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R. SAXON

2,994,623

INSULATED ELECTRICAL CONDUCTOR AND METHOD OF MAKING THE SAME

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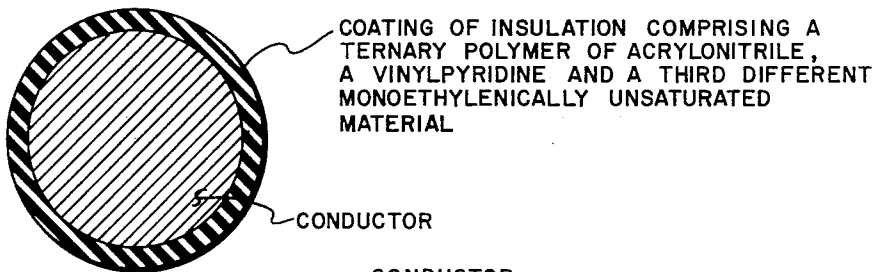


FIG. 1

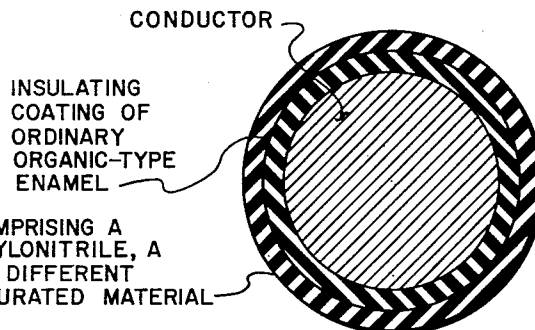


FIG. 2

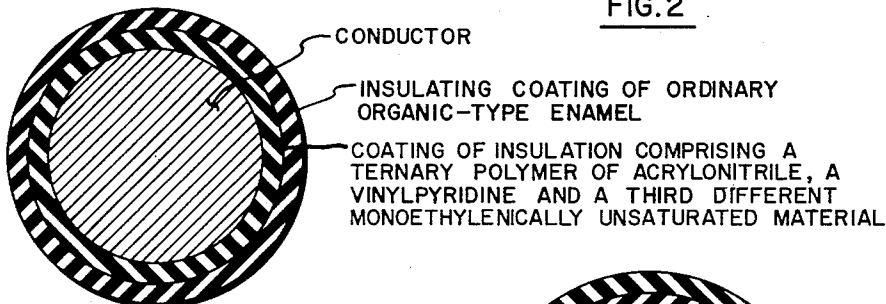


FIG. 3

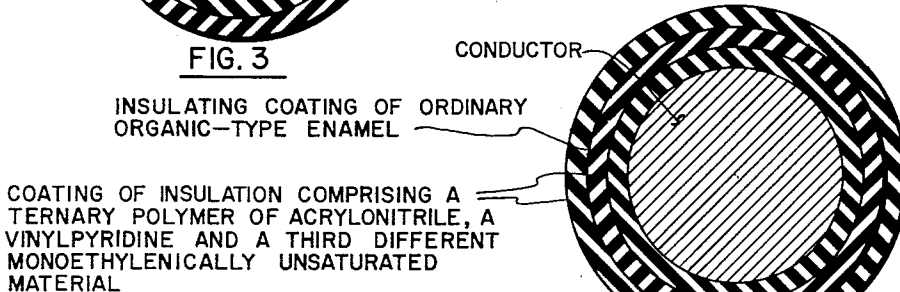


FIG. 4

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2,994,623

INSULATED ELECTRICAL CONDUCTOR AND METHOD OF MAKING THE SAME

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14 Claims. (Cl. 117-232)

This invention relates to insulated electrical conductors and to a method of making the same. More particularly, the invention is concerned with the manufacture of insulated electrical conductors having insulation of the organic-enamel type thereon.

In accordance with the present invention, metallic conductors, e.g., copper wire, aluminum wire, etc., are insulated with a particular ternary polymer. More specifically, the insulation on the conductor comprises a ternary polymer of, by weight, from 80% to 96% acrylonitrile, from 2% to 10% of a vinylpyridine and from 2% to 10% of a third, different, monoethylenically unsaturated material. The insulation coating is hard, flexible, moisture- and abrasion-resistant and has a high dielectric strength. It is also resistant to attack by such ingredients as oils, solvents, varnishes, and various chemicals.

