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S. RUBEN

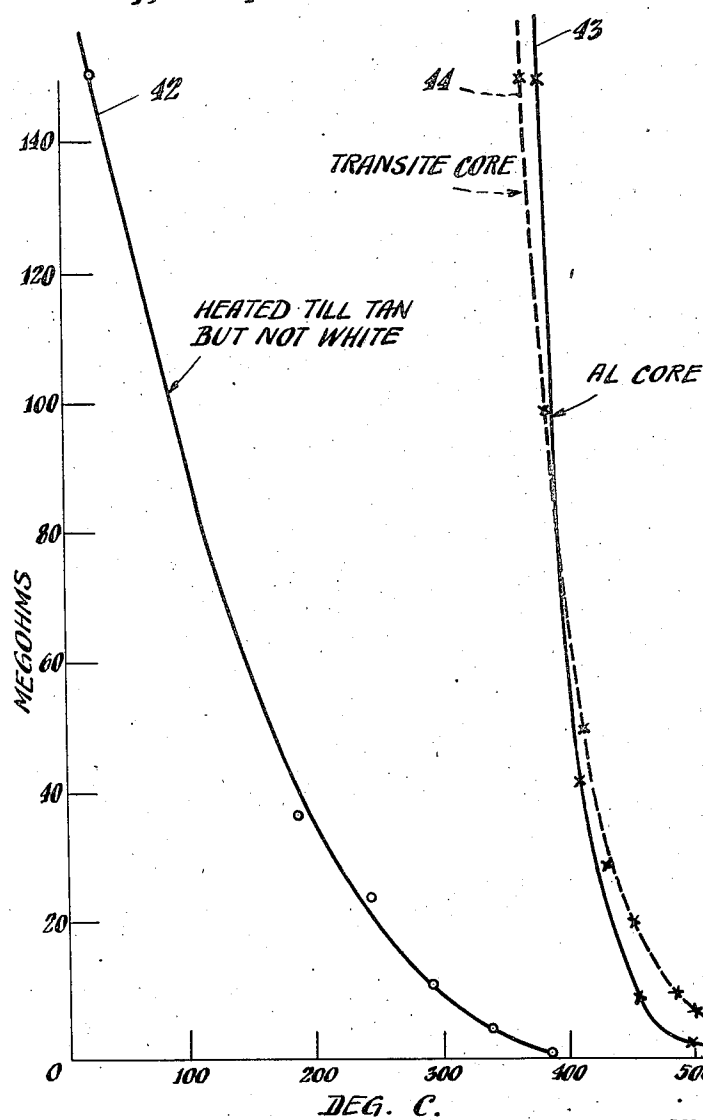
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ELECTRODEPOSITION OF INSULATING MATERIALS

Original Filed Aug. 12, 1939 2 Sheets-Sheet 1

Fig. 1.

