

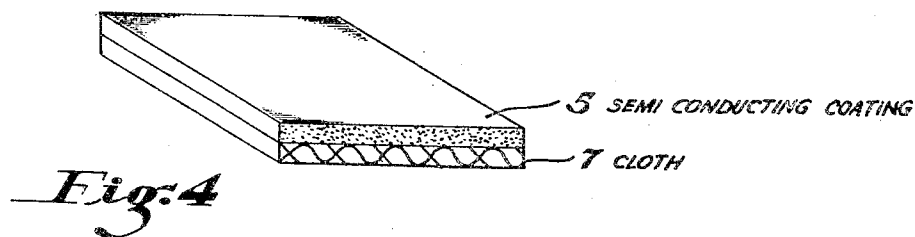
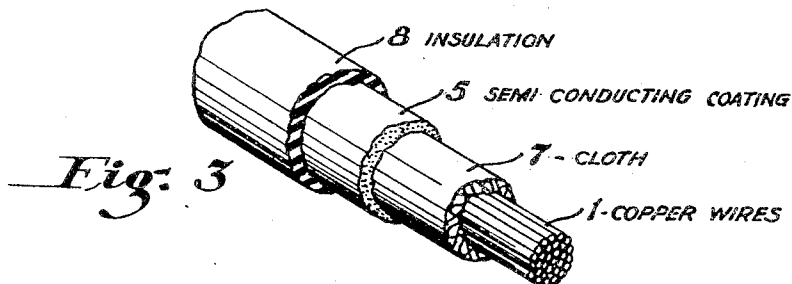
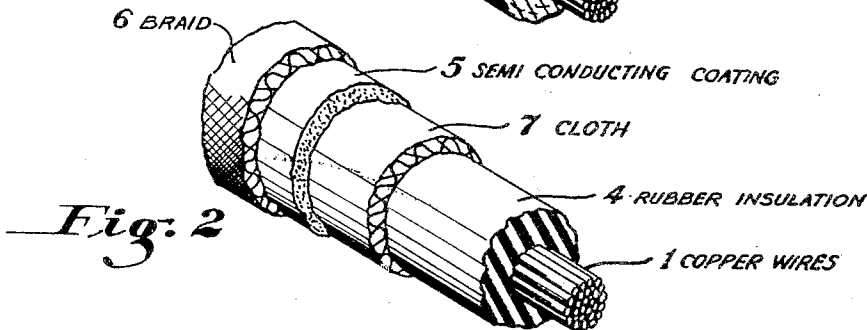
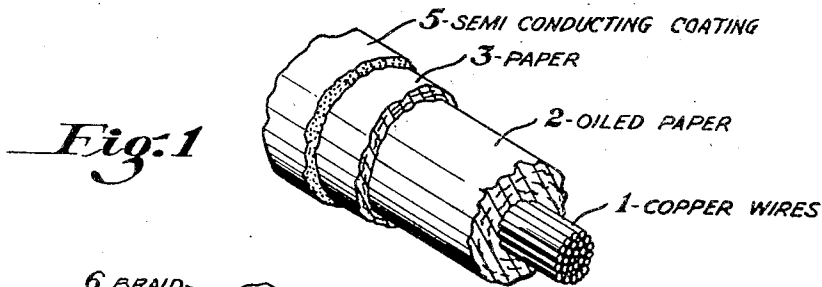
March 16, 1948.

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2,437,708

SEMI-CONDUCTING TAPE FOR ELECTRIC CABLE

Filed Feb. 18, 1944



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2,437,708

SEMICONDUCTING TAPE FOR ELECTRIC CABLE

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Application February 18, 1944, Serial No. 522,980

7 Claims. (Cl. 174-102)

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This invention relates to a semi-conducting oil impervious coating material for use as an electrostatic shield on high tension insulated electrical conductors where it is desirable to maintain the voltage gradient at the surface of the insulation below a value above which harmful electrical disturbances occur.

