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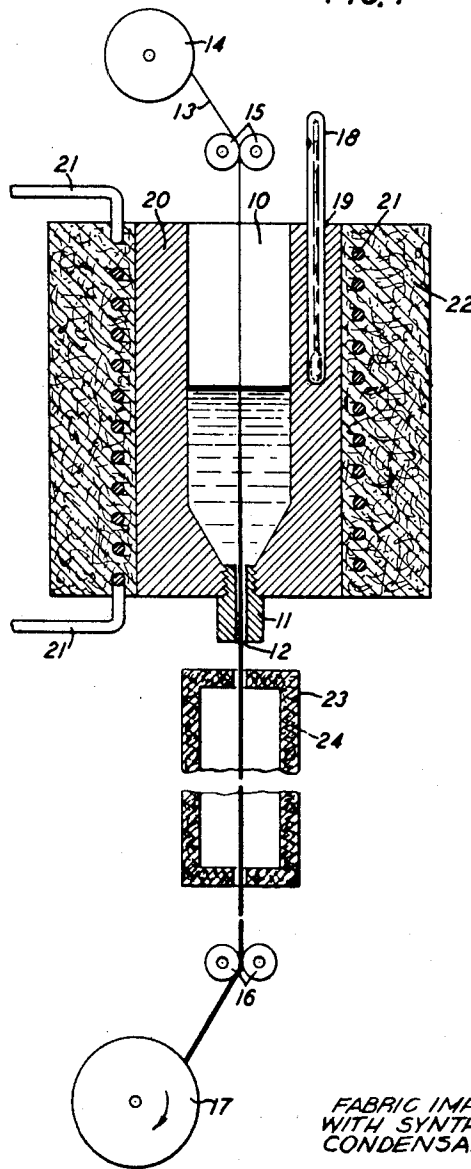
C. S. FULLER ET AL

2,349,951

ELECTRICAL CONDUCTOR

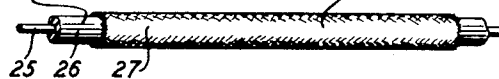
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FIG. 1



RUBBER

FIG. 2



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2,349,951

ELECTRICAL CONDUCTOR

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Application November 16, 1938, Serial No. 240,630

7 Claims. (Cl. 174-121)

The present invention relates to electrical conductors. More particularly it relates to conductors covered with an abrasion resistant layer containing a synthetic linear condensation polymer of high molecular weight or more particularly to conductors covered with a layer of fibrous material impregnated with such a polymer. It also relates to insulated conductors in which the insulation is protected against the destructive action of light, weathering and abrasion by means of a protective covering containing a synthetic linear condensation polymer of high molecular weight. The invention is also concerned with conductors in which the conducting element is covered directly with a fibrous material impregnated with such polymers.

An object of the present invention is a conductor having a protecting or insulating and protecting covering which is more effective than those previously available.

A further object is to effect the thorough impregnation of fibrous coverings on conductors with synthetic linear condensation polymers of high molecular weight.

When insulated electrical conductors, particularly those insulated with rubber or rubber-like materials, are to be subjected to outdoor use or to other conditions under which the insulation would be exposed to the deteriorating influences of light, weather or abrasion, they are provided with a protective covering designed to prevent injury to the insulation. The common protective covering consists of a textile braid impregnated with a suitable water-proofing, light-excluding and abrasion-resistant material. To be satisfactory as an impregnant such a substance must be economical, resistant to destruction and easy to apply to the wire.

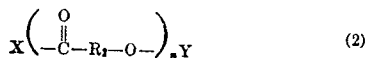
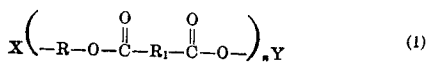
Such a substance is difficult to find. Few materials which are flexible enough and tough enough to withstand abrasion are capable of forming a sufficiently fluid melt at a sufficiently low temperature to permit impregnation. At present impregnation in the molten state is the most satisfactory and the only economically feasible method of saturating the fibrous coating on the wire.

Up to the present the most commonly used saturants and finishes have consisted of asphalts and asphalt-stearin pitch mixtures. The most

important reasons for their use have been their relative cheapness and ability to be melted into comparatively fluid liquids at low temperatures. These materials form reasonably good protective coatings. Other materials, such as resins or cellulose derivatives, which might be expected to form a coating which is just as good or better than those previously used, have not been adopted since they are too viscous to be impregnated into a fibrous layer by the economical method of impregnation in the molten state.

