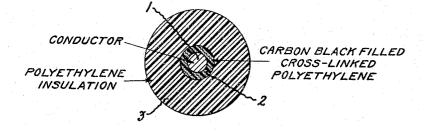
R. A. WARD
METHOD OF MAKING POLYETHYLENE INSULATED
ELECTRICAL CONDUCTORS
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3,325,325 METHOD OF MAKING POLYETHYLENE INSU-LATED ELECTRICAL CONDUCTORS Robert A. Ward, Scotia, N.Y., assignor to General Electric Company, a corporation of New York
Original application May 21, 1958, Ser. No. 736,760.
Divided and this application Dec. 17, 1962, Ser. No.

2 Claims. (Cl. 156-56)

This application is a division of my copending applica- 10 tion Ser. No. 736,760, filed May 21, 1958 (now abandoned). This invention is concerned with polyethylene insulated conductors. More particularly, the invention relates to a polyethylene insulated conductor composed of a metallic core, an outer insulation of polyethylene, and an intermediate semiconducting layer of insulation comprising a cross-linked, carbon-black filled polyethylene.

Polyethylene insulated conductors and equipment have within recent years become important improvements in the insulating field. In combination with such polyethylene insulated conductors, it is often required that there be present a means for eliminating or minimizing electrical breakdown of equipment due to high voltage discharges (corona damage). In order to effect this desired result, the use of semiconducting layers between the metallic core and the outer polyethylene insulation for the purpose of distributing high voltage stress gradients have been found to be an essential feature of such insulated conductors. However, heretofore, any semiconducting layer used in an insulating system has not been satisfactory in combination with polyethylene insulated conductors.

This is due to the fact that when corona, which is an electrical discharge occurring between two electrodes when a critical voltage is exceeded, causes localized high temperatures and chemical action from ions or radicals formed, thereby resulting in mechanical erosion and reduction in the efficiency of the primary outer insulation. In the usual cases, corona discharge takes place in air spaces or gaps between the conductor and the ground insulation.

Where corona discharges take place in the air spaces or gaps between the conductors and the ground insulation. usually such gaps are present because of the porosity of the cotton strand insulation and the crevice formed by the radius of curvature of the individual strands. Normal procedure for high voltage insulation entails compounding by vacuum and pressure processing. This fills in voids in the basic structure and also compresses the insulation into any gaps next to the conductor. However, this procedure is both time consuming and costly and even when used 50 does not produce a satisfactory insulated conductor which is as free of corona discharge as is desired.

It is, therefore, one of the objects of this invention to prevent corona attack of a polyethylene insulated con-

It is another object of the invention to employ a semiconducting layer in combination with polyethylene insulated conductors which is compatible with the poly-

It is still a further object of the invention to prepare an 60 insulated conductor whose primary insulation is based on polyethylene in which the insulation will expand and contract with temperature changes without the appearance of voids in any substructure underneath the outer polyethylene insulation.

It is an additional object of the invention to obtain polyethylene insulated conductors which are free of moisture sensitivity and which have high thermal stability at temperatures as high as 150° C.

Other objects of the invention will become apparent 70 from the description thereof which follows.

All the foregoing objects of the invention are obviated

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by employing an insulated conductor in which the outer insulation is polyethylene and there is present between the outer insulation and the metallic conducting core an intermediate layer of insulation comprising a cross-linked, carbon-black filled polyethylene.

The conducting core which comprises the subject of the present invention may be any one of those normally used in the electrical arts, for instance, copper, aluminum,

alloys of copper, alloys of aluminum, etc.

The polyethylene employed in the practice of the present invention is a solid, polymeric material formed by the polymerization of ethylene at various temperatures and pressures. Such material is described in U.S. Patent 2,153,553-Fawcett et al., and in "Modern Plastics Encyclopedia," New York 1949, pages 268-271. Specific examples of commercially available polyethylene are the polyethylenes sold by E. I. du Pont de Nemours and Company, Inc., Wilmington, Del., under the name of "Alathon;" those sold by Bakelite Company, such as DE-2400, DYNH, etc.; polyethylene sold by Phillips Petroleum Company, such as Marlex 20, 50, etc. Other polyethylenes which are included in the practice of the present invention and which may be prepared by either high or low pressure polymerizations, are found described in recently issued United States Patents 2,816,883 and 2,882,357.