Heretofore it has been common to dissipate high voltage charges which surround electric cables carrying high voltages, that is, of the order of 2000 volts or more, by means of a metallic conducting shield over an insulating medium which may be in the form of oil saturated paper, rubber, varnished cambric and the like. In ordinary use it is necessary to dissipate or discharge the charges which surround such a cable and this has been done by various means, such as surrounding the cable with the thin metallic sheath mentioned above. Metals, however, have the disadvantage that frequent bendings of the cable tend to develop air gaps because of the separation of the metal shield from the adjacent insulation. When such gaps are formed, arcing across the air gap may occur which eventually causes a failure of the insulating medium or ozone may be formed in the air gap which deleteriously affects the insulation. It has also been proposed to provide a shield which is more flexible than metal. Such shields have been prepared by a conducting paint, compositions of rubber, or other film-forming agents in combination with metallic particles. None of these expedients has been entirely satisfactory when used in combination with oil impregnated insulation due primarily to the attack of the oil on the film-forming agents whereby the conducting properties of the films are deleteriously affected.

In U. S. application for Letters Patent Ser. No. 373,181 of Peterson, now Patent No. 2,322,702, granted June 22, 1943, a method for producing satisfactory shielded cables is disclosed. The present invention relates to a modification of the method therein disclosed which offers several desirable advantages, specifically a type of conducting coating or film that embodies enhanced resistance to the solvent action of materials common to cable insulation, permanence of properties when exposed to the effects of aging and electrical discharges, and a means of providing a

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readily controlled degree of electrical conductivity.

We have now found that many disadvantages of prior art rubber compositions and similar semi-conducting shields have been overcome by the use of a tape having a composition containing a special type of polyamide and a special type of carbon black on its surface or impregnated therewith, especially when used in combination with oil impregnated insulation.

The special types of polyamides are those which are soluble in a lower aliphatic monohydric alcohol, such as those disclosed in U. S. Patent 2,285,009 to Brubaker et al., granted June 2, 1942, and N-alkoxymethyl polyamides disclosed in Cairns application Ser. No. 445,635, filed June 3, 1942 (now abandoned).

The latter are a new class of nitrogen-substituted polyamides formed by reacting with an aldehyde and a formaldehyde-reactive organic compound having a hydrogen attached to an element of groups V and VI of series 2 and 3 of the periodic table, in the presence of an oxygen-containing acid catalyst, polyamides of the general type described in U. S. Patents 2,071,250, 2,071,253 and 2,130,948. The polyamides of this kind, generally speaking, comprise the reaction product of a linear polymer-forming composition containing amide-forming groups, for example, reacting material consisting essentially of bifunctional molecules each containing two reactive groups which are complementary to reactive groups in other molecules and which include complementary amide-forming groups. These polyamides can be obtained by the methods given in the above mentioned patents and by other methods, for example, by self-polymerization of a mono-aminomonocarboxylic acid, by reacting a diamine with a dibasic carboxylic acid in substantially equimolecular amounts, or by reacting a monoaminomonohydric alcohol with a dibasic carboxylic acid in substantially equimolecular amounts, it being understood that reference herein to the amino acids, diamines, dibasic carboxylic acids, and amino alcohols is intended to include the equivalent amide-forming derivatives of these reactants. The preferred polyamides obtained from these reactants have a unit length of at least 7, where "unit length" is defined as in United States Patents 2,071,253 and

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2,130,948. The average number of carbon atoms separating the amide groups in these polyamides is at least two.

These linear polyamides include also polymers, as for instance the polyester-amides, obtained by admixture of other linear polymer-forming reactants, as for instance glycol-dibasic acid mixtures or hydroxy acids, with the mentioned polyamide-forming reactants. Both the simple and modified linear polyamides contain the recurring amide groups



in which X is oxygen or sulfur and R is hydrogen or a monovalent hydrocarbon radical, as an integral part of the main chain of atoms in the polymer. On hydrolysis with hydrochloric acid the amino acid polymers yield the amino acid hydrochloride, and the diamine-dibasic acid polymers yield the diamine hydrochloride and the dibasic carboxylic acid, and the amino alcohol-dibasic acid polymers yield the amino alcohol hydrochloride and the dibasic carboxylic acid.

