

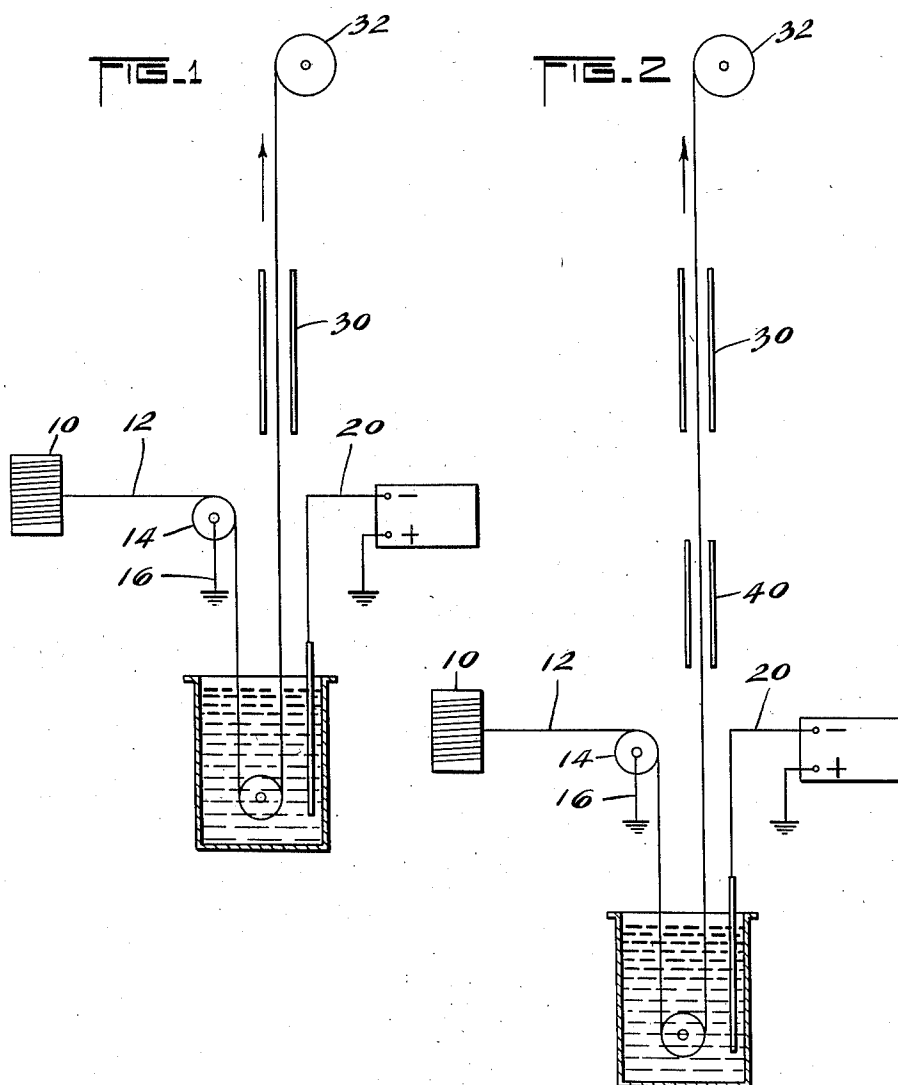
May 26, 1953

R. E. PALMATEER

2,640,024

ELECTROPHORETIC BORATING OF COPPER WIRE

Filed Nov. 2, 1948



INVENTOR.
Russell E. Palmateer
BY *AtB Richardson*
Attorney

UNITED STATES PATENT OFFICE

2,640,024

ELECTROPHORETIC BORATING OF
COPPER WIRE

Russell E. Palmateer, Emporium, Pa., assignor to
Sylvania Electric Products Inc., a corporation
of Massachusetts

Application November 2, 1948, Serial No. 57,994

2 Claims. (Cl. 204—181)

1

This invention relates to a method of coating wire; more particularly it relates to a method of coating wire with a vitreous material by an electrophoretic process.

