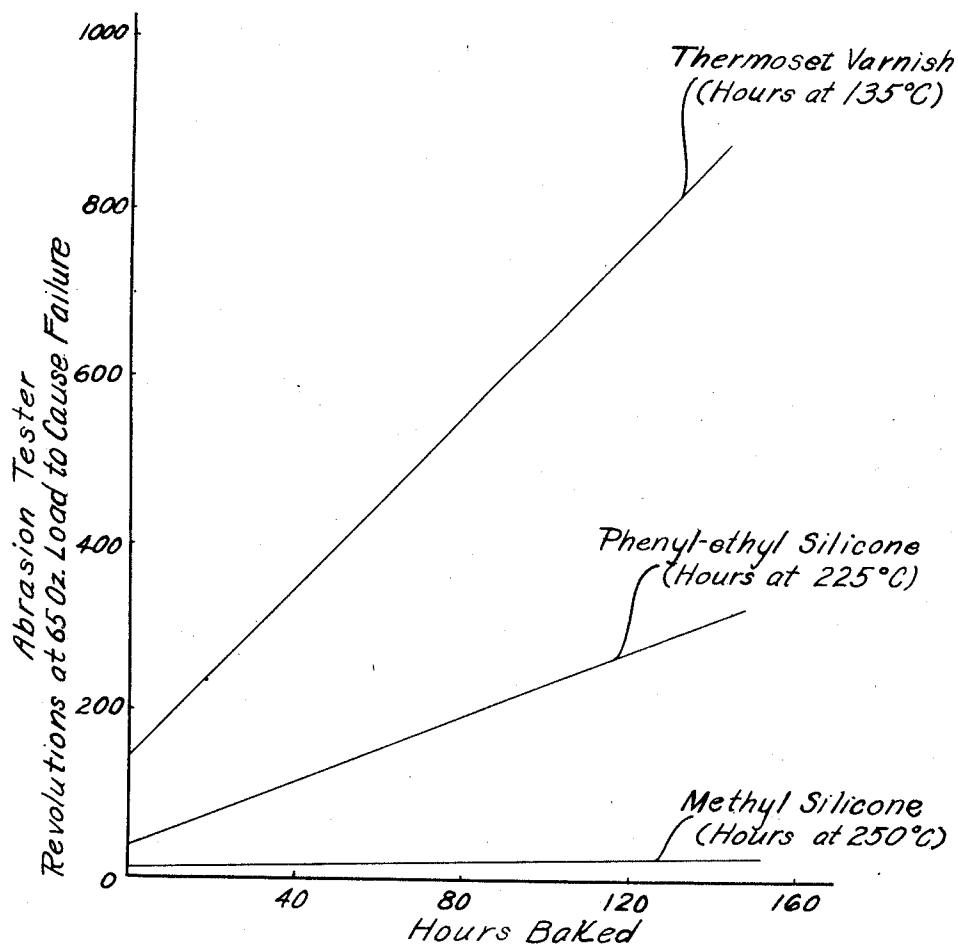


June 5, 1945.

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SEMI-CONDUCTING COMPOSITIONS

2,377,600

Filed Feb. 10, 1943



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2,377,600

SEMICONDUCTING COMPOSITION

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Application February 10, 1943, Serial No. 475,460

4 Claims. (Cl. 201-76)

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

In order to eliminate the phenomenon known as corona, which is produced when air or other gaseous medium is subjected to certain critical electrical stresses, it has been heretofore proposed to apply to the surfaces of electrical members semi-conducting or resistance paints to reduce the voltage gradient to below that value at which ionization of gases takes place.

A satisfactory semi-conducting composition for application to surfaces of members must meet several requirements. The composition should have such ohmic resistance that the voltage gradient is so reduced that excessive electrical currents will not flow along the surface of the conductor. For most purposes, a composition which when applied as a coating has a resistivity of from 1 to 1000 megohms per square of area for a film 3 to 4 mils thick has been found to meet satisfactorily the resistance requirements for such service.

Since electrical apparatus must operate satisfactorily for many years without requiring continual maintenance and repairing, it is a requisite for semi-conducting coatings that they retain a predetermined resistance throughout the normal life expectancy of the apparatus to which it is applied. One of the many disadvantages of prior semi-conducting compositions employed to prevent corona resided in the fact that the resistance rapidly increased with ageing, whereby in a few years of time, the composition was ineffective for the purpose of lowering the voltage gradient along the surfaces of the electrical conductors.

