March 26, 1946. H. H. BARKER 2,397,082

SEMICONDUCTING MATERIALS

Filed Dec. 3, 1942 2 Sheets-Sheet 1

Fig. 5.

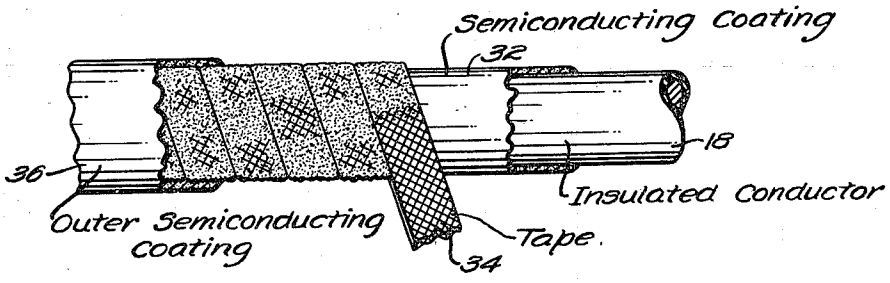
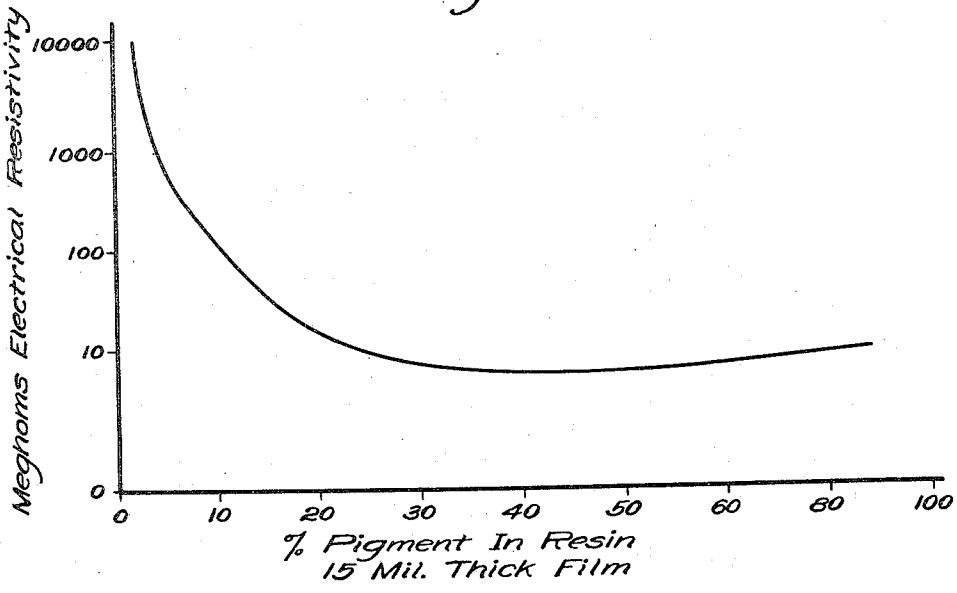


Fig. 1.



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SEMICONDUCTING MATERIALS

Filed Dec. 3, 1942 2 Sheets-Sheet 2

Fig. 3.

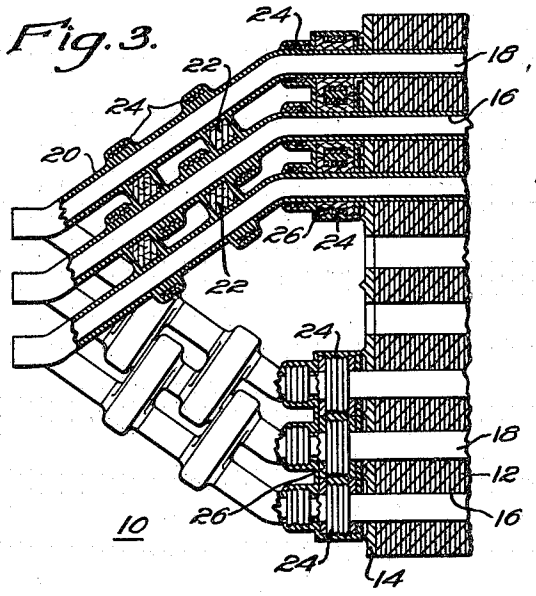


Fig. 4.