The outer insulation may be thermoplastic polyethylene which may be readily extruded over the metallic core and the intermediate semiconducting polyethylene layer. Alternatively, the polyethylene may be wrapped around the latter two components in the form of a tape or sheet and thereafter subjected to a molding operation to effect compacting of the outer insulation over the metallic core and intermediate layer of semiconducting polyethylene.

In addition to employing thermoplastic polyethylene as the outer insulation, it is also intended to include within the scope of the invention the use of an outer cross-linked polyethylene, for instance, polyethylene which may be cross-linked to the substantially infusible and insoluble state, as, for instance, by irradiation with high energy electrons (for instance, with a dose of from 4×106 rep to 5×10^8 rep) as is more particularly disclosed and claimed in the copending application of Lawton and Bueche, Ser. No. 324,552, filed Dec. 6, 1952 (now abandoned). In addition, the polyethylene may be chemically cross-linked. usually in situ, by means of a specific class of organic peroxides (e.g., dicumyl peroxide in amounts ranging from 0.1 to 10 percent of the weight of the polyethylene) as is more particularly disclosed and claimed in U.S. 2,826,570 and in the copending application of Precopio and Gilbert, Ser. No. 509,388, filed May 18, 1955 (now Patent 3,079,370), both of the aforesaid applications being assigned to the same assignee as the present invention and by reference being made part of the discloures of the instant application.

Alternatively, the outer polyethylene insulation may be cross-linked, for instance, by chemical means or by irradiation with high energy electrons and thereafter subjected to a milling operation and thereby made suitable for extrusion over the metallic core and over the intermediate semiconducting carbon-black filled, cross-linked polyethylene. The use of such milling techniques to make crosslinked polyethylene extrudable is more particularly disclosed and claimed in the copending applications of Ouintin P. Cole, Ser. No. 561,937, filed Jan. 27, 1956 (now Patent 2,919,475), and Ser. No. 437,477, filed June 17, 1954 (now Patent 2,919,473), both applications being assigned to the same assignee of the present invention and by reference being incorporated as part of the instant ap-

The outer insulation of polyethylene when applied in

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tape form preferably comprises a flat stock material (e.g., tape) which has been oriented, i.e. stretched at least 10 percent up to 50 percent or more, in at least one direction, preferably in at least the lengthwise direction of the tape, and advantageously in both transverse and lengthwise directions. This orientation generally comprises stretching the polyethylene either after, during, or before irradiation of the polyethylene with high energy electrons to crosslink the polyethylene. This orientation of the polyethylene can also be exercised in connection with chemically crosslinked polyethylene referred to above. Thereafter, when the oriented or stretched polyethylene is applied to the metallic core and the intermediate semiconducting crosslinked polyethylene layer, and subjected to heat, the heat void-free structure around the intermediate layer of semiconducting, cross-linked polyethylene and around the metallic core. By means of this void-free structure, the possibility of corona discharge taking place in air spaces or gaps between the conductor and the ground insulation is materially eliminated. The heat shrinking of oriented polyethylene is more particularly disclosed and claimed in Stirrat et al. application, Ser. No. 518,403, filed June 27, 1955 (now abandoned) and assigned to the assignee of the present invention.

The carbon-black filled, cross-linked polyethylene used as an intermediate layer in the above-described insulated conductor may contain from 10 to 300 percent, by weight, carbon-black, based on the weight of the cross-linked polyethylene. Stated alternatively, one can use from 0.1 to 3 parts carbon-black per part of polyethylene. Among the types of finely divided carbon-blacks which can be employed in the practice of the instant invention are, for example, animal or vegetable, channel, furnace and thermal carbon-blacks, etc. A good description of the preparation of carbon-blacks is contained in the book Industrial Chemicals by Faith et al., pages 174-182, published by John Wiley & Sons, New York (1950). Among the various grades of suitable carbon-black are channel; channel, conducting; channel, hard processing; channel, medium processing; channel, easy processing; furnace, conducting; furnace, fine; furnace, high modulus; furnace, high elongation; furnace, reinforcing; furnace, semi-reinforcing; thermal fine; thermal medium; acetylene; lamp black, etc. These carbon-blacks are of very fine particle size and may range in average particle size from about 1 to 100 millimicrons.

