Feb. 21, 1950 L. J. BERBERICH ET AL 2,498,238

RESISTANCE COMPOSITIONS AND PRODUCTS THEREOF

Filed April 30, 1947

Fig. 4.

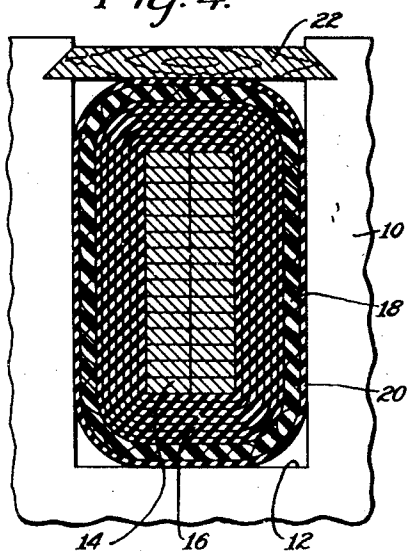


Fig. 3.

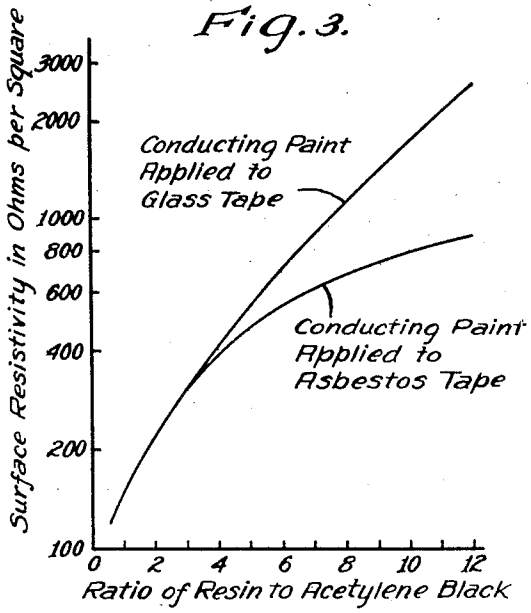


Fig. 1.

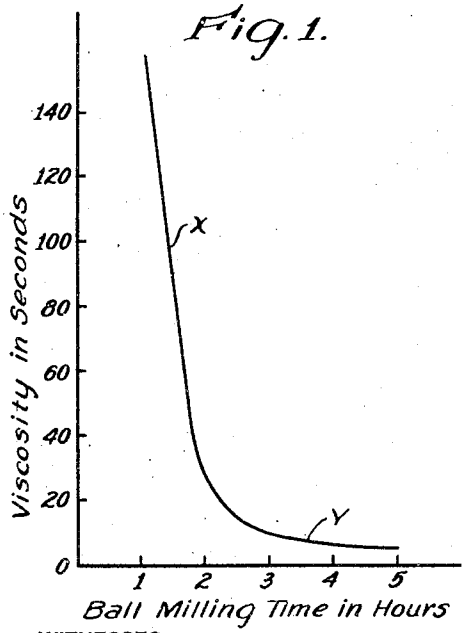
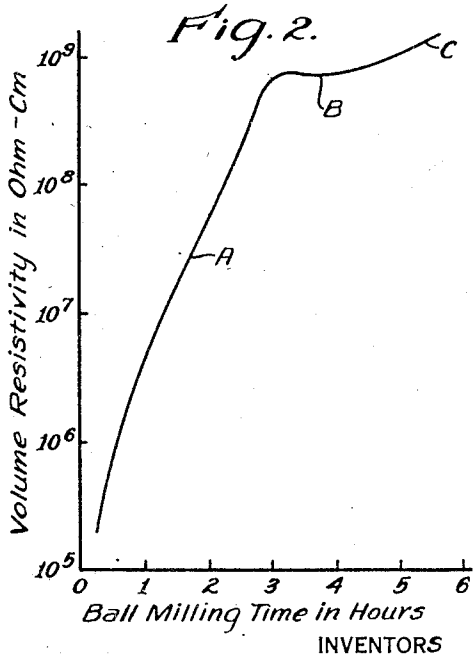


Fig. 2.