These nitrogen-substituted polyamides are typified by N-methoxymethyl polyhexamethylene adipamide, which was prepared as follows:

A solution of 1 part of polyhexamethylene adipamide (intrinsic viscosity=1.0) in 3.7 parts of formic acid (commercial grade, specific gravity=1.20) was prepared at 60° C. in a stainless steel reaction vessel equipped with a mechanical stirrer and an opening for the addition of reagents. To this was added at 60° C. a solution of 1 part paraformaldehyde dissolved in 1.33 parts methanol containing 0.0006 part sodium hydroxide to depolymerize the paraformaldehyde and render it soluble in the methanol. The resulting solution was maintained at 60° C. for 30 minutes during which time an additional 0.3 part of methanol was added. This solution was poured into a mixture of 9 parts acetone and 11.5 parts of cold water with stirring. The resulting solution was then made basic to litmus by the addition of concentrated aqueous ammonia, the mixture being maintained below 40° C. and stirred vigorously during this step. The reaction product, N-methoxymethyl polyhexamethylene adipamide, separated from the mixture as a white granular solid. This product was removed by filtration, washed thoroughly and dried in vacuum at 50° C.

The carbon black which is used may be prepared according to an article published in "Canadian Chemistry & Metallurgy," May, 1933, pages 93 to 95 by Charles Kaufmann.

In addition to this carbon black, there are now on the market many blacks with high conducting properties. Chapter 7, page 67 of the book "Columbian Colloidal Carbons," published in 1938 by the Columbian Carbon Company, defines a suitable type of black as having an electrical resistance in ohms per 1" cube of .152 to .217, although a somewhat higher resistance up to about 1.0 ohm per 1" cube is satisfactory. In the claims such blacks are termed "low resistance carbon blacks."

In the drawing Figures 1, 2, and 3 are diagrammatic partial sections of a high tension cable prepared according to the present invention. Figure 4 is a diagrammatic section of a piece of semi-conducting tape. In the drawing, 1 represents a conductor which may be solid or made up of a bundle of wires as shown. In Figure 1 an oiled paper layer 2 surrounds the

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conductor 1. Over this oiled paper layer is applied a semi-conducting tape made up of a base 3 which may be paper 3 as shown in Figure 1, or the paper may be replaced by a suitable fabric. The tape with the paper or fabric base is provided with a semi-conducting coating 5. The tape is prepared by impregnating or coating the base with a semi-conducting composition and cut into strips of suitable width, which is then wound around the insulated cable. Figure 2 is a modification of Figure 1 showing a rubber insulation 4 next to the conductor 1 instead of the oiled paper shown in Figure 1. The semi-conducting tape also differs from Figure 1 in the cloth base 7 instead of the paper base 3. In Figure 2 the semi-conducting coating is covered with a conventional braid 6.

Figure 3 represents a modification of Figures 1 and 2 in which the semi-conducting tape is applied directly to the copper conductor 1. An insulation 8 is provided over the semi-conducting coating 5. This insulation may be rubber shown as 4 in Figure 2 or oiled paper shown as 2 in Figure 1 or other types of electrical insulation. Figure 4 illustrates a section of the semi-conducting tape which has a cloth base 7 and a semi-conducting coating 5, the composition of which will be more fully described in the following examples.

In some cases it may be desirable to encase the improved cable or a plurality of such cables in a lead sheath or equivalent protective means according to common practice to make the assembly more impervious to water and more resistant to mechanical abrasion and to function also as a fault current carrying medium to ground.

The resistance of the tape or unsupported layer should be of the order of 300 to 1000 ohms per inch square. Under some conditions the tape may have a resistance of up to 2000 ohms or even more. When a cloth base is used, it is preferable to coat the same with about 2 to 4 ounces per square yard of polyamide-carbon black composition. When a paper base is used, about 1 ounce per square yard is satisfactory. The composition applied to the fabric or paper base may be prepared in any known manner or by methods illustrated by the following examples.

Example I

The following ingredients were heated to about 80° F. with stirring for 12 hours in a suitable mixer, such as a Werner & Pfleiderer:

	Parts by weight
Polyamide prepared according to Example I of U. S. Patent 2,285,009	10
Isopropyl alcohol	30
Water	10
Low resistance carbon black	3

The water, alcohol, and polyamide were placed in the mixer first and after about 12 hours' mixing the low resistance carbon black was added and mixing continued for an additional 12 hours. Immediately before applying the composition to the fabric or paper base, it was stirred vigorously in a high speed mixer for another hour.

Example II

While the coating composition of Example I functions well when the semi-conducting tape is formed from paper, it may penetrate an open weave fabric unduly. To prevent penetration of

the base support, the following composition may be applied:

	Parts by weight
Polyamide ¹	25
Ethyl alcohol	110
Water	45

¹ The polyamide used in this example was an N-alkoxymethyl polyhexamethylene adipamide as disclosed above.