The manner whereby the carbon-black filled, crosslinked polyethylene may be prepared may be varied widely. One method comprises incorporating the carbon-black in 50 the polyethylene and thereafter irradiating the carbonblack filled polyethylene to cross-link the same with high energy electrons with a dose of from about 3×106 rep to 5×108 rep employing the method disclosed and claimed in the copending application of Gilbert and Precopio, Ser. 55 No. 488,304, filed Feb. 15, 1955 (now Patent No. 3,084,-114). Alternatively, one can incorporate a chemical curing agent for the purpose of cross-linking the polyethylene, for instance, an organic peroxide, such as di-alpha cumyl peroxide, more particularly disclosed and claimed in the copending application of Precopio and Gilbert, Ser. No. 509.387, filed May 18, 1955 (now Patent 2,888,424). After incorporation of the peroxide, and the carbon-black in the polyethylene, the latter is heated at elevated temperatures of about 150° to 175° C. in order to effect crosslinking (i.e., curing) of the carbon-black filled polyethylene. Generally, this cross-linked, carbon-black filled polyethylene which is advantageously used in tape form, is then wound around the metallic core to form the intermediate semiconducting layer and thereafter the outer 70 polyethylene insulation may be applied. The application of the outer insulation may be in the form of a tape wrapped around the metallic core covered with the semiconducting layer of cross-linked, carbon-black filled polyethylene or the outer polyethylene insulating surface may be extruded 75 broke down. 4

over the latter two members of the conductor assembly. When employing tapes of either the semiconducting layer or of the outer layer of polyethylene, the tape is advantageously from one-half to six inches or more wide and in thickness may range from about 0.5 to 50 or more mils, e.g., from 1 to 20 mils. When making the insulated conductor, it may be desirable to employ more than one layer of both the cross-linked, carbon-black filled polyethylene and of the outer insulation of polyethylene.

The drawing accompanying this description shows a preferred embodiment of the claimed invention. In the metallic core and the intermediate semiconducting cross-linked polyethylene layer, and subjected to heat, the heat causes the oriented polyethylene to shrink into a tight, void-free structure around the intermediate layer of semi-conducting, cross-linked polyethylene and around the substantially infusible and insoluble state.

In order that those skilled in the art may better understand how the present invention may be practiced, and in 20 order to show the marked advantages derived from the practice of said invention, the following example is given by way of illustration and not by way of limitation. All parts are by weight.

Example 1

A copper stranded coil form about 1/4 inch wide by 1 inch in height was wound with an irradiated semiconducting tape composed of carbon-black (Vulcan 9-super abrasion carbon manufactured by Godfrey L. Cabot Company) filled polyethylene (in which the carbon-black comprised about 30 percent, by weight, of the total weight of the polyethylene and the carbon-black) which had been irradiated with about 8×106 rep (by means of electrons from a high voltage accelerating apparatus). The semiconducting tape, which was about 4 mils thick, was wrapped around the coil form with half laps until a thickness of about 6 to 8 mils of the carbon-black filled, crosslinked polyethylene was obtained on the insulated conductor. Unfilled, oriented (40 to 50 percent orientation) polyethylene tape which had been irradiated with about 9 to 11×10^6 rep was then wrapped around the assembly comprising the metallic core and the carbon-black filled, crosslinked polyethylene to a thickness of about 40 mils. The entire assembly (insulation being about 48 mils thick) comprising the outer irradiated polyethylene insulation, the intermediate layer of carbon-black filled, cross-linked polyethylene and the metallic core were heated at 105-115° C. for one hour to shrink the outer polyethylene layer, and then at 150° C. for 15 minutes to effect a tight seal between all the layers of polyethylene. This procedure gave a smooth, dimensionally reproducible insulation which was essentially void-free. The 150° C. treatment was sufficient to effect a seal between the semi-conducting layers and the outer insulating, unfilled, irradiated polyethylene.