Since corona is essentially a gas phenomenon, it tends to occur at surfaces where gases come in contact with electrically charged members. Semi-conducting compositions are, therefore, primarily applied to surfaces exposed to air or other gases in order to reduce the voltage gradient at such points. However, these surfaces are exposed and subject to abrasion as will occur when electrical apparatus is in operation, or is cleaned to remove dust and the like. Consequently, it is necessary that the semi-conducting composition be resistant to abrasion and the usual wear and tear that takes place at exposed surfaces. Furthermore, the composition must resist the effects of high temperature, particularly in conjunction with the accelerated oxidation and other chemical effects of air and moisture at elevated temperatures.

The object of this invention is to provide a semi-conducting material which may be readily applied with commercial quality control and

which is stable when subjected to high temperatures and has good abrasion resistance.

A further object of this invention is to provide a semi-conducting composition capable of retaining a substantially constant predetermined resistance when utilized at high temperatures to which dynamo-electric machines and other electrical apparatus are subjected.

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 the invention, reference should be had to the single figure of the drawing, which is a plot of the abrasion resistance of several resinous coating materials heat-treated for periods of time.

This invention is directed to a combination of metallo-organic resins employed as the vehicle for a semi-conducting pigment or filler, which is stable at elevated temperatures for long periods of time.

According to this invention, it has been discovered that anthracite coal properly selected and treated is an exceptionally desirable semi-conducting pigment or filler suitable for incorporation into organic film-forming materials in producing a semi-conducting coating 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. There are relatively few sources of anthracite coal suitable for the practice of this invention. The electrical resistivity of coals from different sources varies greatly. 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 predetermined electrical resistivity may be secured. Six samples of anthracite coal were selected which were obtained from different geographic locations in Pennsylvania. These samples in a dry powdered state were tested for electrical conductivity. The per cent of volatile matter and its relation to electrical resistivity for the several coals were as follows:

Table

Sample No.	Percent volatile matter	Electrical resistance
1	2.9	As rec'd. 20 mesh.
2	3.1	.008 megs.
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 this value is not the re-

sistivity 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, however, will vary according to some proportionality to the resistivity indicated in the tables, but the values may be of an entirely different order.

Anthracite coal may be purchased in a finely broken state such as No. 5 Buckwheat ($\frac{3}{4}$ inch diameter or finer). The anthracite coal is prepared by blending two or more available anthracite coals as determined by prepared tables and experience. It is only rarely that anthracite coal from one source is of exactly the correct resistivity for a given purpose. A semi-conducting paint may be prepared from the anthracite coal, as purchased or pre-ground to around 100 mesh, by incorporating a predetermined quantity of the anthracite coal in a suitable film-forming vehicle, such as a metallo-organic insulating varnish. The selection of the vehicle will depend on the stability, toughness, hardness and other requirements to be met by the paint when applied.

In producing a paint-like composition from a resinous substance and the anthracite coal, it has been found that the best results are obtained when the anthracite coal and the resin with a suitable solvent are milled together, for example, in a ball mill, for a period of time of from 2 to 24 hours. While the coal and resin may be milled concurrently for the entire time, another method of achieving this result is to initially subject the anthracite coal suspended alone in the solvent to ball milling until it nearly reaches the desired degree of colloidal fineness. The resin or other vehicle is added at this time. The ball milling of the resin, anthracite coal and solvent is continued for at least one-half hour to secure an intimate and homogeneous paint. Resins which polymerize readily are preferably thoroughly mixed with the anthracite coal by this short milling time after the resin is added. After either method of mixing, it may be said that the coal is incorporated in the resin.

It has been found that incorporation of the anthracite pigment into the metallo-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 toluol or acetone, and determine the relative light transmission through a standard photo-electric colorimeter. A 5% light transmission is believed to correspond to an average particle size of about one (1) micron. Light transmission values of from $\frac{1}{4}$ of 1% to 10% are regarded as indicative of sufficient milling.