Effect of Oxidation



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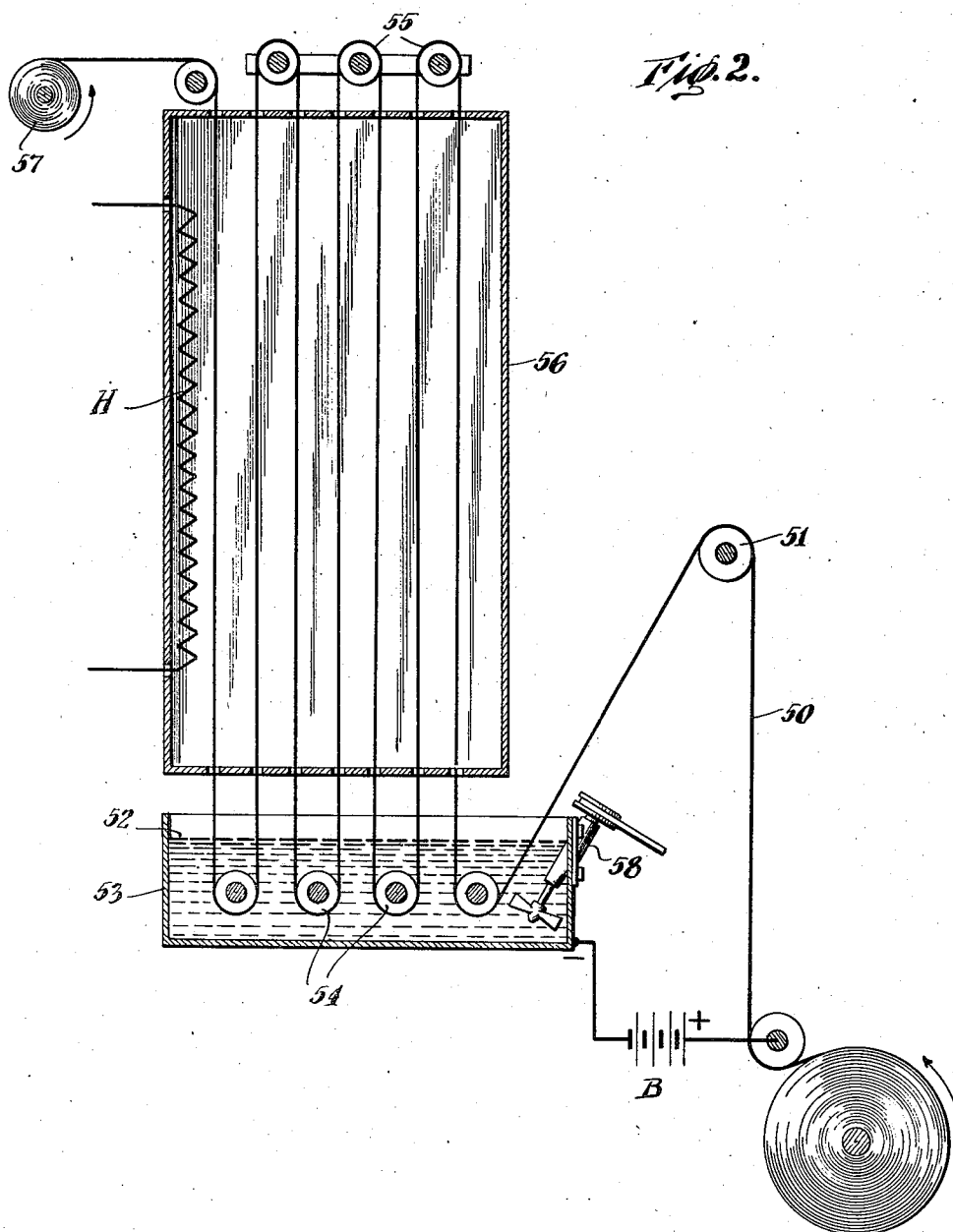
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ELECTRODEPOSITION OF INSULATING MATERIALS

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Original application August 12, 1939, Serial No. 289,810, now Patent No. 2,327,462, dated August 24, 1943. Divided and this application March 23, 1943, Serial No. 480,146

16 Claims. (Cl. 204—181)

This invention relates to a method of electrically depositing insulating materials on metals, particularly resistance wire formed of refractory metal compositions. This application is a division of my copending application Serial No. 289,810, filed August 12, 1939.

An object of the invention is to provide a method whereby an insulating material may be electrically deposited on metal surfaces.

A further object is the provision of a process whereby metal members of very fine or unusual dimension may be coated with an insulating material.

Another object is the provision of a method for coating refractory wire with an insulating material having a high resistance to heat.

Still another object is the provision of a process for electrophoretically depositing and bonding a thin hard high temperature resistant insulation upon refractory wire elements to be used as electrical resistors.

Other objects of the invention will be apparent from the following description and accompanying drawings taken in connection with the appended claims.

The invention comprises the features of construction, combination of elements, arrangement of parts and methods of manufacture and operation referred to above or which will be brought out and exemplified in the disclosure hereinafter set forth, including the illustrations in the drawings.

In the drawings:

Figure 1 is a graph showing the effect of oxidation of the coating in respect to increase in resistivity; and

Figure 2 illustrates the process of applying the insulating coating to the refractory wire.

While a preferred embodiment of the invention is described herein, it is contemplated that considerable variation may be made in the method of procedure and the construction of parts without departing from the spirit of the invention. In the following description and in the claims, parts will be identified by specific names for convenience, but the invention is not intended to be limited beyond the scope of the claims.