As a control, another insulated conductor was prepared similarly as above, with the exception that the intermediate semi-conducting layer of carbon-black filled, cross-linked polyethylene was omitted and the outer electron cross-linked polyethylene insulation was increased in thickness from 40 mils to 48 mils, so that this control insulated conductor had the same thickness of insulation as the one described previously.

Each of the insulated conductors was stressed to breakdown using sheet lead wraps as ground at 167 volts per
mil. If only the unfilled, irradiated polyethylene insulation was considered, the stress was 200 volts per mil.
As the result of these tests (average of five tests on each
type of insulation assembly) it was found that the insulated conductor which did not contain the intermediate
layer of carbon-black filled, cross-linked polyethylene
took an average of about 6 hours under dielectric stress
to breakdown, whereas the insulated conductor which had
the intermediate layer of carbon-black filled, cross-linked
polyethylene took an average of about 67 hours before it
broke down.

The above example illustrates the ability to use a conducting layer to distribute voltage stress and eliminate ionization. The corona damage in the insulation and on the conductor has been greatly reduced, if not completely eliminated, and this same principle can be applied to other similar situations where the insulation is separated from high voltage or from ground by voids. The invention herein described avoids the necessity for using vacuum-pressure compounding techniques and can be used in the encapsulation of various electrical conductors and coils. 10

The insulated conductors of the present invention have a firm bond between the outer insulation and the conductor core through the medium of the intermediate semiconducting layer and eliminates difficulties upon flexing, bending or vibration, where conventional non- 15 bonding semiconducting tapes become embrittled and discontinuous and pull away from the insulation with resultant void formation. Because of the compatibility of the outer insulation with the intermediate layers of carbongeneous structure obtained which is able to obviate the difficulties heretofore encountered when using non-compatible layer systems. This means that voids will not develop in the composite insulation structure due to thermal system due to temperature cycling. Because the intermediate layer is non-melting, it can withstand extrusion temperatures when, for instance, thermoplastic polyethylene, or milled, cross-linked polyethylene (referred to in the above-mentioned two Cole applications) is ex- 30 truded over the carbon-black filled, cross-linked polyethylene and the metallic core.

It will, of course, be apparent to those skilled in the art that other carbon-blacks may be employed, many examples of which have been given above, without departing from the scope of the invention. In addition, instead of using irradiated polyethylene both for the outer insulation and for the intermediate carbon-black filled, crosslinked polyethylene, one can also use chemically crosslinked polyethylene employing, for instance, dicumyl 40 peroxide as the curing agent as is recited in the abovedescribed Precopio and Gilbert aplications, Ser. No. 509,-387 (now Patent 2,888,424) and Ser. No. 509,388 (now Patent 3,079,370).

6 What I claim as new and desire to secure by Letters

Patent of the United States is:

1. The process for forming an insulated electrical conductor of improved corona resistance which comprises (1) forming a coating of carbon-black filled cross-linked polyethylene on the surface of an electrical conductor, (2) wrapping a stretched, cross-linked polyethylene tape in overlapping fashion about said coating and (3) heating the resulting assembly above the temperature at which said tape tends to shrink, whereby the shrinkage of said tape compresses said coating between said conductor and said tape to form an insulated electrical conductor having a substantially void-free semiconducting layer in contact with said conductor and a substantially void-free outer insulating layer surrounding and in contact with said semiconducting layer.

2. The process for forming an insulated electrical conductor which comprises (1) forming a coating of carbon black filled cross-linked polyethylene on the surface of an black filled, cross-linked polyethylene, there is a homo- 20 electrical conductor, (2) wrapping a stretched, crosslinked polyethylene tape in overlapping fashion about said coating, (3) heating the resulting assembly at a temperature of about 105 to 115° C. for a sufficient time to shrink said outer polyethylene layer, and (4) then heating said working, i.e., expansion and contraction of the insulation 25 entire assembly at a temperature of about 150° C. to effect a seal between said inner coating and said outer coating, whereby an insulated electrical conductor is produced which is substantially free of voids and which has

improved corona resistance.

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EARL M. BERGERT, Primary Examiner. P. R. WYLIE, T. R. SAVOIE, Assistant Examiners.