According to the present invention, certain synthetic linear condensation polymers of high molecular weight are employed in the protective layer on this type of conductor. These polymers have been found to give far superior results for this purpose than materials previously used. Thus abrasion tests show that certain wire coverings impregnated with these polymers have from 10 to 20 times the abrasion resistance of those impregnated with asphalt-stearin pitch. Further, these polymers can be chosen to have a sufficiently low melting point and to be sufficiently fluid when molten to permit impregnation in the molten state.

The polymers used are of the type described in U. S. Patents 2,071,250 and 2,130,948 to W. H. Carothers. From a practical standpoint the most important for the present use are the polyesters, polyamides, polyester-amides and various co-polymers of the aforementioned types. The polyesters may have either of the two following general structural formulae:



Where

R is a divalent organic radical having a chain length greater than 1 atom,

R₁ is a divalent organic radical having a chain length of 0 or greater,

R₂ is a divalent organic radical having a chain length greater than 3 atoms,

X and Y are suitable monovalent terminal groups, and n is an integer having an average value sufficient to insure the proper degree of polymerization.

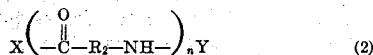
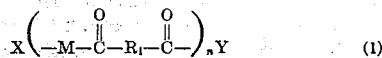
R, R₁ and R₂ may be chosen from the suitable aliphatic, aromatic, alicyclic, araliphatic or heterocyclic radicals.

The first type of polyester is prepared by the reaction of a glycol with a dicarboxylic acid, the reaction being carried on until the desired degree of polymerization is obtained. This may be accomplished by any suitable method, such as that described in the above-mentioned patents to Carothers or by the methods described in the copending application of C. S. Fuller, Serial No. 210,677, filed May 28, 1938, which has matured to Patent No. 2,249,950 dated July 22, 1941.

The polyesters of the second type may be prepared by the reaction of molecules of a hydroxy acid with one another.

Copolyesters, formed by the reaction of two or more different glycols with a dicarboxylic acid, two or more dicarboxylic acids with a glycol, or two or more different members of both types of reactants, or by the reaction of two or more hydroxy acids, are also suitable for the present invention. Physical mixtures of polyesters, which may be formed by melting polyesters together without reaction, may also be employed.

The polyamides have the two following general types of structural formulae:



Where M is any suitable aliphatic, araliphatic, alicyclic or heterocyclic organic radical containing two amino nitrogen atoms, the radical being linked by means of these nitrogen atoms to the adjacent carbon atoms in the polyamide chain, the radical preferably having a chain length greater than 5 atoms including the nitrogen atoms,

R₁ is a divalent organic radical preferably having a chain length greater than 3 atoms,

R₂ is a divalent organic radical preferably having a chain length greater than 5 atoms,

X and Y are suitable monovalent terminal groups, and

n is an integer having an average value sufficient to insure the proper degree of polymerization.

The first type of polyamide may be prepared by reacting any suitable diamine with a dicarboxylic acid or a reactive derivative of a dicarboxylic acid. The second type may be prepared by the autoreaction of an amino acid.

Copolyamides, formed by using, in each case, more than one member of each type of reactant, are also suitable. Physical mixtures of various polyamides, formed by melting them together without reaction, may also be employed. Polyester-amides, formed by reacting a diamine and a glycol with a dicarboxylic acid, or by reacting an hydroxy acid with an amino acid, or by reacting an hydroxy amine with a dicarboxylic acid, are also desirable impregnants.

The properties of high molecular weight synthetic linear polymers are such as to render them almost ideally suited for the purposes of the present invention. They are of a crystalline or semicrystalline structure. When their average molecular weight is sufficiently high, they have the property of cold drawing under stress. Thus when thin fibers are formed from

these materials and subjected to tensile stress, the fibers are permanently elongated and a change in the physical properties of the material takes place. The fibers become transparent and increase in tensile strength and elasticity. X-ray examinations show that the crystals of the substances become permanently oriented in the direction of the fiber axis after such tensile stress is applied.

This property is of great value when the polymers are used as a protective or insulating coating for wire. A somewhat similar crystal orientation is believed to take place when the protective coating is subjected to abrasion or any other type of stress which will tend to destroy the covering. Thus, the already tough and elastic covering has its toughness and elasticity increased by the very forces which would ordinarily tend to destroy it. Any rubbing or shearing stress tends to orient the crystals in such a direction that the polymers offer the greatest possible resistance to destruction through a continuance of the application of the force.

When wire is strung outdoors as, for instance, in telephone or telegraph communication, it is often necessary to run the wires in proximity to the swaying branches of trees. When the wire of the present invention is employed for this purpose, the rubbing of the limbs of trees tends to orient the crystals of the polymers in such a manner as to resist destruction from this cause. Therefore, there is, in effect, a self-protective action.