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RESISTANCE COMPOSITIONS AND PRODUCTS THEREOF

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3 Claims. (Cl. 174—120)

1

This invention relates to resistance compositions, and more particularly resinous coating compositions containing conductive carbon for producing low resistance films when applied to electrical conductors.

It has been proposed heretofore to treat the insulating surfaces of high-voltage (6600 volts and higher) conductors with semi-conducting and resistance compositions in order to reduce the potentials to a value below that at which corona is generated. Depending on the nature of the conductors and its relationship to the electrical apparatus with which it is associated, certain optimum resistances per unit area of the conductor treated have been ascertained. Thus while a resistance of from 1 to 100 megohms per square of surface is required to eliminate corona from end windings, the slot portions of these conductors requires a radically different resistivity of the order of from 400 to 2500 ohms per square to prevent corona.

There is great difficulty in producing a resistance coating, stable for the life of electrical equipment, within the range of from 400 to 2500 ohms per square of surface area for the slot portions. Graphitic resistance coatings such, for example, as colloidal graphite in a water soluble resin gum, will not produce resistance values this low, since the median value of a reasonably thick mechanically acceptable film is approximately 12,000 ohms per square. Any lower resistivity can be secured only with such heavy thick coatings of graphite-gum that mechanical difficulties occur. Flaking, rubbing off or chalking readily takes place. One reason for this appears to be due to the fact that, while graphite is a good conductor of electricity, a relatively poor contact is made between the colloidal graphite particles, raising the apparent resistivity of a film. A second reason is that the dried film is weak mechanically and movement as by thermal expansion and contraction produces many small cracks which extend the current path and raise the resistivity. If excessive loading of colloidal graphite in a gum or resin film is employed, the composition will vary radically in resistivity with minute changes in proportion of graphite. In one case, doubling the amount of graphite in a resinous binder changed the resistance approximately 100,000 times.

Tests with high conductivity colloidal carbonaceous powders, including graphite, in organic water-insoluble resins also show that the same type of high resistivity coatings as in water soluble resins are produced unless the pigment loading is

2

increased to an excessive amount. Here again the particles are insulated from one another by resin films unless an excess of pigment is employed.

Other problems, encountered in commercial application of resistance coatings to the slot portions of insulated windings, have been the problem of incorporating the conducting material, such as a form of carbon, in a binder capable of resisting deterioration with time when employed in electrical apparatus. Thus numerous resinous film forming compositions slowly oxidize or harden internally when subjected to the normal operating temperatures of electrical apparatus over a period of months or years. Most present day electrical apparatus is intended to have a life of the order of 20 years at an operating temperature of from 80° C. to 100° C.

Experience with resistance coatings embodying carbonaceous pigments in resinous binders shows that, first, the resin cures to a denser film having a progressively decreasing resistivity compared to its initial value, then on further aging the resinous film forms fine cracks which raises the surface resistivity to progressively higher values. This aging property depends on the nature of the resin and the activity and the structure of the carbon. Therefore, it is desirable to combine a stable resin which ages at a minimum rate with a low activity carbon having a structure least sensitive to changes in the resin.

Furthermore, the resinous films must withstand normal wear and tear both in assembly and operation in, for example, high-voltage generators. It is, therefore, desirable that a resinous film forming composition should cure rapidly to a stable condition, wherein the composition does not age markedly. The resinous films containing the conducting carbon materials should be resistant to abrasion from dust laden air and other influences. It is particularly necessary that the resinous compositions be so proportioned to a powdered carbonaceous conducting pigment that it is relatively non-dusting. Other desirable properties of such compositions will be disclosed hereinafter.

It has been discovered that there are a few relatively unusual carbon blacks that are characterized by a structure comprising chains of carbon particles when viewed in a dispersed state under magnification of 10,000 to 25,000 or over. Most conducting carbonaceous materials, when viewed at this magnification, consist of discrete particles, plates or similar structures. Tests indicate that the long chain type of carbon blacks

when dispersed in a carrier, such as a resin, have excellent conductivity at a low pigment ratio to the carrier and the conductivity varies but slightly with considerable change in proportion of the carbon black to the carrier. One outstanding example of such carbon black is the product known as "acetylene black."