Tape Coated With Resin And a Distribution Of Anthracite Coal

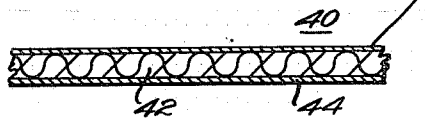
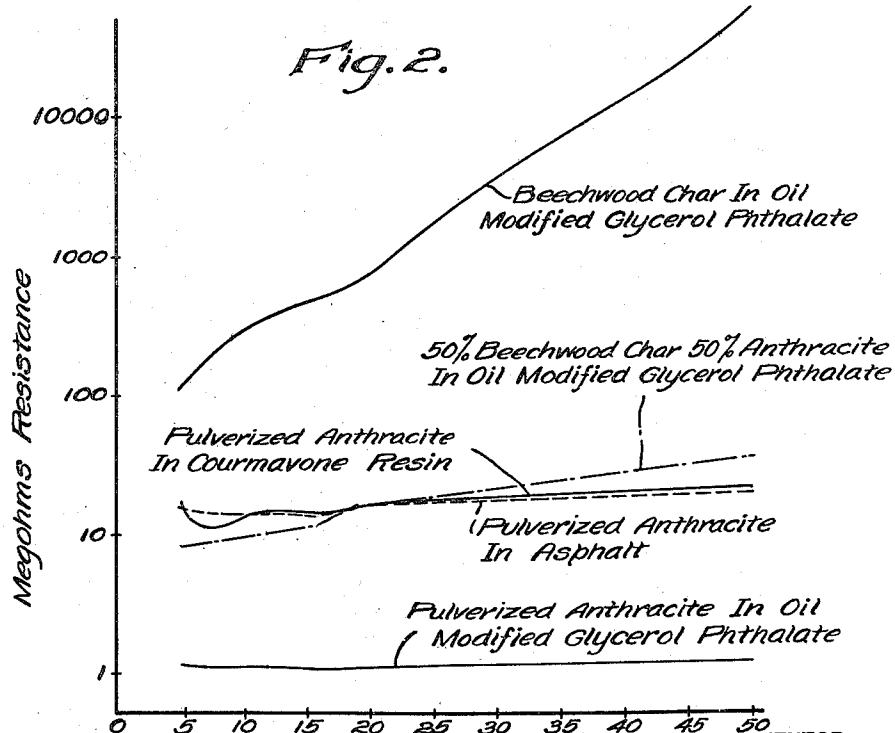


Fig. 2.



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UNITED STATES PATENT OFFICE

2,397,082

SEMICONDUCTING MATERIAL

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Application December 3, 1942, Serial No. 467,727

12 Claims. (Cl. 174—105)

This invention relates to means for preventing corona in high voltage conductors and electrical members disposed in air or other gaseous medium.

More particularly, this invention relates to a semiconducting material for application to insulated conductors, the material having predetermined electrical resistivity and a high degree of stability.

In high voltage machines, the formation of corona tends to limit the life and thereby limits the permissible voltage in electrical members and conductors since corona can be so destructive that organic insulation may be destroyed or so impaired that the electrical insulation is rendered ineffective. The phenomenon leading to corona in electrical apparatus is that of gas ionization occurring when air or other gaseous medium is subjected to an electrostatic voltage gradient high enough to cause the molecules of air or other gas to become highly active chemically and electrically. Ozone, nitrous gases and other powerful chemical substances may be formed under these conditions. The decomposition or deterioration of organic insulation occurs so readily due to these chemicals and to such an extent that in some cases in a few months organic insulation may fail and become useless for its intended purpose. In cases where the insulation comprises inorganic materials, such, for example, as mica combined with an organic binder, corona may be sufficiently destructive of the organic binder as to require refinishing of the insulation at frequent intervals.