It was known prior to the present invention to use a variety of resinous and polymeric materials dissolved in a suitable solvent as a so-called "wire enamel" or coating material in place of, or in addition to, the various enamels of the conventional varnish type that have been used for many years in the electrical industry. These older types of insulating coatings have been generally described as oleo-resinous coating compositions or enamels. Such oleo-resinous varnishes are not entirely resistant to mineral oil and mineral-oil-containing materials, and hence have been replaced to a large extent in recent years by wire enamels containing various synthetic resinous and polymeric materials.

One of the most effective and widely used wire enamels of the synthetic resin type is that described in Patent No. 2,085,995 and a modified form thereof in Patent No. 2,307,588. The first-named patent describes insulated conductors wherein the insulation is a polyvinyl acetal resin, specifically a polyvinyl formal resin, which is produced by condensing an aldehyde, e.g., formaldehyde, with a product of hydrolysis of a polyvinyl ester, e.g., polyvinyl acetate. The last-named patent involves a wire enamel comprising a polyvinyl acetal resin of the kind just described, which resin has been modified with a phenol-aldehyde resin, specifically a cresol-formaldehyde resin.

Other patents involving the use of wire enamels containing a synthetic resinous or polymeric material are Patent No. 2,271,233, directed to the use of a phenol-aldehyde resin-modified superpolyamide, by which is meant specifically a synthetic linear condensation product of the kind described in British Pats. 461,236 and 461,237, and now known generically as nylon; and Patents 2,191,584 and 2,249,498. In both of these last-named patents reference is made to the use of certain synthetic materials of the "polymerized acrylic compound" or "polymerized acrylic acid" types. By this language the respective patentees include polymerized methyl and ethyl esters of acrylic acid, polymerized acrylonitrile, separately or conjointly polymerized mixtures of methyl and ethyl esters of acrylic acid and separately or conjointly polymerized mixtures of either or both of the aforesaid esters with acrylonitrile.

The novel features of my invention are set forth in the appended claims. The invention itself, however, will be

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understood most readily from the following more detailed description when considered in connection with the accompanying drawing in which:

FIG. 1 is a cross-sectional view of an electrical conductor provided with insulation in accordance with the present invention;

FIG. 2 is also a cross-sectional view showing the conductor provided with a coating of insulation of ordinary organic-type enamel and a superimposed coating of the insulating material hereinafter more fully described;

FIG. 3 is another cross-sectional view illustrating a further modification of the invention; and

FIG. 4 is also a cross-sectional view showing a still further modification of the invention.

The present invention is based on my discovery that a ternary polymer of the kind broadly described in the second paragraph of this specification and more fully hereinafter provides an improved electrically-insulating coating on electrical conductors that permits the construction of more compact electrical equipment or, alternatively, more powerful equipment, e.g., motors, of about the same size than heretofore has been possible with the oleo-resinous wire enamels of many of the available wire enamels containing a synthetic resin or polymer. This is because the insulating materials used in practicing the present invention have a high degree of temperature resistance, particularly for a thermoplastic polymer; and, therefore, heat buildup due to passage of electric current through the conductor during the use of the apparatus containing the insulated conductors of this invention does not cause failure of the insulation.

It was quite surprising and unexpected that a thermoplastic polymer should give such good heat resistance, while maintaining all of the other desirable properties of a wire enamel since, by their inherent nature, thermoplastic polymers are subject to flow or deformation. The improved and unexpected results obtained from the insulated conductors of the present invention are due in part to the presence of a relatively small but critical amount of a vinylpyridine, more particularly an alkyl vinylpyridine, and specifically 2-methyl-5-vinylpyridine, as an essential ingredient of the ternary polymer component of the wire enamel; and to the use of a solvent comprising essentially dimethylformamide as the volatile (volatilizable) solvent employed in the wire enamel.

In order that those skilled in the art may better understand how the present invention can be carried into effect, the following examples are given by way of illustration and not by way of limitation.

EXAMPLE 1

Preparation of ternary polymer

A ternary polymer is made from a monomeric mixture of 7.5% vinyl acetate, 7.5% 2-methyl-5-vinylpyridine and 85% acrylonitrile by continuously polymerizing the aforesaid mixture in an aqueous medium using an oxidation-reduction catalyst system comprised of chloric acid and sulfuric acid and following the general procedure described in Mallison U.S. Patent No. 2,777,832. The resulting ternary polymer contains, in combined state, about 86.0% acrylonitrile, about 6.3% 2-methyl-5-vinylpyridine and about 5.4% vinyl acetate. This ternary polymer is dried and made into a wire enamel as described in Example 2.

