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SEMICONDUCTING COMPOSITION

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This invention relates to semi-conducting compositions for application to electrical members, in order to reduce or eliminate corona when subjected to high voltages.

When electrical conductors operate at voltages of about 6600 or higher, air or other gas surrounding the conductors is subjected to electrostatic voltage gradients of such order that the molecules of the air or other gas become highly active. At these critical voltage gradients, ozone and nitrous oxide gases tend to form and produce oxidizing acids which are destructive to organic insulation. Accordingly, the functioning of electrical apparatus at 6600 volts and higher is dependent upon the ability of the insulation to resist corona and its effects, or the elimination or prevention of corona. Since, in the present state of the art, organic insulation is regarded as a necessary element of high quality electrical insulation, it is necessary to eliminate corona as much as possible.

It has been proposed heretofore to apply semi-conducting paints to the surface of organic insulation on high voltage conductors, in order to grade the potential to a value below that at which corona occurs. However, many of the semi-conducting paints are difficult to apply and, accordingly, their utility is greatly diminished for this reason. In other cases, the semi-conducting elements in the paints deteriorate with age, whereby changes in resistance occur to such an extent that the paint rapidly fails in its intended function, and then corona occurs.

The object of this invention is to provide a semi-conducting composition that may be applied to the insulation of high voltage conductors with ease and having a life equal to that of the expected life of the apparatus in which the conductor is embodied.

A further object of the invention is to provide a semi-conducting tape for application to electrical conductors, thereby to prevent the formation of corona on the conductors.

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

In building high-voltage electrical apparatus, semi-conducting compositions in the form of paint or tape has been applied as a coating to the exterior surface of the electrical conductors thereof in order to grade the electrostatic potential on the surfaces exposed to air or other gaseous medium. While in theory the application of such semi-conducting materials appears simple and easy to carry out, unexpected difficulties are met with in practice. The selection of

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semi-conducting compositions having a suitable range of resistivities to adequately reduce the electrostatic potential below the threshold values at which corona is formed is limited due to the fact that high resistivity compounds will not grade the potential sufficiently while low resistivity compounds will permit relatively enormous currents to flow along the surface of the insulated conductors and give rise to excessive heating. As is well known, high temperatures are as destructive to organic insulation as is corona. It has been discovered that for conductors having voltages of the order of 6600 or greater, the semi-conducting compositions should have a surface resistivity of the order of from 1 to 1000 megohms per square of 3 to 4 mils thick film in order to avoid excessive heating and to prevent corona. Where a tape is employed in combination with the composition, this order of resistance is obtained by applying sufficient composition to 10 mils thick tape to produce a final thickness of about 12 mils.

From experience and research, it has been found that while certain carbonaceous substances, such as wood chars, may be applied in combination with a vehicle such as varnish to insulated conductors to produce semi-conducting coatings having the resistances of the order of 1 to 1000 megohms per square of 3 to 4 mils thick film, such coatings do not maintain a constant resistivity. The coatings ordinarily increase in resistivity with time at such a rate that in a few years the semi-conducting coating is ineffective for its intended purpose.

Application of semi-conducting coatings as a paint to insulated conductors in order to eliminate corona is not favored in certain cases, since painted coatings are so susceptible to injury from flaking or the like due to the normal expansion and contraction of the members, accidental abuse, corrosive conditions, and similar occurrences. It has also been proposed heretofore to employ a tape coated with semi-conducting material as the means of applying semi-conducting composition to the surfaces of insulated conductors instead of painted coatings. In practice, it has been found that tape prepared by incorporating a conventional carbonaceous semi-conducting material in an organic film-forming resin is not entirely effective for eliminating corona. Between each lap of semi-conducting tape prepared in this manner and applied to the insulated conductor, there apparently exists an air gap of such character that corona may be formed therein. This phenomenon is ascribed to the fact that the successive spirals

of tape do not contact each other sufficiently to produce an effective electrical conducting relationship.

According to this invention, it has been discovered that members of a group of water soluble organic film-forming materials may be combined with natural anthracite coal comminuted to substantially colloidal dimensions whereby a semi-conducting paint may be prepared. Semi-conducting tapes may be prepared by the use of this paint which are not subject to the defects of tapes prepared heretofore.