The object of this invention is to provide a coating composition which will produce durable films and coatings having a relatively constant resistivity of from 400 to 2500 ohms per square inch when applied to fibrous materials of 10 mils in thickness.

A further object of the invention is to provide the slot portion of an insulated electrical winding with a durable resinous coating carrying a predetermined amount of acetylene black to produce an average surface resistivity of about 1500 ohms per square.

Other objects of the invention will in part be obvious and will in part appear hereinafter. For a better understanding of the nature and objects of the invention, reference should be had to the following detailed drawing and description, in which:

Figure 1 is a graph plotting viscosity against ball milling time in hours,

Fig. 2 is a graph plotting resistivity against ball milling time in hours,

Fig. 3 is a graph plotting the surface resistivity of a composition against various ratios of resin to acetylene black, and

Fig. 4 is a fragmentary vertical cross section through the slot portion of a dynamo-electric machine.

It has been found that exceptionally durable and stable cured resinous films having a predetermined resistivity of from 400 to 2500 ohms per square when applied to a fibrous tape may be prepared from a drying oil modified glycerol-phthalate resin and from ¼ to ½ the weight of the resin of colloidal acetylene black or other carbon black showing a long chain structure.

The resinous composition is prepared by reacting from 45% to 60% by weight of a drying oil compound selected from the group consisting of linseed oil and linseed oil acids such as oleic, linoleic and linolenic acids from 40% to 30% by weight of phthalic anhydride and the balance 10% to 15% by weight, glycerol. The ingredients may be reacted in a closed reaction vessel for a period of time of from 1 to 8 hours at a temperature of from 80° C. to 150° C. until there results a resin soluble in aromatic solvents, such as toluene or xylene, and of a viscosity suitable for coating purposes. The linseed oil may be employed alone or in admixture with acids derived therefrom. A mixture of oleic, linolenic, and linoleic acids may be employed in preparing the resin. The resin may be dissolved in a suitable volatile organic solvent having a boiling point of 30° C. to 200° C. A petroleum hydrocarbon consisting of a fraction boiling between 100° C. and 180° C. may be used to dissolve the resin. Aromatic solvents alone or admixed with the petroleum fraction may be employed. It is desirable that the solvent be present in the amount of at least 150 parts for each 100 parts of resin. As much as 500 parts of solvent for each 100 parts of resin may be employed though the solutions may be uneconomical to use industrially because of their high dilution.

The oil modified glycerol-phthalate resin must be curable in 24 hours at room temperature or temperatures below about 50° C. This is required because the composition must be applied to resin treated, highly compacted insulation which may swell or change in shape if heated much above 50° C. After the resistance composition is cured on the insulation the conductor is placed into slots and wedged tightly. Any swelling of the conductor that takes place when the electrical apparatus is further treated or placed in service can only force the resistance coating into contact with the iron core laminations.

For embodiment of a carbon black having a long chain structure when observed at a magnification of from 10,000 to 25,000 and higher, it is necessary to mill the solution of resin in the solvent and the admixed carbon black until a colloidal dispersion is obtained. It has been found that when the carbon black is admixed with the solution of oil modified glycerol phthalate and placed within a ball mill or other mill capable of producing a colloidal dispersion, that the viscosity drops regularly for a period of time of milling and then gradually reaches a relatively constant viscosity condition. Likewise, the volume resistivity of the composition increases steadily until a certain relatively stable or plateau value is reached. Tests appear to indicate that when the relatively stable viscosity and resistivity values are attained, that the carbon black has reached an optimum dispersion of chains of particles. Prolonged ball milling after this condition is reached succeeds only in breaking up the carbon particle chains without appreciably modifying the viscosity thereby causing a rise in resistivity. Excessive milling will be detrimental to the intended use of the composition. In practice, we have found it to be desirable to control the milling time by measuring at intervals either the viscosity or resistance or both. For the purpose of this invention, it is desirable to preserve the chain particle structure of the carbon black, since the resistivity of the cured compositions is remarkably constant and stable when this condition attains.