EXAMPLE 2

Preparation of wire enamel

One hundred and sixty (160) parts of the dried, finely-divided ternary polymer of Example 1 is dissolved in 840 parts of dimethylformamide to form a wire enamel. This wire enamel is used in producing an insulated electrical conductor as described in Example 3.

EXAMPLE 3

Preparation of insulated electrical conductor

The wire enamel of Example 2 is used to coat No. 17 A.W.G. copper wire at a speed of 17 feet per minute in a wire-coating tower held at about 300° C. The so-called "build," that is, the increase in wire thickness as a result of the coating operation, is 2.9 mils. A smooth coating is formed on the wire. The coated wire successfully passes a flexibility test in which, after the coated wire has been given a 35% stretch, it is wound around a mandrel which is the same diameter as the wire. The so-called "scrape hardness" is 63, this being the number of ounces of load on a 9-mil diameter knife-edge to scrape enamel from the wire. The coated wire also shows excellent abrasion resistance, as evidenced by the fact that, in order to cause failure, from 78 to 186 strokes with a 16-mil knife-edge under a 740 g. load are required. In a heat-shock test, the coated wire is heated around its own diameter, heated at 200° C. for 15 minutes, and then cooled. Under this test, the coated wire does not show cracking or other evidence of failure of the insulation. The insulated electrical conductor shows a dielectric breakdown, in duplicate tests, of 3.0 and 4.0 k.v.

Instead of the ternary polymer made as described in Example 1, one can use a terpolymer made from a monomeric mixture of 7.5% methyl acrylate, 7.5% 2-methyl-5-vinylpyridine and 85% acrylonitrile which has been produced as broadly described in Example 1 and in the patent to which reference is there made. The resulting ternary polymer contains, in combined state, about 85% acrylonitrile, about 5.4% 2-methyl-5-vinylpyridine and about 7.5% methyl acrylate. This ternary polymer is made into a wire enamel as described in Example 2, which enamel is then used in making an insulated, coated wire as described in Example 3. The properties of the resulting insulated electrical conductor are much the same as the properties of the insulated electrical conductor of Example 3.

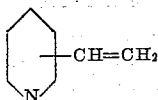
Various other ternary polymers comprising acrylonitrile, a vinylpyridine, and a third, different, monoethylenically unsaturated material, using the ranges of proportions of these ingredients that are given in the second paragraph of this specification, can be used instead of the two specific ternary polymers described hereinbefore. A preferred sub-class of ternary polymers that are useful in practicing the present invention is the one which comprises ternary polymers of, by weight, from 80% to 90% acrylonitrile, from 5% to 10% of a vinylpyridine including 2-methyl-5-vinylpyridine, and from 5% to 10% of a vinyl ester, specifically vinyl acetate. Additional examples of ternary polymers falling within this preferred sub-class are those made from a monomeric mixture of, by weight,

- (a) 84% acrylonitrile, 8% acrylamide and 8% 2-methyl-5-vinylpyridine,
- (b) 90% acrylonitrile, 5% methyl methacrylate and 5% 2-methyl-5-vinylpyridine,
- (c) 86% acrylonitrile, 7% methacrylonitrile and 7% 2-vinyl-5-ethylpyridine (or 7% 2-methyl-5-vinylpyridine).

The specific ternary polymers of (a), (b), and (c), and others employed in practicing this invention, can be prepared, used in making wire enamels, and the latter employed in manufacturing insulated electrical conductors in the manner described under Examples 1, 2, and 3.