Heretofore, in the commercial manufacture of resistance elements, several methods have been employed. In one, the wire was wrapped with a layer of thick insulating fibrous material such as asbestos; in another, the wire was embedded in a mass of plastic cement after which the mass was baked to dry and harden the cement; a third means of obtaining insulation was to wind the

bare wire on an insulating form with sufficient spacing between turns to avoid short-circuiting contact between them.

Units of the above types could not conveniently or efficiently be made in multi-layer coil form. It will be appreciated that the asbestos or cement coverings of the type described are inherently and necessarily relatively thick or massive resulting in excessive heat insulation. This produces a high temperature differential between the inside and outside of the element. The element is thus not as quickly responsive to electric current through the wire nor can high current values be safely handled by the element without danger of burn-outs. Likewise the space occupied by the insulation seriously limits the amount of wire which can be contained in an element of a given size. The space factor is also very poor in a bare wire element and added precautions are necessary to avoid danger of contact with the bare wire.

The present application describes a method for producing a flexible, high-temperature, electrical heating element comprising a wire of refractory metal coated with a thin, hard and adherent insulating layer of uniform thickness, the layer being hard, adherent and non-conductive at temperatures at which the heating element is operated. The layer is composed of inorganic insulating material and a much smaller amount of organic resinous binder, the percentage of latter material present being insufficient to render the insulating layer conductive at temperatures beyond its carbonization point. The coating is applied by making the wire the anode in a suitable bath, such as an aqueous ammonia reacted shellac solution which has in suspension finely divided inorganic insulating material, the container for the bath, acting as the cathode. When current is discharged through the assembly, inorganic insulating material and shellac are simultaneously deposited upon the wire, the inorganic refractory material being deposited in a much greater amount than the shellac.

Finely divided hydrated materials of the kaolinite and talc type are the most desirable insulating compounds, due to the fact that they are excellent suspension materials in the electrolytic method of coating used and also because they are highly suitable for the firing and sintering operation. While kaolinite alone may be used, the presence of talc increases the smoothness of the coating and increases its resistivity at high temperatures. Finely divided chromium oxide, beryllium oxide or titanium oxide may be substituted

for the talc or kaolinite with less satisfactory results, the latter materials being superior. The most desirable combination appears to be a mixture of kaolinite and talc in bentonite. Before the mixture is applied to the wire, it is ball-milled for about twenty-four hours in order to eliminate any possible large particles and to insure a fine grain deposition. It is important that the materials after being ground should have a grain size not larger than 400 mesh and preferably smaller.

The wire used for the resistance element may be of any suitable composition, such as nickel-chromium, iron-chromium, tantalum-iron-chromium, etc., and of any desired size. The invention makes it possible to use very fine wire, as low as 0.001 inch in diameter and the coating may, of course, also be deposited upon larger wires of all commercial sizes.

The coating is electro-deposited on the wire, next heated and dried and may thereafter be passed through a firing or sintering oven. For some purposes the wire may be used in this form but where considerable handling is required and where the coated wire is to be wound upon mandrels of relatively small diameter it is desirable to apply a flexible waterproof top coating of a material such as methyl methacrylate, cable lacquer, tung oil, indene or other resin, etc. Accordingly, the sintered wire may be directly passed through a solution of 7% methyl methacrylate polymer in acetone and thereafter dried at a temperature of about 150° C. and spooled for future use. The wire so produced is sufficiently tough and flexible to be wound or bent into any form ordinarily required in the finished element without danger of chipping or cracking. It is likewise resistant to mechanical shocks and abrasion so that the coated wire may be handled by a winding machine. In the manufacture of resistance units, the organic top coating may be expelled as a gas or vapor from the finished unit, either immediately after the wire has been wound into form or where a metal casting is used at the time of or prior to the application of the metal to the unit. Alternatively, the top coat may be allowed to remain, in which case it may gradually volatilize after the resistor has been put in use.