Referring to Figs. 1 and 2 of the drawing, there are illustrated curves of change in viscosity with time and change in volume resistivity with time for a composition comprising 8 parts of resin and 1 part of acetylene black when milled in a high speed ball mill. It will be noted in Fig. 1 that the drop in viscosity is regular and rapid along portion X of the curve for approximately the first two hours of ball milling and then the curve of viscosity changes gradually to a relatively stable or constant state as indicated by portion Y or the curve at approximately 3 hours ball milling time. Thereafter the rate of change of viscosity is quite low. Fig. 2 of the drawing shows a relatively rapid increase in volume resistivity at portion A of the curve for approximately 3 hours until a plateau B of relatively stable resistivity values occurs. The change in resistivity for the next hour is substantially constant. However, it is not desirable to ball mill for any prolonged period of time once the stable or plateau values of resistivity have been reached, since the resistance begins to rise as shown at C, indicating a breaking up of the carbon particle chains.

It should be understood that various ball mills have different rates of operation and are constructed to function more or less rapidly so that while similar curves of viscosity and resistivity are attained with different ball mills, the time factor may differ greatly. Thus with a given laboratory type of ball mill, the viscosity did not become constant until approximately 20 hours of

ball milling had taken place. Similarly, the resistivity would not approach a constant value until approximately 20 hours of ball milling had occurred in the same apparatus. However, in each case, a stable or plateau portion was reached indicating a satisfactory dispersion of the carbon into relatively separate chains.

The following compositions were prepared according to the milling practice above set forth:

TABLE

Percentage of constituents by weight in experimental batches of conducting paints

Batch No	1	2	3	4	5	6
Resin-to-Pigment Ratio	6:1	8:1	8:1	8:1	10:1	10:1
Acetylene Black..per cent	5.0	4.4	4.4	3.9	3.9	3.2
Resin.....do	30.0	26.3	35.6	31.1	31.0	32.0
Total Solvent.....do	65.0	69.3	60.0	65.0	65.1	65.0

The resin used in making the compositions in the table comprised the reaction product of 33% to 36% phthalic anhydride, 51% to 55% of linseed oil and 12% to 15% of glycerol. It had a saponification value of 360 to 400. The solvent was composed of approximately equal parts by weight of toluene and petroleum naphtha.

Referring to Fig. 3 of the drawing, there is illustrated the surface resistivity in ohms per square when the compositions are applied to 10 mil glass tape and 10 mil asbestos tape, respectively, and cured by drying at room temperature. The difference in the relative resistivity between glass tape and asbestos tape is ascribed to the fact that the glass fibers are continuous filaments forming a comparatively slick surface, whereas the asbestos tape was matted much like blotting paper and the resin was subject to a more pronounced filtering action, leaving a higher proportion of the acetylene black at the surface of the asbestor fibers than was on the surface of the glass fibers. Any other fibrous material treated with the compositions will have values of surface resistivity between the two curves shown in Fig. 3. From the curves it will be apparent that a resin to pigment rates of 4:1 to 12:1 is satisfactory for treating slot cell portions of windings.

The unusual characteristics of acetylene black and other blacks characterized by long carbon particle chains is the relatively low resistivity considering the proportion of the carbon black to the resin. Ordinarily, graphite would be required in an amount or proportion several times that of the acetylene black to give the same resistivity. Wood chars likewise would be required in a considerably greater amount. All other known carbonaceous powders exhibit a higher resistance for a given loading in the resin than does acetylene black. The low ratio of acetylene black to resin enables a much harder and more fully cured film having high abrasion resistance to be produced for a given resistivity than with any other known form of conducting carbon.

Extensive aging tests have been made to determine the change in resistivity with time at elevated temperatures. These tests have indicated a decrease in resistivity with aging time. Thus when aged 2500 hours at 50° C., a tape containing the composition of Example 4 of the table decreased in resistivity approximately 30%. At 100° C. and 2500 hours, the decrease in resistivity was approximately 50%. At 150° C. for 10,000 hours, the decrease in resistivity was estimated to be approximately 38%. For the prevention of corona, a decrease of resistivity with time of

this order, particularly within the range of temperatures in which this test was conducted, is considerably more desirable than an increase in resistivity.

Comparison with many other semi-conducting and resistance compositions indicates that the compositions of the present invention change less in resistivity on aging than any other known composition. A further desirable property is the low temperature coefficient of resistance. Thus the resistivity decreases 8% between 25° C. and 100° C. Both of these characteristics are believed to be inherent in the chain structure of the carbon.