Anthracite coal has a resistivity depending on the source or nature of the coal such that when incorporated in suitable proportions in an organic film-forming material, any surface resistivity within the range of about 1 to 1000 megohms per square of 3 to 4 mils thick film may be obtained. The resistivity may be closely controlled by blending anthracite coal from two or more independent sources since the anthracite coal from different sources varies markedly in resistivity, though each is usually within a relatively narrow range. It has also been found that the resistivity of the anthracite coal is closely related to the percentage of volatile matter therein. The following table was prepared from six samples of anthracite coal found in the State of Pennsylvania.

Table I

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

For the practice of this invention the average volatile matter in the anthracite coal should be above 1% and below 10%. Volatile content outside this range does not give a product that can be used in semi-conducting composition of the kind specified.

The electrical resistivity of the 20 mesh anthracite coals in Table I is of an entirely different order from the resistivity which will be secured when the anthracite coal is applied in combination with a vehicle. However, the resistivity of the anthracite coal in combination with the vehicle varies almost directly with resistivity of the several powdered coals.

The compositions of this invention are composed of natural anthracite coal. By natural anthracite coal it is intended to mean anthracite coal 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 semi-conducting coatings.

Anthracite coal of high quality may be purchased in No. 5 buckwheat size, though the size as purchased is not critical. In preparing semi-conducting compositions, anthracite coal is prepared initially by blending two or more anthracite coals secured from different sources in such proportions as determined by experience and tests that will give a mixture of predetermined resistivity. It is, of course, infrequently found that a single variety of anthracite coal is suitable for a given application requiring a selected resistivity.

The natural anthracite coal may be preground

to 100 mesh fineness if desired. Thereafter the coal is subjected to milling in ball or tube mills or the equivalent in water for a period of the order of 24 hours until the coal has been reduced to a substantially colloidal condition. By "milling" we refer to the use of any apparatus capable of comminuting a substantial proportion of the coal to colloidal fineness. For ball milling, a 30% coal suspension in water is suggested. Tests of the physical state of the coal during the ball milling operation will indicate whether or not the coal has been reduced to suitable fineness. One suitable test is to prepare a dispersion of the ball mill product in water having 0.01% coal by weight. The dispersion so prepared is introduced into a cell of a photoelectric colorimeter. When the light transmission of the coal dispersion is about 5%, then the ball milling may be considered satisfactory. Light transmission value of $\frac{1}{4}$ of 1% to 10% are indicative of satisfactory comminution. A 5% light transmission value is believed to correspond to an average particle size of under one micron. The product of the ball mill is strained through a fine mesh fabric in order to remove extraneous and oversize material therefrom.

The substantially colloidal coal suspended in water is mixed with a water soluble organic film-forming resin, gum or other substances. Gum arabic has been found particularly satisfactory for this purpose. However, gum tragacanth and gum gatti are also suitable for this purpose. Polyvinyl alcohol which has been derived by hydrolyzing the polyvinyl ester to the degree that the polyvinyl alcohol is water soluble which occurs at a hydrolysis of about 50% and higher may be employed in this application. Methyl cellulose and casein glue are other examples of suitable water soluble organic materials.

As an example of the invention, the preparation of a gum arabic suspension will be described in detail. The amount of gum arabic to the colloidal coal may vary over a range of from 75 parts to 10 parts by weight of gum arabic and from 25 parts to 90 parts by weight of coal. Sufficient water should be added to dissolve the resin and suspend the coal. Customarily three or more parts of water per part of coal and resin is sufficient for this purpose. In order to stabilize the suspension and prevent deterioration of the gum, approximately $\frac{1}{2}$ of 1% of ammonia based on the weight of the gum arabic is added. Other stabilizers for this purpose may be substituted. A thorough mixing of the colloidal anthracite coal, gum arabic, water, and ammonia will give a stable suspension suitable for application to members as a semi-conducting composition. A composition viscosity of 10 to 100 seconds No. 1 Demmler cup is satisfactory for application.

It has been found that in treating oily or hydrophobic materials with the gum arabic suspension that the coating wets improperly and is incomplete in that the aqueous film tends to break and gather into heads. It is important that the coating cover the surface of the conductor insulation substantially completely. Therefore, the suspension is treated to include a water soluble monohydric alcohol, preferably having from 1 to 4 carbon atoms or with a wetting agent, or both. A suspension containing from 5 to 25 parts by weight of a monohydric alcohol such, for example, as ethyl alcohol or isopropyl alcohol will render the suspension capable of forming continuous films on asphalt-covered

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conductors or, when applied to tape, the suspension will produce a uniform coating.