The coated wire having the characteristics above described may be used to form resistance elements of various types and for various purposes such as fixed resistors for radio circuits and the like, heating elements, soldering iron elements, hot plates, energy dissipating units and the like. It may be wound on forms of metal or ceramic either in ordinary spiral or in non-conductive form.

If greater rigidity and higher abrasive resistance is desired in the finished element it can be obtained by applying a glazing material prior to any of the above heat treatments. For example, the wound element, before heating, can be sprayed, dipped or painted with a hydrolyzed ethyl silicate solution, preferably with finely divided kaolinite and talc suspended therein. A suitable mixture consists of 50% kaolinite and 50% talc added to an equal weight of hydrolyzed ethyl silicate. This glazing layer gives the coating a smooth surface and bonds adjacent turns of the winding together into a rigid integral unit. Upon heat treatment the organic ethyl silicate is decomposed leaving a silica binder. Methyl or glycol silicate can be substituted for ethyl silicate. Likewise a water solution of sodium silicate may be applied if high voltages are not encountered.

The best glazing effects can be obtained by heating at least to 1000° C.

When shellac or other organic binder is used, it may either be removed by a subsequent heating operation in which case the finished coating will consist solely of inorganic materials, or a relatively small amount of shellac may be left in the coating.

The most practical working limits for shellac are 10% to 30%. The preferred proportions of shellac will vary somewhat, however, with different sizes of wire. Thus with 1 and 2 mil wire the preferred amount of shellac is 10%, with 4 to 6 mil wire 16% and with 10 mil wire about 22%.

Other organic binders than shellac can be used such as the various resins (natural or synthetic), for example, rosin, copal and the like, the various gums, for instance, dammar, arabic, tragacanth, and rubber latex and certain oils such as tung oil and linseed oil. However, none of these has been as satisfactory as shellac.

When shellac is used, it is desirable in most cases to employ the high temperature heating only after the wire has been wound on the resistance element. In such cases the resistance element may be heated up to 1000° C. after the wire has been wound into final form.

For use where low voltage insulation only is required it may only be necessary to heat the winding above the volatilizing or decomposition temperature of the shellac or other organic binder. For shellac a temperature of about 420° C. may be sufficient. At this temperature the shellac appears to decompose, the majority of the product going off as vapor and only a small amount of non-volatile residue remaining, probably in the form of carbon. If the unit is to be used in this form it is to be preferred that the original coating shall have a lower percentage of binder so that the amount of carbon left in the coating will be insufficient to cause any material current leakage. For a shellac binder, the percentage of shellac originally in the coating should preferably be not larger than 30%. The heating may be carried on in an oven or by passing current through the winding and may take place in air or in an inert gas atmosphere.

While the above heating may be sufficient for low voltage operation it will generally be preferred especially where high voltage will be encountered to heat the element to a higher temperature, namely one at which the residue (carbon) will burn out leaving a coating free from organic matter. For this purpose the temperature should be raised to 455° C. or above. The resulting coating is highly resistant to current leakage, the resistance normally amounting to several megohms per linear inch of coated wire. This coating is suitable for high voltage high temperature use. A metal sheath can be cast directly against the coated wire if desired in which case the coating will fully insulate the wire from the cast sheath. In this case it is of advantage, however, to keep the percentage of shellac originally in the coating to a minimum (preferably below 5% to keep down the porosity in the final coating from which the organic material has been volatilized and oxidized out).

When a greater abrasion resistance is desired, as where the coated wire is to be used without any protective sheath, it is preferred that the wire element be sintered and fired at 1000° C. The resulting sintered element is ready for use without further treatment either with or without a protective sleeve or a cast metal sheath. The

sintering temperature can be reduced by adding a small percentage of fusible borates or silicates to the coating material before applying to the wire but for minimum leakage at high temperatures the use of such additional agents is not desired.