A single coat of this composition is applied by any suitable means to a moderately open weave fabric sheeting. After the base coat has dried, it is treated as in Example I with about 4 ounces per square yard of the composition therein disclosed.

Example III

It was found that tape with either paper or fabric backing, more particularly with fabric backing, produced from the coating compositions described in Examples I and II, while highly serviceable, could be improved as to some of the desired characteristics, such as shortness, conductivity, elasticity, extensibility, and absence of flakiness of the coating, if the resin base included the N methoxy methyl polyhexamethylene adipamide type disclosed above. The compounding of the Brubaker composition has already been described. The N-alkoxymethyl polyamide base composition is produced as follows:

	Parts by weight
N-alkoxymethyl polyhexamethylene adipamide	25
Ethyl alcohol	90
Water	36

The resin and solvents are heated and slowly agitated for 12 hours at 140° F. or higher. 75 parts of low resistance carbon black were then added and slow agitation is continued for 12 hours. The mixture is agitated for 1 hour with a high speed agitation. Equal parts of the two compositions, those from the Brubaker patent and the above described N-alkoxymethyl polyamide type, are mixed together, after which coating proceeds as in Examples I and II. While equal parts yield highly serviceable products, we are not limited to such proportions; our invention comprehends mixtures in all proportions.

The time of mixing is important since if the carbon black is entirely surrounded by a film of polyamide, the composition is not sufficiently conducting. The grinding of the carbon black and polyamide mixture should be controlled to give the desired resistance. This time is usually between 6 to 15 hours. In the examples, the supporting base is coated on one side only. If desired, both sides may be coated or the fabric may be impregnated by drawing it through a bath of the polyamide-carbon black mixture suitably diluted. The paper base may be any suitable type but cable insulating paper sold by Union Mills having a thickness of about .003 to .0035 inch is preferred. Suitable fabric is a cotton sheeting of 40 inch width weighing about 6.25 yards per pound. Usually three coats are applied to obtain the necessary thickness although a fewer or greater number may be applied as desired. After the paper or fabric base is coated, it is cut into convenient widths in the form of a tape which is then used for wrapping about the conductor in any conventional desired manner. The particular type of polyamide used is critical and only those which are soluble preferably in an alcoholic solution may be used. The ratio of polyamide to low resistance carbon black should

be between .25 and 4 parts of polyamide to each part of carbon black.

In addition to the soluble polyamides illustrated in the examples, any of those described in U. S. Patents 2,252,554, granted August 12, 1941, 2,252,555, granted August 12, 1941, and 2,252,556, granted August 12, 1941, are likewise suitable. Those melting below about 175° C. are particularly preferred. Examples of these are the multi-component polyamides prepared from hexamethylenediamine, adipic acid, sebacic acid, and caprolactam as described in U. S. Patent 2,285,009, and the alkoxy-methyl polyamides such as methoxymethyl hexamethylene adipamide described above. These latter materials may be prepared by the condensation of a polyamide with formaldehyde and an alcohol. While the invention has been illustrated with certain polyamides, the polyesteramides, formed from combinations of ester- and amide-forming reactants, including dibasic acids, diamines, glycols, hydroxy acids; amino acids, and amino alcohols which are described in U. S. Patents 2,071,250, granted February 19, 1937, and 2,312,879, granted March 2, 1943, may be used. Polyesteramides which have been converted to higher molecular weight products by reaction with a diisocyanate as described in U. S. Patent 2,333,639, granted November 9, 1943, are also suitable. Such products may be subsequently converted after calendering to insoluble, infusible products by treating them with formaldehyde or formaldehyde liberating substances.

Cables prepared according to the present invention have been found to have an exceptionally long life and maintain uniform electrical characteristics much longer than any heretofore tested. The compositions applied to the tape are particularly resistant to the oil with which the sublayers of paper have been impregnated. The breakdown of the older type materials, rubber, etc. is accompanied with an emanation of decomposition products which contaminate the insulating oil and ruin its insulating properties. The stability of the nylon base in oil contributes to the longevity of the insulating phase. While the composition of matter which we have discovered is particularly adaptable to use as a conducting shield for high tension cables, it is also equally useful for other related applications where it is desirable to obtain an electrically conducting surface or film.

It is apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof; and, therefore, it is not intended to be limited except as indicated in the appended claims.