It has been proposed heretofore to employ certain resistance compositions available to the trade for application to the surfaces of insulation subjected to voltage gradients leading to the formation of corona. For example, a colloidal suspension of graphite in a vehicle, sold to the trade as Aquadag, has been applied to conductors to produce semiconducting coating to ground the surface voltage present on the electrical insulation, and thereby the formation of corona was prevented. When applied closely to the surface of electrical insulation so that there is no air gap between the insulation and the applied semiconducting Aquadag paint coatings, corona is not formed since the entire surface of the insulation is at very nearly the same relative electrical potential.

Aquadag and similar semiconducting coatings, while having a substantial ohmic resistivity, nevertheless are so low in resistivity that these prior art materials are only useful for application to low voltage electrical members and for certain specialized applications, such, for example, as slots in laminated armatures. The resistivity of the conducting coatings is of the order of from 100 to 10,000 ohms per square inch of 3 to 4 mil thick film. Such low resistance is not entirely satisfactory in grading potentials for various reasons. Since the amount of current flowing in the conducting paint is inversely proportional to the resistance, and directly proportional to the voltage developed by the conductor, a relatively large current will flow in these prior art medium resistivity conducting coatings when the voltage is of the order of 6600 volts or higher in the conductor to which they are applied. In fact, the insulation surface may become too hot to touch due to the flow of a considerable quantity of electrical current. Excessive heat is just as detrimental to organic insulation as is corona. Therefore, many prior art conducting compositions are unsuitable for application to high voltage insulation.

It is not practical to reduce the proportion of graphite in a composition, such as Aquadag, to produce a high resistivity of the order of 1 megohm or more for example, since the quantity of graphite would be relatively small and small errors in compounding or applying it would give enormous differences in resistivity. Furthermore, the resultant coatings would be relatively unstable since the barest film of graphite particles is required for such high resistance and would be so thin that ageing, expansion, wear and other factors would easily render the coating ineffective. Likewise, such thin graphitic coatings have an excessive change in resistivity with voltage change.

In order to produce a much higher resistivity composition, it is known to subject wood to a predetermined temperature of heat treatment, thereby securing a carbonized or charred material providing a much higher resistivity coating when incorporated in practical amounts in a vehicle and applied, as compared to the Aquadag material referred to herein. Unfortunately, the coating including chars prepared by heat-treating wood is not sufficiently stable, and the coating increases in resistance with time so that in a few years it is unsatisfactory for the purpose. It is believed that, among other factors, the wood chars carry large quantities of absorbed gases which react with the vehicle or binder in which they are embodied, thereby causing progressive change in the vehicle. Since it is necessary to incorporate a large quantity of char into the vehicle in order to prepare a suitable composition, organic base vehicles and the like are subject to a continual and undesirable change.

Investigation of the requirements of a semiconducting paint or composition for application to insulation on high voltage conductors indicates that the semiconducting paint should have a resistivity of from 1 to 1000 megohms per square of area of 3 to 4 mils thick film in order to adequately grade the surface potential whereby to

prevent the generation of corona without electrical currents of such magnitude being produced by high voltage that the surface of the conductor is subjected to undue heating. Since resistance of an area is determined by the ratio of length to width of the area, and all squares having a constant ratio, the resistance is independent of the dimensions of squares. The resistivity desired depends on the voltage of the conductor, the length of the conductor being coated, and other factors, and no particular value can be given.

The object of the invention is to provide a high resistance conducting material which may be readily applied with commercial quality control and which is stable under the operating conditions to which it may be subjected in use.

Another object of this invention is to provide on an insulated conductor a semiconducting surface coating which will prevent the generation of corona.

Other objects of the invention will, in part, be obvious and will, in part, appear hereinafter.