The proceeding description of the various possible heat treatments which may be employed when an organic binder is used may be briefly summarized as follows: The wire is first provided with a coating consisting of a finely divided inorganic insulating material and an organic binder whereby a coated wire is produced of sufficient flexibility to enable winding or otherwise forming into a resistance element of desired shape by hand or with a winding machine or other forming apparatus. The wound (or formed) element can be used in this form where low temperatures only are to be encountered. Where higher temperatures are to be encountered the coated wire element is given a heat treatment which changes the composition and physical properties of the coating. The composition is thus changed so as to reduce or eliminate the organic material which could not stand up under the higher temperatures which the element is expected to encounter during the coating of the metal sheath or in subsequent use. The physical characteristics are changed by the heat treatment to produce a more rigid, less flexible coating which would ordinarily be chipped or cracked if it were attempted to manipulate or rewind the coated wire in this condition. However, since the element has already been formed or wound prior to the heat treatment it is unnecessary to apply any further manipulations after treatment and hence the coating is preserved intact.

The heat treatment, as described above, may extend to one of the following temperatures:

(1) Volatilizing temperature at which the volatile constituents of the organic binder are driven off. Suitable for low voltage operation at high temperatures preferably with metal sheath, 375° C.

(2) Oxidizing temperature at which any residual carbon left by the organic binder is burned out. Suitable for high voltage 450° C. operation at high temperatures preferably with cast metal sheath.

(3) Sintering temperatures at which the particles of inorganic material are sintered together. Suitable for high voltage operation at high temperatures with or without any protective sleeve or sheath.

The effect of the heat treatments and resultant oxidation of the shellac binder wire coating is illustrated in Figure 1 which is a graph, the curves of which show resistivity of insulation on units formed from resistance wire having a 0.003" insulating coating and in which the total contacting area of the insulation is 4.6 sq. in. Curve 42 shows the resistivity of such a unit, the insulating coating of which has been heated only up to the point at which the coating becomes tanned. Curve 44 shows the result of heating such a unit to a temperature where the coating becomes white due to oxidation and/or elimination of any carbonaceous material, the heating temperature being in excess of 450° C. The insulated wire, the characteristics of which are shown in curve 44, was wound on a transite core. Curve 43 illustrates the resistivity of a coated wire identical with that referred to in curve 44, excepting that in this case the wire was wound on an aluminum core.

Figure 2 illustrates a simple continuous method of applying the insulating coating to the resistance wire. The positively charged uncoated nickel-chromium wire 50, passes via pulley 51, into talc-kaolinite-aqueous shellac bath 52, held in negatively charged metal container 53. Pulleys 54 and 55 serve to direct the course of the wire through the solution and up through electrically heated oven 56. It will be noted that the coated wire is baked after each pass into the bath. The finished wire completely coated, is wound on spool 57. Battery B provides the plating current and heater H supplies the temperature for the baking oven. The solution 52, is continuously agitated by propeller 58.

Where it is desired to add an organic waterproof top coating to the wire, an additional bath of a suitable material such as indene resin, may be added, the wire passing through the resin bath after the inorganic coating has been completed, and being again heated to drive off volatilizable vapors prior to being spooled.

It will be seen that the present invention provides a method for producing an insulated resistance wire element in which the insulation, fired in situ upon the wire, is thin, hard, uniform, continuous, adherent, indestructible, of sufficient flexibility to permit of its being wound into coil form, which may be constructed in compact multi-layers without danger of short-circuiting between turns and which conveniently allows the casting of a protective and heat-radiating hard metal sheath directly against and around the insulated wire without damage to the wire.

What is claimed is:

1. In the method of insulating a flexible conductor, said conductor constituting the anode in an electrophoretic assembly, the steps comprising electrophoretically depositing upon said conductor from an aqueous dispersion, a mixture of finely divided refractory inorganic insulating material of the class consisting of kaolinite and talc and an insulating organic binder, the amount of inorganic insulating material being greater than the amount of said organic binder.

2. In the method of insulating a flexible conductor, said conductor constituting the anode in an electrophoretic assembly, the steps comprising electrophoretically depositing upon said conductor from an aqueous dispersion, a mixture of finely divided inorganic insulating material and shellac, the amount of inorganic insulating material being greater than the amount of shellac.