Tests have shown that electrical resistivity of the paint composition is best controlled by preparing a composition with from 15% to 90% of anthracite coal based on the total weight of coal and resin. In this range of proportions, small errors or changes do not produce an undue change in the electrical resistivity. For most purposes, highly satisfactory coatings may be secured when the composition consists of approximately 50% of anthracite coal and 50% of resin. The amount or proportion of solvent is optional in order to secure proper brushing, spraying, or

dipping consistencies. Inasmuch as a volatile solvent is employed, the solvent will evaporate on further processing the coating when applied to an electrical member.

If a particular resistivity is 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 incorporated into the resin. Not only is the stability of the semi-conducting coating improved when larger quantities of pigment are employed, but 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 usually does occur when any carbonaceous pigment is present in a film in amounts of about 10% or less.

In producing semi-conducting coatings for electrical members which are to be subjected to high temperatures, it has been discovered that the effect of the oxygen and moisture in the atmosphere as well as the thermal effect tends to cause harmful changes when the usual resins are employed. In some cases, the resinous material changes in its properties due to continuing polymerization to a brittle stage with adverse results. Cracking of the resin film and other undesirable physical changes may take place. Corona will take place at such cracked or broken portions, thereby defeating the intended purpose of the coating.

It has been discovered that a metallo-organic vehicle or resin may be employed in combination with anthracite coal to produce coatings capable of maintaining predetermined resistivity for prolonged periods of time at temperatures of above 100° C. to 225° C. and higher. Metallo-organic compounds which have been found to be particularly satisfactory for this purpose are the phenyl ethyl silicones. The phenyl ethyl silicones produce a polymerized resinous material when subjected to certain catalysts under elevated temperature conditions, the polymerized silicone being soluble in a solvent when in an intermediate stage of polymerization. A solution of such intermediate polymerized silicone may be applied to members, and when subjected to heat treatment, further polymerization takes place, and the phenyl ethyl silicone gives a hard resistant film or coating capable of withstanding high temperatures for prolonged periods of time.

Polymerized phenyl ethyl silicone is believed to consist of a series of alternate silicon and oxygen atoms attached to one another with a phenyl and ethyl radical attached to the silicon atoms. In some cases, two phenyl groups may be attached to one silicon atom, and in others two ethyl groups to one silicon atom. The average composition indicates that approximately one phenyl and one ethyl group is present in the polymer for each silicon atom. The ratio of phenyl to ethyl radicals may be varied slightly in some cases.

A commercial source of phenyl-ethyl silicones for practicing the invention is the resin sold as "990-A" by Dow-Corning Sales Company.

For the purpose of this invention, polymerized phenyl ethyl silicone is preferred to other organic silicones. While nearly all the silicones apparently have a high degree of resistance to thermal effects, not all the silicones are equally resistant to abrasion. Referring to the figure of the drawing, there is shown a plurality of curves of the abrasion resistance of several resinous

materials plotted against the hours at which the resins have been subjected to baking. The abrasion test was performed on a standard known type of abrasion tester, wherein a rotating wheel loaded with a given weight is operated in contact with a wire carrying the resin to be tested. The samples from which the curves have been prepared each consisted of No. 15 copper wire covered with a layer of continuous filament of glass fibers. The resin was applied as a varnish or enamel to the glass fiber covered wire and baked for the times indicated. The total thickness of the wire samples varied from 0.065 to 0.073 inch. The upper curve was that secured by applying a standard thermosetting varnish consisting of entirely organic materials sold to the trade as Westinghouse Thermoset Varnish. The middle abrasion curve was that secured by employing the phenyl ethyl silicone polymer specified herein. While the relative abrasion resistance of the thermoset varnish appears to be superior to that of the phenyl ethyl silicone, it should be noted that the baking temperatures are so much greater in case of the phenyl ethyl silicone that the abrasion resistance of the latter is under these conditions unexpected. Thermoset varnish could not be subjected to temperatures of 225° C. for similar periods of time with any reasonable abrasion resistance being secured.

For comparative purposes, a methyl silicone polymer was applied to the same types of glass fiber covered conductor. As will be noted, the abrasion resistance was almost negligible. The conductors failed under the abrasion test in a few revolutions. If the methyl silicone treated conductor were to be employed in electrical apparatus, vibration, particles of dust, and other atmospheric abrasives would soon cause the material to fail by wearing away. Accidental contacts with tools while the apparatus was being adjusted or repaired would likewise undoubtedly cause considerable damage. Consequently, a methyl silicone polymer would be unsatisfactory on the ground of abrasion resistance.