For a fuller understanding of the nature and objects of this invention, reference should be had to the figures of the drawings, in which:

Figure 1 is a graph plotting the per cent of anthracite coal pigment in a resin film against the electrical resistance of the film;

Fig. 2 is a graph of an accelerated ageing test plotting the days to which the semiconducting materials were tested against the resistance;

Fig. 3 is a fragmentary view partly in section of the end windings of a dynamo-electric machine;

Fig. 4 is a fragmentary cross-sectional view of a tape coated with resin and anthracite coal; and

Fig. 5 is a partly broken view in elevation of a conductor in process of treatment.

According to this invention, it has been discovered that anthracite coal properly selected and treated is an exceptionally desirable semiconducting pigment or filler suitable for incorporation into organic film-forming materials in producing a semiconducting coating composition having stability and predetermined resistivity. For the purpose of this invention, the anthracite coal employed should contain less than 10% volatile matter and be free from earthy matter and other undesirable impurities. Since there are relatively few sources of anthracite coal suitable for the purpose of this invention and the electrical resistivity varies considerably at the source, it has been found that for most applications, two or more grades of anthracite coal must be blended in suitable proportions in order that a specific electrical resistivity may be secured. For example, six samples of anthracite coal were selected from Pennsylvania anthracite coal and the dry powdered samples were tested for electrical conductivity. The per cent of volatile matter and its relation to electrical resistivity for the several coals was as follows:

Table

Sample No.	Percent vol. matter	Electrical resistance
		As rec'd 20 mesh
1	2.9	0.009 megs.
2	3.1	.009
3	4.9	.23
4	6.4	.38
5	6.7	1.4
6	7.7	7.6

The electrical resistance of the coal was determined directly, and is not the resistivity which will be obtained when the anthracite coal is suitably treated and incorporated in various organic film-forming materials employed as a vehicle. The resistivity of the final product, of course, will vary almost directly with the resistivity indicated in the table, but the values will be of an entirely different order.

Anthracite coal may be purchased in a finely broken state such as No. 5 buckwheat ($\frac{3}{32}$ inch diameter or finer). The anthracite coal is prepared by blending two or more available anthracite coals as determined by experience. It is only rarely that anthracite coal from one source is of exactly correct resistivity for a given purpose. A semiconducting composition may be prepared from the anthracite coal, as purchased or preground to around 100 mesh, by incorporating a predetermined quantity of the anthracite coal in a suitable film-forming vehicle, such as an insulating varnish. Both natural and synthetic resins may be used as a vehicle for the coal. The selection of the vehicle will depend on the stability, toughness, hardness and other requirements of the coating. For example, one part of coal and two parts of a linseed oil modified glycerol phthalate resin dissolved in 2 parts of petroleum spirits, or other suitable solvent is a suggested combination. One part ethyl cellulose and 3 parts anthracite coal are another specific combination. The anthracite coal and vehicle including a solvent are put into a ball mill and ball milled for a period of time from 2 to 24 hours.

The anthracite coal may be initially ball milled in the solvent alone until at nearly the desired degree of fineness. The resin is then added at this point and ball milling continued for at least one-half hour to secure an intimate and homogeneous composition. Easily polymerized resins are preferably incorporated with the anthracite coal in this fashion.

It has been found that incorporation of the anthracite pigment into the organic film-forming material by milling in a ball mill, tube mill or other device is necessary in order to secure desirable coating properties to provide for uniformity of electrical resistivity. The milling operation reduces the anthracite coal to substantially colloidal fineness. A convenient method of determining the degree of comminution of the anthracite coal is to place a 0.01% suspension of coal in a solvent carrier, such as acetone, and determine the relative light transmission through a standard photoelectric colorimeter. A 5% light transmission is believed to correspond to an average particle of about one (1) micron. Light transmission values of from ¼ of 1% to 10% are regarded as indicative of sufficient milling.