We claim:

1. An oil-impervious semi-conducting tape comprising a flexible supporting base and a semi-conducting coating thereon, said coating comprising an alcohol-soluble synthetic linear polyamide having an intrinsic viscosity of at least 0.4, a unit length of at least 7, and an average of at least 2 carbon atoms separating the amide groups, said synthetic linear polyamide being selected from the group which consists of (a) linear polyamides formed by reacting 30-45% of caprolactam, 10-50% of hexamethylenediammonium adipate, and 10-45% of hexamethylenediammonium sebacate, (b) linear polyamides formed by reacting 20-60% of 6-aminocaproic acid and not less than 10% each of at least two of the following polyamide-forming compositions: hexamethylenediammonium sebacate, hexa-

methylenediammonium adipate, and a mixture of hexamethylenediammonium suberate and hexamethylenediammonium azelate in approximately 15:85-30:70 proportions, and (c) linear polyamides formed by reacting synthetic fiber-forming linear polyamides having hydrogen-bearing amide groups separated by an average of at least 2 carbon atoms with a mixture of formaldehyde and an alcohol in the presence of an oxygen-containing acid catalyst, and a carbon black which has a resistance of less than about 1 ohm per 1-inch cube, these components being present in the ratio of between approximately .25 and 4 parts of said polyamide to 1 part of said carbon black.

2. The semi-conducting tape of claim 1, in which the polyamide is a polyester-amide having a melting point below 175° C.

3. The semi-conducting tape of claim 1, in which the base is a fabric base.

4. The semi-conducting tape of claim 1, in which the base is a paper base.

5. An oil-impervious semi-conducting coating composition, particularly adapted for the manufacture of high tension electric cables, comprising an alcohol-soluble synthetic linear polyamide having an intrinsic viscosity of 0.4, a unit length of at least 7, and an average of at least 2 carbon atoms separating the amide groups, said synthetic linear polyamide being selected from the group which consists of (a) linear polyamides formed by reacting 30-45% of caprolactam, 10-50% of hexamethylenediammonium adipate, and 10-45% of hexamethylenediammonium sebacate, (b) linear polyamides formed by reacting 20-60% of 6-aminocaproic acid and not less than 10% each of at least two of the following polyamide-forming compositions: hexamethylenediammonium sebacate, hexamethylenediammonium adipate, and a mixture of hexamethylenediammonium suberate and hexamethylenediammonium azelate in approximately 15:85-30:70 proportions, and (c) linear polyamides formed by reacting synthetic fiber-forming linear polyamides having hydrogen-bearing amide groups separated by an average of at least 2 carbon atoms with a mixture of formaldehyde and an alcohol in the presence of an oxygen-containing acid catalyst, and a carbon black having a resistance of less than about 1 ohm per 1-inch cube, in the proportion of between approximately .25 part and 4 parts of said polyamide to 1 part of said carbon black.

6. A high tension insulated electric cable com-

prising a high tension electric conductor, a layer of oil-impregnated insulation therearound, and an oil-impervious organic electric shielding layer over and in contact with the insulation, the shielding layer containing approximately .25 part to 4 parts of an alcohol-soluble synthetic linear polyamide having an intrinsic viscosity of 0.4, a unit length of at least 7, and an average of at least 2 carbon atoms separating the amide groups, said synthetic linear polyamide being selected from the group which consists of (a) linear polyamides formed by reacting 30-45% of caprolactam, 10-50% of hexamethylenediammonium adipate, and 10-45% of hexamethylenediammonium sebacate, (b) linear polyamides formed by reacting 20-60% of 6-aminocaproic acid and not less than 10% each of at least two of the following polyamide-forming compositions: hexamethylenediammonium sebacate, hexamethylenediammonium adipate, and a mixture of hexamethylenediammonium suberate and hexamethylenediammonium azelate in approximately 15:85-30:70 proportions, and (c) linear polyamides formed by reacting synthetic fiber-forming linear polyamides having hydrogen-bearing amide groups separated by an average of at least 2 carbon atoms with a mixture of formaldehyde and an alcohol in the presence of an oxygen-containing acid catalyst, to 1 part of a carbon black which has a resistance of less than about 1 ohm per 1-inch cube.

7. The article of claim 6, in which the resistance of the polyamide-carbon black mixture is between 300 and 2,000 ohms per square inch.

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