The resistance compositions of this invention are particularly adapted for application to the slot portions of insulated conductors. For the maximum durability and life, it has been found desirable to combine a fibrous covering and the resistance composition into an exterior coating on the insulated conductor. Particularly desirable results are obtained if the fibrous covering comprises a glass fiber or asbestos or other inorganic fiber tape thoroughly impregnated and bonded to the insulation on the slot portion of the conductor with conducting varnish.

Referring to Fig. 4 of the drawing, there is illustrated a magnetic core 10 provided with a slot 12 in which there is disposed an insulated electrical conductor comprising the copper conductor 14 and insulation 16 wrapped thereon. Insulation 16 may comprise mica tape or fibrous fabrics, resinous impregnants, such as phenolic varnishes, alkyd resins or organo polysiloxane resins or natural resins, such as asphalts, and the like. To the exterior of the insulation 16 there is applied a fibrous covering 18 such as glass fiber or asbestos tape or sheeting. The fibrous covering 18 may be cemented to the insulation by a suitable adhesive resin, the glycerol-phthalate resistance compositions may be used to advantage for this purpose. The fibrous covering 18 is thoroughly coated and impregnated with the resinous resistance composition disclosed herein, an excess thereof forming a surface layer 20. The oil modified glycerol phthalate resin cures rapidly at room temperature to a relatively stable condition. The layer 20 is hard and smooth.

After complete curing of the insulated conductor, the insertion of the insulated conductor 14, 16 into the slot 12 and applying the slot stick 22 causes the insulation to come in contact with some pressure with the grounded laminations 10 at close intervals, thereby grounding the resistance coating. Tests and calculations indicate that the currents flowing in the resistance coating due to the induced voltage will be of such a magnitude that the heat generated in the coating is less than 3% of the copper loss in an average machine when the resistivity is about 100 ohms per square inch.

This value of 100 ohms per square should not be reached in service if satisfactory results are to be had.

Films of the resinous composition applied to a non-porous surface, such as a glass plate, have been found to have a resistance of 3000 to 6000 ohms per square. When applied to 10 mil thick glass fabric, the average resistance has been approximately that shown in the upper curve in Fig. 3 of the drawing. This difference is believed due to the relative change in concentration of the acetylene black by reason of the straining or filtering action of the fibrous material.

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. A resistance composition composed of 100 parts by weight of an oil modified alkyd resin derived by reacting from 45% to 60% by weight of a drying oil compound selected from the group consisting of linseed oil and linseed oil acids, from 40% to 30%, respectively of phthalic anhydride, and the balance glycerol, from 8 to 25 parts by weight of acetylene black and at least 150 parts by weight of a volatile organic solvent, the composition having been milled until the viscosity and resistivity attain relatively constant values, and cured films of the composition having a resistivity of from 3000 to 6000 ohms per square of surface area.

2. A resistance composition composed of 100 parts by weight of an oil modified alkyd resin derived by reacting from 45% to 60% by weight of a drying oil compound selected from the group consisting of linseed oil and linseed oil acids, from 40% to 30%, respectively of phthalic anhydride, and the balance glycerol, from 8 to 25 parts by weight of a carbon black characterized by long chains of carbon particles when viewed at a magnification of over 10,000, and at least 150 parts by weight of a volatile organic solvent, the composition having been milled until the viscosity and resistivity attain relatively constant values, and cured films of the composition having a resistivity of from 3000 to 6000 ohms per square of surface area.

3. An electrical winding comprising, in combination, an electrical conductor having a slot portion, electrical insulation applied to the electrical conductor at the slot portion, the insulation including an exterior fibrous covering, and a cured resistance composition applied to the slot portion of the exterior fibrous covering, the cured resistance composition composed of a drying oil modified glycerol-phthalate resin containing 45% to 60% by weight of the drying oil, from 40% to 30% by weight of phthalic anhydride and from 10% to 15% of glycerol, and from ¼ to 1/12 of its weight of colloidal acetylene black, the whole having been milled to a relatively constant volume resistivity, the fibrous covering so treated having a resistivity of 400 to 2500 ohms per square of surface area.

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