The compositions of this invention are composed of natural anthracite coal. By natural anthracite coal it is intended to mean anthracite coal that has not been subjected to any decomposition processes, such as would reduce the volatile content, except mechanical operations to reduce it to proper particle size for use in semiconducting coatings.

Referring to Fig. 1 of the drawings, there is shown a graph plotting the percentage of anthracite coal pigment in an organic resin against the electrical resistivity for coating brushed into 10 mil thick tape, the total thickness being about 12 mils. Since the resistivity varies so rapidly with change in proportions when about 10% or less of pigment is present, electrical resistivity is better controlled by preparing a semiconducting

composition with from about 15% to 90% of pigment to the total weight of pigment and resin. Small changes in compounding do not produce an undue change in the electrical resistivity in this range. For most purposes, it has been found that highly satisfactory coatings are produced when approximately 50% of the semiconducting coating is anthracite coal and 50% is resin. When over 90% of a film is anthracite coal, the film is usually too weak mechanically and dusts easily on contact. Almost any proportion of solvent may be employed to provide for proper brushing, spraying, or other methods of applying the composition to the conductor insulation being treated therewith.

If variations in resistivity are desired, the blend of anthracite coal should be initially selected in order to give predetermined values in preference to varying the resistivity by varying the quantity of anthracite coal pigment. Not only is the stability of the semiconducting coating improved when larger quantities of pigment are employed, but likewise the variation of resistivity with voltage is not objectionable when from 15% to 90% of anthracite coal pigment is present in the resin. An undesirable rate of change of resistivity with applied voltage does occur when any carbonaceous pigment is present in a film in amounts of 10% or less.

Numerous resins may be employed as vehicles in preparing a coating composition by milling the resin with the anthracite coal. Reactive resins which continue oxidizing, polymerizing or condensing after being applied as painted films to surfaces may be selected for the practice of this invention. Coumarone resins, various alkyd resins such as glycerol-phthalate and maleic anhydride-glycol resins, shellac and phenol-aldehyde resins, including the modified phenolics are examples of this class. Non-polymerizing resins and other non-reactive organic substance such as asphalt and similar organic film-forming materials have been found to be satisfactory for carrying the anthracite pigment and providing durable semiconducting coatings on electrical insulation. Ethyl cellulose, cellulose acetate and other cellulosic esters and ethers are examples of the latter class. Other examples are given in the Barker, Hill and Atkinson patent application, Serial No. 467,728, filed December 3, 1942.

Inorganic film material such as silicates or properly prepared bentonite may be employed as a vehicle in some cases for the anthracite coal.

Reactive resins usually exhibit certain film properties which are desirable. The property of oxidation or further polymerization after being applied to a surface generally increases the solvent resistance and reduces the degree of softening with temperature rise. The thermoplastic non-reactive resins typified by cellulose acetate while not as desirable due to their heat softening properties, are superior in some features for the purpose of this invention since semi-conducting coatings produced by their use attain a substantially constant resistivity on fully drying. Furthermore non-polymerizing resins need not be heat treated to attain their optimum properties, while polymerizing resins must be heat treated to some extent.

The prime characteristic that renders the anthracite organic film-forming material superior to known semiconducting paints is the relative non-ageing properties of the material. Reference should be had to Fig. 2 of the drawings in which curves plotted from accelerated ageing tests disclose some of the advantages of the present invention. In each case one part of carbonaceous pigment per one part of solid resin was applied to 1¼ inch tape 10 mils thick by saturating the tape with the composition and drying. The curves of Fig. 2 were secured by plotting the number of days at which films of different semiconducting materials in several resins have been aged at 200° C. against the electrical resistivity of the films during the test. The uppermost curve is that of a beechwood char in a linseed oil-modified glycerol phthalate resin which exhibited a resistivity at five days of slightly over 100 megohms. Thereafter, the coating increased in resistance extremely rapidly, and at the end of fifty days had a resistivity of approximately 16,000 megohms. This final resistivity value is entirely too high for any practical use and would not appreciably prevent corona.