3. The method described in claim 2 characterized in that the inorganic insulating material comprises kaolinite.

4. In a continuous process for making a flexible insulated resistance wire capable thereafter of being wound in coil form to provide a resistor unit in an electrical circuit, the steps which comprise making a wire of electrical resistance material the anode in an electrophoretic assembly containing an aqueous dispersion of an organic binder and finely divided refractory insulating material of the class consisting of kaolinite and talc, the amount of refractory insulating material being greater than the amount of said organic binder, providing a cathode in contact with said dispersion, passing said resistance wire through said dispersion whereby the organic binder is deposited upon said wire simultaneously with said finely divided inorganic insulating material, said coated wire thereafter passing through an oven to dehydrate the coating and eliminate any remaining water.

5. The method described in claim 4 character-

ized in that a top coating is finally applied to said coated wire.

6. The method described in claim 4 characterized in that the coated wire is heated in an atmosphere of at least 375° C.

7. The method described in claim 4 characterized in that the coated wire is heated to a temperature at which the organic binder is substantially removed.

8. The method described in claim 4 characterized in that an insulating inorganic top coating is finally applied to said coated wire.

9. In a continuous process for making a flexible insulated resistance wire capable thereafter of being wound in coil form to provide resistor units in electrical circuits, the steps which comprise making a wire of electrical resistance material the anode in an electrophoretic assembly containing an aqueous dispersion of shellac and finely divided refractory insulating material, the amount of refractory material exceeding the amount of shellac providing a cathode in contact with said dispersion, passing said resistance wire through said dispersion whereby the shellac is deposited upon said wire simultaneously with said finely divided insulating material, said coated wire thereafter passing through an oven whereby the coating is baked and further bonded to the wire.

10. The process described in claim 9 characterized in that the shellac comprises not more than 30% of the total amount of solids in the aqueous dispersion.

11. In a continuous process for making a flexible insulated resistance wire, the steps which comprise making the wire the anode in an electrophoretic assembly containing an aqueous dispersion of insulating resinous binder having in suspension finely divided refractory insulating material comprising kaolinite and talc, the amount of refractory insulating material exceeding the amount of resinous binder, providing a cathode in contact with said dispersion, passing said resistance wire through said dispersion whereby the resinous binder is deposited upon said wire simultaneously with said finely divided kaolinite and talc, and thereafter baking the coated wire to drive off water.

12. In a continuous process for making a flexible insulated resistance wire, the steps which comprise making a wire of electrical resistance material the anode in an electrophoretic assembly comprising a dispersion containing water and an insulating organic binder, said dispersion hav-

ing suspended therein finely divided refractory insulating material of the class consisting of kaolinite and talc, the amount of refractory insulating material exceeding the amount of organic binder, providing a cathode in contact with said dispersion, applying a potential to said electrodes whereby the organic binder and said finely divided insulating material are simultaneously deposited upon the wire, and thereafter repeating said steps with the coated wire until the desired thickness of insulation is obtained.

13. The process described in claim 12 characterized in that the wire is baked after the application of each coating.

14. A continuous method of providing a flexible refractory insulating coating for a resistance wire of the nickel-chromium type which comprises making said wire the anode in an electrophoretic assembly containing an aqueous dispersion of an insulating organic binder having kaolinite suspended therein, the amount of kaolinite being greater than the amount of organic binder, providing a cathode in contact with said dispersion, passing said wire through said dispersion whereby the kaolinite is deposited upon said wire and simultaneously therewith the organic binder is likewise deposited upon said wire, the kaolinite being deposited in a greater amount than the organic binder, and thereafter baking said coated wire to a temperature sufficient to dehydrate the deposited material.

15. A method of electrically insulating a flexible electrical conductor which comprises electrophoretically depositing upon the surface of said conductor a mixture of an organic binder and a finely divided refractory inorganic insulating material of the class consisting of kaolinite and talc, the amount of inorganic insulating material being greater than the amount of organic binder, heating said mixture to bond it to the conductor, and applying thereto an insulating inorganic top coating.

16. A method of electrically insulating a flexible electrical conductor which comprises electrophoretically depositing upon the surface of said conductor a mixture of an organic binder and a finely divided refractory inorganic insulating material of the class consisting of kaolinite and talc, the amount of inorganic insulating material being greater than the amount of organic binder, heating said mixture to bond it to the conductor, and applying thereto a flexible, waterproof organic top coating.

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