In addition to being self-toughening, as described above, the polymeric substances are unusually tough in their unoriented state, are fusible without decomposition, can be chosen to be sufficiently fluid in their molten state to permit impregnation of fibers in that state, and can be chosen to have a melting point sufficiently low so as to make it possible to impregnate heat destructible fibers in the molten state.

In some instances a covering consisting of a fibrous material impregnated with a synthetic linear condensation polymer may advantageously be used directly over the metal wire without a separate insulating layer between. In this case the covering functions as a tough insulating layer, highly resistant to destruction by abrasion or exposure to the atmosphere. In power lines, where the power factor of the insulation is not of great importance, a common insulation consists of one or more layers of textile braid impregnated with a suitable material for waterproofing and protecting the textile, such as asphalt-stearin pitch. Much the same advantages result from substituting synthetic linear condensation polymers for asphalt-stearin pitch in this type of wire as in wires insulated with rubber or other materials.

The polymers may be applied to wire in several ways. The preferable method is to cover the insulated wire with a fibrous covering, such as a braid of textile or mineral fibers, paper braid or paper pulp and to impregnate this fibrous covering with a molten polymer. This procedure may be better understood by reference to the accompanying drawing, in which:

Fig. 1 represents a sectional view of an apparatus for impregnating the fibrous covering on wire; and

Fig. 2 shows a conductor having a rubber or rubber-like insulation and a protective covering.

In Fig. 1 a reservoir 10 in a block of metal 20 contains the molten polymer. A replaceable bushing 11 having an orifice 12 through which the conductor 13 passes is mounted at the bottom of the reservoir. The conductor may be, for instance, a rubber insulated wire covered with a textile braid. The orifice 12 is of a diameter slightly greater than the conductor. The conductor 13 is supplied from a drum 14 and passes between rollers 15 which serve to guide the conductor through the reservoir 10 and the orifice 12. From the orifice 12 the wire passes through a long heating chamber 23, which insures the thorough penetration of the polymer into the braid. The heating chamber may be heated by any suitable means such as the electrical heating coil 24. The wire then passes over a second set of guide rollers 16 to a collecting drum 17. A thermometer 18 is placed in a thermometer well 19 to indicate the temperature of the polymer in the reservoir. A resistance winding 21 embedded in an insulating material 22 completely surrounds the block 20 to supply the necessary heat for maintaining the polymer at the desired temperature.

To coat the wire it is drawn through the reservoir, the orifice and the heating chamber. Since the wire is relatively cool when it enters the bath of molten polymer, it tends to chill the molten substance and prevent it from completely penetrating the textile covering. The heating chamber is maintained at a temperature sufficiently high to maintain the polymer already deposited on the wire in a molten state. The heating chamber is of such a length and the wire is passed through at such a speed that the polymer is permitted to penetrate the textile thoroughly by the time the wire emerges from the heating chamber. After it emerges the polymer should be permitted to solidify before the wire passes through the rolls 16. If desired, water cooling may be used to speed up solidification.

In place of the heating chamber at the outlet of the reservoir, a heating chamber at the inlet may be employed. If the wire is sufficiently heated by this means before it enters the pool of molten polymer, it does not tend to chill the impregnant and, therefore, impregnation takes place much more readily. An advantage of this procedure is that the heating chamber may be of a more convenient shape since the wire, which is not yet wet with the polymer, may be passed over rolls within the chamber. If desired, heating chambers at both the inlet and outlet may be employed. If the reservoir 10 is of sufficient depth and the wire is passed through sufficiently slowly, the heating chambers may, in some instances, be dispensed with entirely. Pressure may also be employed to force the polymer into the interstices of the braid.

Alternatively the wire, covered with polymer which has not yet thoroughly penetrated the fibrous covering, may be wound on a reel and the entire reel placed in an oven for a sufficient time to insure complete impregnation. After this treatment the wire should be unwound from the reel while still hot and passed through a polishing die, if desired.

If desired, a small amount of volatile solvent may be added to the molten polymer to decrease the viscosity and facilitate impregnation. In such a case provision must be made for the removal of the solvent from the coating on the wire after it leaves the molten bath. In all cases pressure may be applied to the reservoir, if desired,

to aid impregnation. Or alternatively the braid may be evacuated in a chamber at a low pressure to remove the air from the interstices of the fiber and subsequently exposed to the impregnant at a higher pressure.

