing alkyl-aryl siloxane had improved burnout resistance compared to the conventional overcoated Isonel 200E.

EXAMPLE 8

Ingredients	Parts by Weight
Epoxy resin (20%) in solution)	310
Cobalt Octoate (6%)	2
Manganese Octoate (6%)	1
Methyl epoxy alkyl siloxane	3.1

The above solution was applied in two coats as a topcoat over a wire with four base coats of a commercial epoxy wire enamel and cured in a wire tower as indicated in example 1. The wire with this composition had a coefficient of friction of 0.197. The same base coat was topcoated with the above epoxy resin without the siloxane and metal driers and had a coefficient of friction of 0.330.

EXAMPLE 9

Ingredients	Parts by Weight
Acrylic resin (24% emulsion in water)	90
Alkyl-aryl siloxane (40% emulsion in water containing a nonionic wetting agent)	1 agent)
Cobalt Octoate (6%)	0.4

A wire coated with the above composition by conventional methods was found to have a coefficient of friction of 0.15 whereas the same composition without polysiloxane had a coefficient of friction of 0.19.

EXAMPLE 10

This example illustrates the useful polyester-polysiloxane polymers in which the siloxane is added to the components during the preparation of the polyester resin. The following ingredients were placed in a four-necked reaction vessel with stirrer, thermometer, inert gas bleed, and a heated condenser:

Ingredients	Parts by Weight
Dimethyl terephthalate	46
Ethylene glycol	31
Trimethylol propane	23
Carboxyethyl methyl polysiloxane	2.3
Zinc Acetate	0.08
(Sufficient xylene or cresylic acid for azeotropic distillation)	

The reaction products were heated to 130° C. in 30 minutes. The zinc acetate catalyst was added and the temperature raised to 240° C. and held for 3 hours. The temperature was then raised to 250° C. with viscosity determination used to indicate termination of the reaction. This period was approximately ½ hour. The reaction was then stopped and the resin quenched with cresylic acid. The resin was then diluted to 30 percent solids with a 1 to 1 blend of cresylic orthocresol acid and aromatic hydrocarbons and applied to wire in multiple layers as a base coat. The wire was cured after each pass through the solution at a temperature from 270° to 450° C. The resultant product was found to have a coefficient of friction of 0.130 while conventional polyesters not top coated had a coefficient of friction of 0.347.

EXAMPLE 11

Another resin was prepared as in example 10 using the following composition:

Ingredients	Parts by Weight
Dimethyl terephthalate	460
Ethylene glycol	210
Trihydroxy ethyl isocyanurate	200
Trimethylol propane	130
Diphenyl silane diol	23
Zinc acetate	0.08
(Sufficient xylene or cresylic acid for azeotropic distillation)	

The above resin was dissolved in a blend of cresylic acid and aromatic hydrocarbons to **30** percent solids. Tetrakis (2-ethyl hexyl) titanate was added as a coreactant catalyst as 2 percent of the solution. A bare copper wire was coated as in example 1 using the above solution. The resultant end product had a coefficient of friction of 0.147 while a conventional polyester had a coefficient of friction of 0.347.

EXAMPLE 12

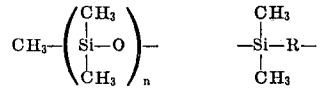
Ingredients	Parts by Weight
Conventional polyurethane wire enamel	98
Methyoctyl polysiloxane	2

Wire coated with the above composition by conventional methods was found to have a coefficient of friction of 0.097 while another wire coated with the resin having no polysiloxane had a coefficient of friction of 0.18

Although in the above examples the wire was coated from solutions of the modified resins, it will be appreciated that the solid resins may be applied to the wire by extrusion without detracting from the desirable properties achieved by the invention.

What I claim is:

1. An insulated electrical conductor having a baked-on resinous coating consisting essentially of the elevated temperature reaction product of a polytrimellitamide-imide film-forming resin and from 0.01 to 25 percent by weight of a two dimensional linear organo polysiloxane having the formula



wherein R is an alkyl group having from two—20 C atoms and n=2 to 10,

said coating being characterized by a low coefficient of friction coupled with varnish adhesiveness.

2. The conductor of claim **1** in which said polysiloxane is methyl tetradecyl polysiloxane.

3. The insulated electrical conductor of claim **1** in which the conductor is copper having a base coat of polyester resin beneath said baked-on resinous coating.

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