Vinylpyridines which can be employed in making the ternary polymers of this invention are those represented by the formula

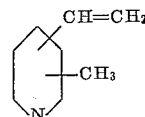
(I)



and which include 2-vinylpyridine, 3-vinylpyridine, and

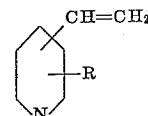
4-vinylpyridine; methyl vinylpyridines represented by the formula

(II)



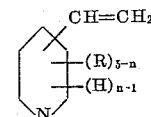
and which include 2-methyl-3-vinylpyridine, 3-vinyl-4-methylpyridine, 3-vinyl-5-methylpyridine, 2-vinyl-3-methylpyridine, 2-vinyl-4-methylpyridine, 2-vinyl-5-methylpyridine, 2-vinyl-6-methylpyridine, 2-methyl-4-vinylpyridine and 3-methyl-4-vinylpyridine. The vinylpyridines embraced by Formula II are a preferred subgroup within a broader class of vinylpyridines that are desirably employed in making ternary polymers for use in practicing the present invention and which may be represented by the formula

(III)



and wherein R represents a lower alkyl radical, more particularly a methyl, ethyl, propyl (including n-propyl and isopropyl) or butyl (including n-butyl, isobutyl, sec-butyl and tert-butyl) radical. Other examples include 2-vinyl-4,6-dimethylpyridine, and 2- and 4-vinylquinolines, 2-vinyl-4,6-diethylpyridine and others embraced by the formula

(IV)



wherein R represents a lower alkyl radical, examples of which have been given hereinbefore, and n represents an integer from 1 to 5, inclusive. One can substitute in the specific ternary polymers mentioned hereinbefore an equivalent amount of any of the vinylpyridines, of which numerous examples have just been given, for the 2-methyl-5-vinylpyridine employed in the previously given formulations.

Illustrative examples of other comonomers with acrylonitrile and a vinylpyridine that can be used as the third, different, monoethylenically unsaturated material are, for example, vinyl esters including the formate, propionate, butyrate; the various acrylic esters including the lower alkyl acrylates and methacrylates such as the ethyl, propyl, and butyl acrylates and the methyl, ethyl, propyl, and butyl methacrylates; the various acrylamides including acrylamide itself and methacrylamide; the various acrylic acids including acrylic acid itself and methacrylic acid; methacrylonitrile and other copolymerizable substituted acrylonitriles; unsaturated alcohols including allyl alcohol; vinyl-substituted aromatic hydrocarbons, e.g., styrene, the various ring-substituted methylstyrenes; isopropenyl toluene; and others including those given by way of example in, for instance, Cresswell U.S. Patent No. 2,558,730, dated July 3, 1951 (column 3, lines 31-55), and Price U.S. Patent No. 2,736,722, dated February 28, 1956 (column 4, line 66 through line 27 in column 5). The "third different monoethylenically unsaturated material" mentioned above includes within its meaning a plurality of such materials. Advantageously the third, different, monoethylenically unsaturated material is a compound which contains a $\text{CH}_2=\text{C}<$ grouping.

The ternary polymers employed in making the wire enamels, which then are used in making the insulated electrical conductors of the present invention, ordinarily have a molecular weight (average molecular weight) within a fiber-forming (fiber-formable) range; that is to say, within the range of from about 15,000 or 20,000 to about 200,00 as calculated from a viscosity measurement

of the ternary polymer in dimethylformamide using the Staudinger equation (reference: Houtz U.S. Patent No. 2,404,713, dated July 23, 1946). The use of ternary polymers having an average molecular weight above 200,000, e.g., about 300,000 and higher, is, of course, not precluded. Ordinarily the average molecular weight of the ternary polymer employed is within the range of from about 50,000 to about 100,000, and more specifically within the range of from about 60,000 to about 90,000.

Optimum results have been obtained by using a solvent comprising or consisting substantially completely of dimethylformamide for dissolving the ternary polymer in order to form the wire enamel. The concentration of the ternary polymer in the solvent comprised (or composed solely) of dimethylformamide may be considerably varied but generally is within the range of from about 5 to about 25 parts ternary polymer to from about 95 to about 75 parts of the aforesaid solvent. A preferred range within this broader range is one wherein the ratio of ternary polymer is from about 10 to about 20 parts of ternary polymer to from about 90 to about 80 parts of solvent comprised or consisting essentially of dimethylformamide.

The "active" or primary solvent, specifically dimethylformamide, may be used in combination with minor amounts (less than 50% by weight) of other solvents for the terpolymer including those described in, for example, U.S. Patents 2,404,714 to 2,404,728, inclusive. This may have cost advantages (without adversely affecting the properties of the insulated conductor) when the added solvent is less expensive than dimethylformamide.