By comparison, a particular blend of anthracite coal selected and pulverized and incorporated by ball milling in the same oil-modified glycerol phthalate resin had an initial resistivity at five days of just over one megohm, as shown in the lowermost curve of Fig. 2. After fifty days, the resistivity had not increased to an appreciable extent over that possessed at five days.

Also shown in Fig. 2, are two curves obtained when a pulverized anthracite blend of a higher inherent resistivity was incorporated both in coumarone resin and in asphalt. The initial resistivity at five days ageing was approximately 18 and 16½ megohms per square respectively, for each material. After the fifty days ageing test, the resistivity had not increased materially, being 22 and 21 megohms per square respectively.

The anthracite coal may be combined with wood chars or other less desirable semiconducting solids in producing a composition which may have desirable features. In Fig. 2 there is a plot of the ageing resistivity of a tape prepared from a mixture of 50% anthracite of the same blend as used in the test for the lowest curve and 50% beechwood char, similar in resistivity to that used in the topmost curve. The resistivity is intermediate in resistance to that shown in the upper and lowermost curves. It indicates a moderate increase of from 9.3 to 43 megohms in resistivity over the test period, which may be acceptable in many cases.

It will be seen, therefore, that pulverized anthracite coal may be incorporated in a variety of organic film-forming materials to give coatings that have a high degree of stability. This feature is exceedingly important since numerous prior art materials are of temporary benefit only, and it is necessary to recoat electrical members periodically in order to secure adequate protection against the generation of corona.

Reference to Fig. 3 of the drawings shows a portion of a generator 10 including the end windings thereof to which the semiconducting composition of this invention has been applied with success. The generator includes laminated magnetic material 12 held together by means of end plates 14. The laminations 12 and end plates 14 are provided with slots 16 to provide for the reception of conductor coils 18. The conductors 18 terminate in end windings 20 that are bent and twisted to provide for proper re-entry into other slots 16. The end windings 20 are braced or blocked by means of spacers or blocks 22 which may be made conventionally of wood or suitable electrical insulating material or semiconducting

material. The end windings are lashed together by means of lashing of rope or tape 24 in the region of the spacers 22. Adjacent the laminations 12 and end windings 14, it is customary to brace the coils by means of channeled wedge blocks 26 and to apply lashings or ties 24 at this point to secure the windings rigidly together. The various blocks and spacers and lashings are necessary in order to prevent vibration of the end windings under the stress of the powerful currents flowing therein as well as to prevent damage from external sources.

At the opposite end of the apparatus 10 the coils terminate in conductor leads that are electrically connected by cross-connectors and attached to rings. The cross-connectors and rings are supported from the frame of the machine 10. Insulation is applied to the cross-connectors and rings.

The high voltage present in conductors 18 establishes a potential gradient of such magnitude that corona would normally be generated at the surfaces of the end windings exposed to the air or other gaseous medium. An anthracite coal and resin film-forming composition prepared as disclosed herein is applied to the entire exterior surface of the end windings including the lashings and the spacer blocks and wedges, preferably before assembly. The semiconducting composition may be applied by brushing or spraying or the like. On drying, the solvent in the composition evaporates leaving a resin film carrying a fine distribution of anthracite coal.

While the semiconducting composition may be applied as a single coating to electrical members, for the best mechanical adhesion, it has been found that the semiconducting composition is preferably applied as shown in Fig. 5 as a first layer 32 to the insulated conductor 18, and while wet, the semiconducting coating is wrapped with a porous fabric tape 34, for example, either of glass fibers or cotton or asbestos, so that the composition will penetrate into the tape and ooze through the interstices thereof. Thereafter the tape is painted with a second layer 36 of semiconducting composition to cover the entire exterior surface. The tape prevents the semiconducting paint from peeling or flaking off under accidental blows, stresses or heat, and thereby increases its durability.