It is believed that the phenyl ethyl silicones constitute a class of silicone resins that are more suitable for use as a semi-conducting paint to be applied to exposed surfaces than other silicones. There is some evidence that this is due to the fact that the ethyl group in the phenyl ethyl silicone under appropriate reaction conditions changes to a vinyl group which may be responsible for producing a tougher and more abrasion resistant polymer than is obtained with other organic silicones.

A semi-conducting composition was prepared by incorporating 260 parts by weight of anthracite coal in 400 parts of phenyl ethyl silicone solution composed of 50% solids in toluene solvent. The composition was ball milled two and one-half hours. The compound was brushed into 10 mil thick tape of glass fibers, the tape being wound on one-inch diameter glass tubes. The resistance of the composition was determined after subjecting to various conditions. After baking 120 hours at 200° C., the resistance was found to be 0.8 times that of the initial resistance secured by baking one and one-half hours at the same temperature. The compound on the glass tape was flexible even after baking 16 hours at 150° C. No hardness or undesirable brittleness was evident. Accelerated ageing tests indicate that this material should retain a resistivity of the same order as the initial re-

sistivity for 10 to 15 years or longer when subjected to normal operating temperatures of electrical apparatus.

The anthracite coal and phenyl ethyl silicone polymer dissolved in a solvent may be applied to conductors or electrical members in several ways. Fully assembled apparatus, such as generators, may be treated by brushing or spraying or even dipping the apparatus in the composition. Upon drying, a uniform film or coating covering all the exposed surfaces will be produced.

An alternate method of application having desirable features is to paint the exposed end windings of the apparatus, for example, with a layer of the composition, and while wet, the applied semi-conducting paint is wrapped with a porous fabric tape, for example, of glass fibers or asbestos so that the paint will penetrate the tape and ooze through the interstices thereof. Thereafter, the tape may be painted with a second layer of semi-conducting composition to cover the entire exterior surface. A highly durable surface coating is produced by following this procedure. In many cases, end windings which are lashed with a tape or twine may be treated to produce the semi-conducting coating on the lashings to grade the potential between successive windings. Spacer blocks and the like may be likewise painted with the resin. In this way, any possible source of a potential gradient above the critical potential for causing corona will be eliminated.

In some cases the conducting pigment need not be entirely anthracite coal, but wood chars or other finely divided conducting material may be added. Wood chars prepared by heat treating wood at predetermined temperatures to a given resistivity, as disclosed in McCulloch Patent No. 2,050,357, may be added up to an equal weight of the anthracite coal and both milled with the polymerized silicone to produce a suitable semi-conducting paint.

It is a requirement that the semi-conducting coating be substantially uniformly effective over the entire end of an electrodynamic machine. 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 end windings of the order of $\pm 20\%$ has been found commercially practicable. 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 a phenyl-ethyl silicone film-forming material by suitably ball milling the whole gives a paint capable of producing semi-conducting coatings characterized not only by a predetermined electrical resistivity of the order of 1 to 100 megohms, but also results in a semi-conducting coating having remarkably stable characteristics, particularly at elevated temperatures, thereby giving it a long operating life. Once the electrical members of apparatus have been prepared with anthracite coal semi-conducting paint of this invention, the apparatus have been prepared with anthracite life without requiring re-treatment with the semi-conducting paint. 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 drawing, shall be interpreted as illustrative and not in a limiting sense.

We claim as our invention:

1. An electrically semi-conducting composition comprising, in combination, finely divided anthracite coal of colloidal dimensions embodied in a polymerized phenyl ethyl silicone.

2. An electrically semi-conducting composition suitable for application to electrical members to provide for a predetermined resistance, comprising finely divided anthracite coal of colloidal dimensions, polymerized phenyl ethyl silicone and a solvent for the phenyl ethyl silicone.

3. A composition for application to electrically insulated conductors for grading the potential on the insulation, comprising finely divided an-

thracite coal of substantially colloidal fineness having less than 10% volatile matter and a vehicle for the finely divided anthracite coal comprising a polymerized phenyl ethyl silicone and a solvent for the polymerized phenyl ethyl silicone whereby when the composition is applied 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.

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 anthracite coal having less than 10% volatile matter and from 85 to 10 parts by weight of polymerized phenyl ethyl silicone, 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 anthracite coal therein having a predetermined ohmic resistivity and characterized by a high degree of stability.

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