Alternatively, the dimethylformamide solvent or mixture thereof with a minor amount, e.g., 5-40% by weight, of a different solvent for the terpolymer may be diluted with a diluent (e.g., acetone) which is normally a non-solvent for the terpolymer, the amount employed being insufficient to cause precipitation of the terpolymer. Such amounts may vary widely depending upon the particular solvent and non-solvent combination, but ordinarily the non-solvent is less than 50% by volume of the total volume of solvent plus non-solvent. Dilution of this nature has the advantage of lowering the cost of applying the wire enamel. Examples of diluents, in addition to acetone, that can be used are phenol and cresol.

Enameled wires are produced by drawing the clean wire, for example clean copper wire, through a bath of wire enamel made as described above. Thereafter the coated wire is subjected to heat, for instance by introducing it into a suitable oven or chamber wherein the applied coating is baked at a suitable temperature. With dimethylformamide alone as the solvent, a suitable temperature is about 250°-300° C. With mixtures of dimethylformamide and a different solvent for the terpolymer and/or a diluent of the kind and in the amount described above, the temperature frequently will be outside of this range. In all cases the temperature should be high enough to volatilize the liquid component(s) of the wire enamel but not so high as to cause blistering of the coating as a result of rapid evaporation.

The coating is baked simultaneously with the annealing of the copper. Usually it is necessary to run the wire successively through the enamel bath and baking oven several times in order to provide adequate insulation thereon. Baking improves the insulating properties of the coating, and may be carried out at any elevated temperature up to the point of incipient decomposition of the ternary polymer. In all cases, the higher the temperature employed, the shorter the period of heating; and, conversely, the lower the temperature, the longer the heating time. The baking treatment results in conversion of the coating on the wire to a hard, tough, abrasion- and moisture-resistant state.

It is to be understood that this invention is not limited to the application of the wire enamel, used in making the insulated conductors of this invention, directly upon

the conductor as shown in FIG. 1. For example, a coating of the insulation may be applied over a coating of regular enamel as shown in FIG. 2. The ternary polymer composition adheres tenaciously to the underlying enamel film, and protects the latter from abrasion and from embrittlement which otherwise results upon prolonged exposure to heat. Also, if desired, a conductor may be provided first with a coating of the ternary polymer, followed by one or more coatings of ordinary enamel as shown in FIG. 3. In this way the adherence of the ordinary organic enamel is improved. Thereafter an outer coating or coatings of the ternary polymer wire enamel may be applied to produce an insulated electrical conductor as shown in FIG. 4.

Wires insulated with the wire enamels of this invention are far superior to those insulated with conventional organic enamels. The heat-treated coating as present on the wire is not only extremely hard and tough, but it is also flexible. The coating on a copper conductor is, in general, more flexible than the copper itself, as evidenced by the fact that it is possible to stretch a coated copper wire of this invention to the breaking point and still wind the wire on itself without evidence of cracking of the film or coating. The film is resistant to almost all commonly used solvents, e.g., petroleum hydrocarbon naphthas, alcohols, and aromatic solvents such as benzene, toluene, xylene, and the like.

The insulation coatings on electrical conductors produced as hereinbefore described are also exceptionally resistant to heat aging. For example, tests indicate that at 105° C. the coated wires of this invention will not lose their extreme flexibility when heated for as long as 2,000 hours at 105° C., whereas ordinary organic-type wire enamels generally will not withstand heating for longer than about 24 hours at 105° C. without cracking on a mandrel test such as has previously been described. Insulated wires of this invention can be elongated to any extent necessary in practical manufacturing, treated with varnish, and immediately placed in an oven at a temperature of 150° C.

The dielectric strength of the insulation of the insulated conductors of this invention is high, and the dielectric losses are low. It is, therefore, possible to use a much thinner overall insulation than previously had been required with most of the prior wire enamels. Because less insulation is required, more copper can be placed in the slot of a motor or generator, resulting in an increased rating of the machine. This applies to transformers, regulators, and other electrical apparatus in which insulated wire is used in the form of a coil. On the other hand, if the rating of the machine is kept constant, there results a material saving of copper and iron.

The insulated electrical conductors of this invention are useful in electrical motors, magnets, coils, and other electrical devices wherein an insulated conductor, such as copper, aluminum or other conducting metallic wire, is tightly wound or packed. The insulated conductors may be used in cables and transmission lines, or for general electrical purposes.