The insulated conductor 18 within the slots 16 is likewise painted to provide a semiconducting surface in order to secure a satisfactory grading of the potential over the surface of the entire electrical conductor. The slot walls of the laminations and the windings 18 therein are coated additionally with a paint of much lower resistance, for example, an Aquadag composition. The surface conducting coating applied to the end windings and conductor is thus grounded through the slots in order to reduce the potential gradient. In this way, any tendency toward the generation of corona is eliminated. The cross-connectors and rings may be similarly rendered semiconducting at their surfaces to reduce the electrostatic potential.

In some cases, the end windings, may be lashed by using a tape or twine of fibrous material previously prepared by applying semiconducting composition thereto and drying. The tape so prepared is wrapped tightly about the insulated windings to equalize the surface potential sufficiently to prevent any substantial amount of corona being generated. A coating of semiconducting composition after tying the tape may be beneficial. Furthermore, after the semiconducting tape or twine is applied to the windings, and additional surface coating of a weather resisting paint may be applied to seal off the air and moisture from the windings.

Referring to Fig. 4 of the drawings, there is shown a semiconducting tape 40 of the type referred to. The tape 40 is prepared by dipping a tape 42 of glass fibers, cotton cloth, asbestos, or other suitable materials or mixtures thereof in the semiconducting composition described herein and drying the applied composition to remove the resin solvents. One or more coatings of the composition may be applied to the tape. The final dry tape will be impregnated with resin carrying a distribution of finely divided anthracite coal. Also a surface coating 44 of resin with the anthracite coal will be present on the tape. The tape so prepared is advantageous for applying to machines which are in service. Tape prepared from glass fibers is particularly good for use as lashing since it has exceptional strength characteristics.

It is a requirement that the semiconducting coating be substantially uniformly effective over the entire end winding. The attainment of a reasonable degree of uniformity should not be too difficult or costly. Commercial quality control has been secured by the practice of the invention described herein easily and conveniently. A maximum variation in resistivity between any portions of the end windings of the order of ±20% has been found commercially practical. It is believed that this degree of uniformity of resistivity has not been possible heretofore and is possible only by the use of the anthracite coal composition set forth.

The incorporation of finely divided anthracite coal of predetermined resistivity in an organic film-forming material by suitably ball milling produces a composition capable of producing semiconducting coatings characterized not only by a predetermined electrical resistivity of the order of 1 to 100 megohms, but also results in a semiconducting coating having remarkably stable characteristics, thereby giving it a long operating life. Once the electrical members of apparatus have been prepared with the anthracite coal semi-conducting composition of this invention, the apparatus will operate successively for its normal life without requiring re-treatment with the semiconducting composition. The protection of organic insulation indefinitely against the destructive action of corona by reducing the potential gradient on the surface thereof will maintain the operating efficiency of the insulation for its full span of life.

Since certain obvious changes may be made in the above procedures and different embodiments of the invention could be made without departing from the scope thereof, it is intended that all matter contained in the above description or taken in connection with the accompanying drawings, shall be interpreted as illustrative and not in a limiting sense.

I claim as my invention:

1. A composition for application to electrically insulated conductors for grading the potential on the insulation, comprising finely divided natural anthracite coal of substantially colloidal fineness having less than 10% volatile matter and a vehicle for the finely divided natural anthracite coal comprising a resin and a solvent for the resin whereby when the composition is appled to the insulation and dried, a resinous film

with a distribution of the finely divided anthracite coal therein is produced, the film having predetermined ohmic resistivity and characterized by a high degree of stability.

2. A composition for application to electrically insulated members for grading the potential on the insulation, comprising from 15 to 90 parts by weight of finely divided natural anthracite coal having less than 10% volatile matter and from 85 to 10% parts by weight of an organic resin, and a solvent therefor, the composition when applied to the member and dried forming a film of resin with a distribution of the finely divided natural anthracite coal therein having a predetermined ohmic resistivity and characterized by a high degree of stability.