In some instances the use of a small amount of a non-volatile low molecular weight solvent which solidifies at atmospheric temperatures may be desirable. An example of such a substance is diphenyl, which melts at about 71° C. At elevated temperatures the diphenyl acts as a solvent and serves to thin the molten polymer so that it may more easily penetrate the fibrous covering on the wire. When the impregnated material is cooled, the diphenyl solidifies out and forms a solid mixture with the polymer. The small amount of diphenyl has no disadvantageous effect on the protective covering.

When the covering on the wire consists of an organic fibrous material and a molten bath is used for impregnation, as described above, an impregnating polymer should be chosen which has a melting point sufficiently low so that the fibers can be thoroughly impregnated without being weakened from excessive exposure to heat. Similarly, care must be taken to prevent damage to the rubber or other insulation from too high a temperature or too long an exposure to heat. When the wire is covered with cellulose fibers, such as cotton braid, paper braid or paper pulp, the impregnating temperature is desirably between 100° and 200° C. To make possible the use of these impregnating temperatures the polymers should preferably have a melting point below about 170° C. By melting point is meant the temperature at which the polymer is converted to a definitely liquid state. However, the polymers should preferably have a softening temperature above about 60° C. so that they will not soften under ordinary atmospheric conditions.

Where the fibrous covering is made up of heat-resistant materials, such as mineral fibers, the impregnating temperature may obviously be higher, limited only by the possibility of destruction of the insulation.

At the temperature of impregnation the polymer should be sufficiently fluid so that impregnation may take place. Preferably the polymers should be capable of being reduced to an absolute viscosity less than about 5000 poises in the molten state.

A polymer which has been found to give very good results for the purposes of the present invention is polyethylene sebacate, which may be produced by the reaction of equal molecular proportions of sebacic acid and ethylene glycol at 200° C. in a stream of an inert gas. It softens at approximately 72° C. and at 130° C. forms a viscous melt which may be readily applied to wire, as described above.

Another very satisfactory polymer is polyethylene propylene sebacate, which may be produced under the conditions described above by the reaction of ethylene glycol, an amount of propylene glycol equal to about 5 per cent of the total glycol, and an amount of sebacic acid equivalent to the total glycol. This substance melts in about the same range as polyethylene sebacate. Similar results are obtained when other glycols, such as diethylene glycol, which form polymers with sebacic acid having melting points below that of polyethylene sebacate are substituted for propylene glycol.

Other suitable polymers are those prepared by the reaction of the following materials:

Polymer melting point (approximately), °C.	
10-hydroxy decanoic acid.....	76
Ethylene glycol and sebacic acid.....	72
Ethylene glycol and succinic acid.....	105
Decamethylene glycol and adipic acid.....	74
Diethylene glycol and sebacic acid.....	39
Hexamethylene glycol and succinic acid.....	57
Ethylene glycol and azelaic acid.....	45
11-amino undecylic acid.....	170
11-methyl amino undecylic acid.....	170
6-amino caproic acid.....	205
Piperazine and sebacic acid.....	155
Pentamethylene diamine and octadecandioic acid.....	167
Ethanol amine and sebacic acid.....	85
Ethylene glycol, propylene glycol and sebacic acid (containing .1 to 10% propylene glycol based on total glycol).....	72
Ethylene glycol, diethylene glycol and sebacic acid (containing .1 to 10% diethylene glycol based on total glycol).....	72

To possess the property of cold drawing which was described above and which is necessary to impart the quality of self-toughening to the finished wire, the polymers must possess a very high degree of polymerization. The degree of polymerization is indicated generally by the relative viscosity of the substance in dilute solution.

Relative viscosity is the ratio between the viscosity of the substance in a suitable solvent and the viscosity of the solvent itself. This value can be obtained conveniently by comparing with the viscosity of chloroform the viscosity of a solution of 0.4 gram of the polymer in sufficient chloroform to form 100 cc. of solution.

The property of cold drawing begins to appear in synthetic linear condensation polymers when their relative viscosity, measured as above, exceeds about 1.2.

The region in which the cold drawing appears may also be expressed in terms of the average molecular weight of the polymer. The average molecular weight may be estimated by means of viscosity measurements according to the following relationship given by Staudinger in his book entitled "Die hochmolekularen organischen Verbindungen" (1932, Berlin):

$$\frac{\eta_r - 1}{C} = K_m M$$

where

η_r =relative viscosity of the solution,

C=concentration of the solution in mols of the repeating group of the polymer per liter of solution,

K_m =a constant characteristic of the series of polymers, and

M=average molecular weight of the polymer.

Cold drawing begins to appear at an average molecular weight of about 7000 but appears more definitely at about 10,000.