I claim:

1. An insulated electrical conductor in which the insulation comprises a ternary polymer of, by weight, from 80% to 96% acrylonitrile, from 2% to 10% of a vinylpyridine and from 2% to 10% of a third, different, monoethylenically unsaturated material.

2. An insulated electrical conductor as in claim 1 wherein the ternary polymer has an average molecular weight within the range of from about 50,000 to about 100,000.

3. An insulated electrical conductor as in claim 1 wherein the vinylpyridine component of the ternary polymer of which the insulation is comprised is a vinylpyridine including 2-methyl-5-vinylpyridine.

4. An insulated electrical conductor as in claim 1 wherein a vinyl ester is the third, different, monoethyl-

enically unsaturated material which is present in the ternary polymer of which the insulation is comprised.

5. An insulated electrical conductor in which the insulation comprises a ternary polymer of, by weight, from 80% to 90% acrylonitrile, from 5% to 10% of a vinylpyridine including 2-methyl-5-vinylpyridine, and from 5% to 10% of vinyl acetate, said ternary polymer having an average molecular weight within the range of from about 60,000 to about 90,000.

6. An insulated electrical conductor as in claim 5 wherein the electrical conductor is copper wire.

7. An electrical conductor having superimposed directly thereon a hard, flexible, tough, abrasion-resistant coating of high dielectric strength, said coating being a heat-treated ternary polymer having the composition defined in claim 1.

8. An electrical cable comprising an electrical conductor provided with a hard, flexible, tough, abrasion-resistant coating of high dielectric strength, said coating being the heat-treated ternary polymer having the composition defined in claim 5.

9. The method which comprises dissolving in a solvent comprising dimethylformamide a ternary polymer of, by weight, from 80% to 96% acrylonitrile, from 2% to 10% of a vinylpyridine and from 2% to 10% of a third, different, monoethylenically unsaturated material, said ternary polymer having an average molecular weight within the range of from about 50,000 to about 100,000 and being dissolved in said solvent comprising dimethylformamide in an amount that will provide a solution having a ratio of ternary polymer to solvent of, by weight, from about 5 to about 25 parts ternary polymer to about 95 to about 75 parts solvent; applying the resulting solution to an electrical conductor to form a coating thereon; and heating the thusly coated electrical conductor at a temperature sufficiently high to volatilize the solvent and to form a hard, flexible, tough, abrasion-

resistant coating of high dielectric strength on said conductor.

10. A method as in claim 9 wherein the ternary polymer is one which has the composition defined in claim 5, the ratio of ternary polymer to the solvent comprising dimethylformamide is, by weight, from about 10 to about 20 parts of ternary polymer to about 90 to about 80 parts of said solvent, and the electrical conductor is copper wire.

11. A method as in claim 9 wherein the solvent consists substantially completely of dimethylformamide.

12. Copper wire in the form of a coil and which is insulated with electrical insulation comprising a ternary polymer of, by weight, from 80% to 96% acrylonitrile, from 2% to 10% of a vinylpyridine and from 2% to 10% of a third, different, monoethylenically unsaturated material, said ternary polymer having an average molecular weight within the range of from about 50,000 to about 100,000.

13. Copper magnet wire having superimposed directly thereon a coating of a ternary polymer of, by weight, from 80% to 90% acrylonitrile, from 5% to 10% of a vinylpyridine including 2-methyl-5-vinylpyridine, and from 5% to 10% vinyl acetate, said ternary polymer having an average molecular weight within the range of from about 60,000 to about 90,000.

14. Electrical apparatus wherein an insulated metallic conductor is tightly wound, the insulation on said conductor comprising a ternary polymer of, by weight, from 80% to 96% acrylonitrile, from 2% to 10% of a vinylpyridine and from 2% to 10% of a third, different, monoethylenically unsaturated material.

References Cited in the file of this patent

UNITED STATES PATENTS

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2,891,035	Price	June 16, 1959

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,994,623

August 1, 1961

Robert Saxon

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 28, for "acrylontrile" read -- acrylonitrile --; line 29, for "descriped" read -- described --; line 30, for "pataent" read -- patent --; column 4, line 75, for "200,00" read -- 200,000 --; column 6, line 22, for "thist" read -- this --.

Signed and sealed this 5th day of December 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

DAVID L. LADD

Commissioner of Patents

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