Furthermore the gum arabic suspension may be prepared with from 1 to 10 parts of a wetting agent to accomplish wetting of oily or other water-repelling materials. Suitable wetting agents are the dioctyl ester of sodium sulfosuccinic acid or other esters of the same acid sold under the trade name "Aerosol," or the sodium salts of either the aryl alkyl polyether sulphates or sulphonates. Many wetting agents are known to the trade and further description thereof is believed unnecessary. Particularly good results have been obtained with approximately 5 parts by weight of ethyl alcohol and 5 parts by weight of a wetting agent in combination with 10 parts by weight of the natural anthracite coal and 10 parts by weight of gum arabic with sufficient ammoniated water to bring the composition to 100 parts.

The suspension so produced may be applied to the insulation on electrical conductors by painting, spraying, dipping, or any other procedure for applying a coating to a surface, and not only the conductor insulation proper, but the lashings, spacers, ties, and other insulating members associated with the electrical conductors may be so coated with the suspension. After drying, an organic film carrying a distribution of the natural anthracite coal will be present over the exterior surfaces of the insulation, whereby to reduce the potential gradient thereon.

In applying the aqueous suspension, it has been found that gloss, porcelain, asphalt coated conductors and other materials will not take a smooth uniform coating required for effective corona reduction unless an alcohol or a wetting agent, or both, are included in the suspension. With these additions present, porcelain bushings, glass tape and asphalt treated conductors could be given a smooth continuous coating of semi-conducting material.

For many purposes, it is desirable to wrap insulated conductors with a semi-conducting tape prepared from the semi-conducting suspension described herein. Tape prepared from glass fibers has excellent tensile strength and other properties making its use in electrical apparatus advantageous. However, in weaving glass fibers into a tape or cloth, an oily lubricant is often employed. The suspensions containing either a simple monohydric alcohol or a wetting agent, or both, have been applied to glass tape with highly satisfactory results. The tape is dipped in the suspension and, when pressed between rollers under predetermined pressure, a predetermined amount of the semi-conducting suspension remains therein. It has been found that for satisfactory manufacturing applications, the tape should be applied while damp. Therefore, the tape coated with the suspension is not dried but is kept in covered receptacles, preferably with a small quantity of water at the bottom of the receptacle to maintain a high humidity and thereby prevent drying out of the tape. When the wet tape is wrapped about an insulated conductor, the wet portions tend to intermingle or unite to produce a continuous electrical conducting surface. With dry tape, the continuity between overlapping or contacting portions of the tape is not maintained and corona may be generated between turns of the tape under the latter conditions.

Fibrous materials in sheet or tape form, other than glass fiber materials, may be employed for

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making the tape. Asbestos, cotton, linen and synthetic silks such as rayon, viscose, super-polyamide fibers are examples of tape fabrics. Likewise, lashings of various fibrous materials may be similarly treated with the suspension to render them semi-conducting.

As an example of the remarkable uniformity and stability of the semi-conducting compounds, a coil was prepared by brushing the colloidal suspension as a 3 to 4 mils thick coating over the insulation and a heavy insulating and weather resisting enamel top coating brushed on after the semi-conducting coating had dried. The coil was heated in an oven at 200° C. under forced draft. The surface resistivity of the semi-conducting paint per square was 0.18 megohm at the end of 16 hours. At the end of 30 days, the resistivity was still 0.18 megohm. The test at 200° C. for one month is equivalent to approximately five years under normal operating conditions. Therefore, it will be seen that the semi-conducting coatings of this invention are exceedingly stable with time even when subjected to elevated temperatures.

When tape is applied to various electrical members, an adhesive may be applied to the surface of the conductor in order to eliminate any possibility of a gas retaining void below the several convolutions of tape. A solution of polyisobutylene or high grade asphalt or other coating substance may be applied to the surface of the coils, and as the tape is applied, the polyisobutylene, for example, will fill the voids under the tape. A further advantage of this modified form of the invention is that of better adhesion of the tape to the conductor.

Semi-conducting tape prepared according to this invention was applied to coils without separately painting the coils before or after the application of the tape, the tape being applied in a humid or moist condition. The dry resistivity of the tape was 20 megohms, the tape being made of 10 mils thick glass cloth with the suspension applied to a total thickness of 12 mils. The coils to which the tape was applied were rated at 13,800 volts. A test voltage of 29,000 volts was applied for one minute without any sign of corona. Subsequently 40,000 volts were applied for a period of time without the observance of any corona at any point on the coils. This high voltage had no ill effect on the tape surfaces of the coils.