In Fig. 2 is shown the finished wire with its protective covering. A metal conductor 25 is surrounded by an insulating material 26 which is in turn surrounded by a protective covering 27. The invention is applicable to any suitable insulating material, which may be enamel or rubber or a composition containing rubber, or which may be any other synthetic or natural elastic polymer having physical and electrical prop-

erties similar to rubber, or which may be a composition containing these materials. It may contain natural materials, such as gutta-percha or balata, or synthetic rubber-like polymers such as polymerized chloroprene or polymerized organic sulphides. In general the insulation is one which is very effective electrically but which should be protected for economic reasons against the deteriorating effects of continued exposure to the atmosphere or other outside or severe environment, such as burial underground.

The protective covering is preferably a fibrous material, such as a braid of textile or mineral fibers, paper braid, paper pulp or a combination covering which is impregnated with a suitable synthetic linear condensation polymer. Preferably the impregnation is as uniform and as thorough as possible, extending to the surface of the insulation itself. If desired, the protective covering may be placed over a bundle of two or more insulated wires instead of over each individual wire.

The impregnation of the wire has been described as conducted with a molten bath. Obviously, the impregnation may be carried on at ordinary temperatures by means of a solution of the polymers in a suitable volatile solvent. When this is done it may sometimes be advantageous to heat the wire above the melting point of the polymer either during or after the removal of the solvent in order to insure uniformity of the impregnation.

Impregnation by means of an emulsion or a suspension of the polymer in a suitable medium may sometimes be desirable. Thus the fibrous material may be impregnated with an aqueous suspension of a finely divided solid polymer at ordinary or slightly elevated temperatures. The water may then be removed by evaporation and the covered wire heated to a temperature sufficient to fuse the deposited polymer and form an impervious coating. In some instances the impregnation may take place at a temperature above the melting point of the polymer, the impregnating medium then consisting of an emulsion of finely divided particles of molten polymer in a suitable medium. As the suspending medium is removed, as by evaporation, the molten particles may coalesce to form an impervious coating.

Instead of impregnating the fibrous material on the wire, individual strands of fibrous material may be impregnated in a molten bath or a solution or suspension and subsequently formed into a braid over the wire. When this is done the finished wire should be heated above the melting point of the polymer for a sufficient time to fuse together the strands and form an impervious coating.

It is to be understood that the invention is not limited to the use of individual polymers in the protective coatings on wire. Thus mechanical mixtures of the various suitable polymers may be employed. Any other desired materials which have no harmful effect, such as mineral or other fillers, dyes, pigments, solvents which are solid at ordinary temperatures, resins and cellulose derivatives, may be added to the polymers to modify their properties or decrease their cost.

Although the invention has been described in terms of its preferred embodiments, certain modifications will be apparent to one skilled in the art and such modifications are intended to be included within the scope of the invention as defined by the appended claims.

What is claimed is:

1. An abrasion resistant covering on telephone wire of the type adapted to be strung outdoors in close proximity to the swaying branches of trees or in close proximity to other objects which subject the wire to rubbing or shearing stresses, comprising a textile fabric impregnated with a material having the property of increased toughness and tensile strength when subjected to stress, said material being a cold drawing superpolyester. 5 10

2. An outdoor, protectively covered, insulated telephone wire, which is subjected to abrasion or other types of stress tending to destroy its protective covering, consisting of a conductor insulated with a rubber composition and having over the rubber insulation a protective covering of high abrasion resistance made up of a textile fabric impregnated with a material having the property of increasing in toughness when subjected to stress, said material comprising a cold drawing superpolyester. 15 20

3. An electric conductor which has an outside covering and which is used for the outdoor transmission of electric current under conditions where it is subjected to abrasion or friction tending to destroy its covering, comprising a conductor having a covering of high abrasion resistance made up of a fabric impregnated with a cold drawing condensation superpolymer. 25 30

4. An outdoor, protectively covered, insulated telephone wire which is subjected to abrasion or other types of stress tending to destroy its protective covering, said wire consisting of a conducting core insulated with a rubber composition and having over the rubber insulation a protective covering of high abrasion resistance made up of a braided fabric impregnated with a condensation superpolymer possessing the property of cold drawing. 10

5. The wire described in claim 4 wherein the superpolymer is polyethylene sebacate.

6. The wire described in claim 4 wherein the superpolymer is polyethylene succinate. 15

7. Outdoor telephone wire for installations where it is subjected to abrasion or other types of rubbing or shearing stress tending to destroy its protective covering, said wire comprising an insulated conductor and a fabric surrounding said insulated conductor, said fabric being impregnated with a material having the property of increased toughness and tensile strength when subjected to stress, said material comprising the superpolyester produced from ethylene glycol and sebacic acid. 20 25

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