3. A composition for application to electrically insulated members for grading the potential on the insulation, comprising from 15 to 90 parts by weight of finely divided natural anthracite coal having less than 10% volatile matter and from 85 to 10 parts by weight of an organic resin, subject to substantially no further reaction when dried as a film, and a solvent therefor, the composition when applied to the member and dried forming a film of resin with a distribution of the finely divided natural anthracite coal therein having a predetermined ohmic resistivity and characterized by a high degree of stability.

4. A composition for application to electrically insulated members for grading the potential on the insulation, comprising from 15 to 90 parts by weight of finely divided electrically conducting material including a substantial proportion of natural anthracite coal having less than 10% volatile matter and from 85 to 10 parts by weight of an organic resin, and a solvent therefor, the composition when applied to the member and dried forming a film of resin with a distribution of the finely divided natural anthracite coal therein having a predetermined ohmic resistivity and characterized by a high degree of stability.

5. The method of incorporating anthracite coal into resin solutions to provide for application to insulated electrical members to produce a predetermined grading of potential stresses which comprises combining finely divided natural anthracite coal having less than 10% volatile matter from different sources in proportions to give a desired electrical resistance, adding the combined coal to a solution of resin and milling the coal to colloidal fineness in the resin solution to provide for uniformity and fineness, whereby when the resin solution and incorporated coal is applied to the electrical members a coating of resin and coal having a relatively high degree of uniformity is produced.

6. A tape for application to insulated electrical members to grade the potential on the surface of the insulation comprising, a fabric tape and a coating of finely divided natural anthracite coal having less than 10% volatile material and of predetermined electrical resistivity applied to the fabric tape.

7. A resistance tape suitable for application to insulated electrical members for grading the potential on the surface of the insulation comprising, a fabric tape, a resin applied to the surface of the fabric, and a distribution of finely divided natural anthracite coal having less than 10% volatile matter and of predetermined electrical resistivity carried by the resin.

8. A resistance tape suitable for application to insulated electrical members for grading the potential on the surface of the insulation comprising, a fabric tape, from 10 to 85 parts of a resin subject to substantially no further reaction when dried as a film applied to the surface of the fabric and from 15 to 90 parts of a distribution of finely divided natural anthracite coal having less than 10% volatile matter and of predetermined electrical resistivity carried by the resin.

9. An insulated conductor comprising, in combination, a conductor, insulation of high ohmic resistance applied to the conductor, and a surface coating of semi-conducting material applied to the insulation, the semi-conducting material comprising 15 to 90 parts by weight of a finely pulverized natural anthracite coal having less than 10% volatile matter and from 85 to 10 parts by weight of a binder.

10. An insulated electrical conductor comprising, in combination, a conductor, insulation of high ohmic resistance applied to the conductor and semiconducting material applied to the surface of the insulation, the semiconducting material comprising a first coating of a semiconducting composition including finely pulverized natural anthracite coal, a layer of porous tape sinking into the first coating and a second coating of a semiconducting composition including finely pulverized natural anthracite coal applied over the porous tape.

11. An insulated electrical conductor comprising, in combination, a conductor, insulation of high ohmic resistance applied to the conductor and semiconducting material applied to the surface of the insulation, the semiconducting material comprising a first coating of a semiconducting composition including from 15 to 90 parts of pulverized natural anthracite coal, and from 85 parts to 10 parts of a film forming resin, a layer of porous tape sinking into the first coating and a second coating of a semiconducting composition including finely pulverized natural anthracite coal applied over the porous tape.

12. The method of incorporating anthracite coal into resin solutions to provide for application to insulated electrical members to provide a predetermined grading of potential stresses which comprises combining finely divided natural anthracite coal having less than 10% volatile matter from different sources in proportions to give a desired electrical resistance, adding the combined coal to a solvent and milling the coal to colloidal fineness in the presence of the solvent, adding a resin soluble in the solvent to the colloidal coal and milling the whole for a period of time sufficient to produce a uniform suspension for application as a coating to insulated conductors to provide a semiconducting coating thereon.

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