The advantages of the gum arabic and the other substantially non-reactive resins set forth in producing semi-conducting coatings over polymerizing resins resides in the attainment of a substantially constant resistance immediately upon drying. Polymerizing resins may take months at operating temperatures to reach a reasonably steady state. The resistivity of such polymerizing resin semi-conducting coatings may easily change twenty-fold from a fully dried condition over a period of 30 days at 100° C. The gum arabic type of composition has a long life with a nearly constant resistivity.

In the application of semi-conducting coatings to end windings and other electrical apparatus, it is highly desirable to secure a reasonable degree of uniformity of resistivity between various portions of the surfaces thereof. Commercial quality control has been attained by the practice of the invention described herein easily, conveniently and economically. By employing colloidal anthracite coal-gum arabic suspensions, for example, a maximum variation in resistivity between any portion of an end winding of the order

of +20% has been found commercially practical.

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 shall be interpreted as illustrative and not in a limiting sense.

We claim as our invention:

1. A composition of matter comprising as essential ingredients, in combination, 5 to 18 parts by weight of finely divided natural anthracite coal having more than about 1% and less than 10% volatile matter, from 2 to 15 parts by weight of gum arabic, from about 5 to 25 parts by weight of a monohydric alcohol having from 1 to 4 carbon atoms, ammonia in an amount of the order of $\frac{1}{2}$ of 1% to enable a good suspension to be produced and from 55 to 70 parts of water, the whole forming a suspension.

2. A composition of matter comprising as essential ingredients, in combination, 5 to 18 parts by weight of finely divided natural anthracite coal having more than about 1% and less than 10% volatile matter, from 2 to 15 parts by weight of gum arabic, from about 5 to 25 parts by weight of ethyl alcohol, ammonia in an amount of the order of $\frac{1}{2}$ of 1% to enable a good suspension to be produced and from 55 to 70 parts of water, the whole forming a suspension.

3. A composition of matter comprising as essential ingredients, in combination, 5 to 18 parts by weight of finely divided natural anthracite coal having more than about 1% and less than 10% volatile matter, from 2 to 15 parts by weight of a water soluble organic film-forming agent, from about 5 to 25 parts by weight of a monohydric alcohol having from 1 to 4 carbon atoms, ammonia in an amount of the order of $\frac{1}{2}$ of 1% to enable a good suspension to be produced and from 55 to 70 parts of water, the whole forming a suspension.

4. A composition of matter comprising as essential ingredients, in combination, 5 to 18 parts by weight of finely divided natural anthracite coal having more than about 1% and less than 10% volatile matter, from 2 to 15 parts by weight

of gum arabic, from about 5 to 25 parts by weight of a monohydric alcohol having from 1 to 4 carbon atoms, from 1 to 10 parts by weight of a wetting agent, ammonia in an amount of the order of $\frac{1}{2}$ of 1% to enable a good suspension to be produced and from 55 to 70 parts of water, the whole forming a suspension.

5. A composition of matter comprising as essential ingredients, in combination, 5 to 18 parts by weight of finely divided natural anthracite coal having more than about 1% and less than 10% volatile matter, from 2 to 15 parts by weight of gum arabic, from about 5 to 25 parts by weight of ethyl alcohol, from 1 to 10 parts by weight of a wetting agent, ammonia in an amount of the order of $\frac{1}{2}$ of 1% to enable a good suspension to be produced and from 55 to 70 parts of water, the whole forming a suspension.

6. A semi-conducting tape for application to electrical conductors comprising, in combination, a sheet fibrous material, and applied thereto a composition composed of 5 to 18 parts by weight of finely divided natural anthracite coal having more than about 1% and less than 10% volatile matter, from 2 to 15 parts by weight of gum arabic, from about 5 to 25 parts by weight of a monohydric alcohol having from 1 to 4 carbon atoms, from 1 to 10 parts by weight of a wetting agent, ammonia in an amount of the order of $\frac{1}{2}$ of 1% to enable a good suspension to be produced and from 55 to 70 parts of water, the whole forming a suspension.

7. A semi-conducting tape for application to electrical conductors comprising, in combination, a sheet fibrous material, and applied thereto a composition composed of 5 to 18 parts by weight of finely divided natural anthracite coal having more than about 1% and less than 10% volatile matter, from 2 to 15 parts by weight of gum arabic, from about 5 to 25 parts by weight of a monohydric alcohol having from 1 to 4 carbon atoms, ammonia in an amount of the order of $\frac{1}{2}$ of the 1% to enable a good suspension to be produced and from 55 to 70 parts of water, the whole forming a suspension.

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