In accordance with prior art practices for coating wire with a vitreous material such as borates or soft glass materials, the vitreous forming material has normally been applied in a purely mechanical manner by dipping or brushing the material onto the surface of the wire. For example, in the borating of copper or copper clad wire as has heretofore been the custom, the wire is first heated in an air furnace to remove contamination and more particularly to oxidize the copper surface since this oxide surface appears to be quite necessary if a satisfactory borate coating is to be applied. The thickness of this oxide and its appearance is, therefore, quite critical. Following this, the borate is applied in a thin coating by painting on or by dipping the wire into a water suspension or solution of the borate maintained at the proper consistency to deposit the most desirable amount of solid material, after which it is dried and heated at a critical temperature to fuse flow the coated material into a skin. In coating wire such as "Dumet" which is a copper clad nickel iron wire used for glass sealing in the electronic industry, a continuous process has been developed wherein the wire is moved successively through these stages and finally after sufficient cooling is wound on spools. Such a process is diagrammatically illustrated in Patent No. 2,316,984.

Although this process has been used commercially for some considerable time, it is understandably not completely satisfactory since it is somewhat dependent upon pre-oxidation of the wire which step needs to be kept under careful control at all times if a satisfactory product is to be obtained. Furthermore, the presence of the water along with the borate also leads to the formation of bubbles in the surface. These are attributable to the hydrated salts that are used thus producing finished products whose coating can by no means be considered smooth and even. Furthermore it is at times difficult to control the coating thickness. Since this mechanical coating method depends in large part upon the heating of the wire, before the dipping operation in order to form a suitable oxide finish, it was not considered the best manner of application on an annealed wire used for such purposes.

It is an object of this invention to provide an improved method of applying a vitreous coating to metals which is adapted to produce an even

2

uniform coating having no bubbles in the finished surface such as those normally encountered due to the use of hydrated salts.

It is a further object of this invention to provide a method of applying a vitreous coating which will require no previous oxidation of the metal.

It is a still further object of this invention to provide a method of applying a vitreous coating in a manner which will not interfere with the annealed condition of the base metal to be coated.

In accordance with this invention these and other advantages which are incidental to its application, can be attained by electrophoretically coating the wire from a suspension of vitrifiable material and metal oxides.

In the accompanying drawing which illustrates the preferred method of this invention:

Fig. 1 is a schematic drawing showing the preferred method and apparatus embodying features of this invention;

Fig. 2 is a schematic drawing showing a modified version of the method and apparatus shown in Fig. 1.

In accordance with this invention, it has been found that metal can be coated with a vitreous material in a manner requiring no preoxidation to obtain even uniform coatings having no bubbles in the finished surface if the material is coated electrophoretically from a bath containing a suspension of the vitrifiable frit material in intimate mixture with an oxide of the material to be covered.

Electrophoretic methods of coating metals with non-conductors are of course quite well known to the art.

However, it has not heretofore been considered possible to apply a vitreous coating to such metals without previously oxidizing the metal if a good adherent coating was desired.

In accordance with the method of this invention however, it becomes unnecessary to oxidize the surface of the wire to produce good adherent coatings. Furthermore it has been found that the presence of the oxide of the base metal in the frit suspension tends to increase the rate at which the vitrifiable material can be applied to the base metal by electrophoresis.

In the case of copper wire, for example, it was found that wire which could only be borated electrophoretically at the slow rate of seven feet per minute could be borated at the rate of 16 feet per minute or more than twice as fast if copper oxide were present in the borating suspension.

In accordance with preferred embodiments of this invention in which clean copper wire is borated without first applying an oxide film to the wire, the spool 10 of the annealed wire as shown in Fig. 1 feeds the wire 12 over a guide pulley 14 electrically grounded by line 16. The wire 12 passing downwardly into a coating bath around a guide pulley at the bottom of it, upwardly out of the bath past a cathode connected to a power line 20. As the wire leaves the coating bath it passes through a furnace 30 which is operated at a temperature of about 900 degrees C. or above to fuse the borate coating. The wire thereupon passes up to a winding spool 32 which is located a sufficient distance above the furnace that the borate will solidify before it reaches the winding spool or pulley 32. As shown in Fig. 2, a dryer 40 may be placed between the coating bath and the furnace for the purpose of evaporating the solvents before the wire reaches the furnace 30 if so desired. This dryer normally operates at 150-200 degrees C. in preferred cases.

In accordance with preferred embodiments of this invention, the coating bath is made up of a suspension of the vitrifiable material in finely divided form and powdered metallic oxide in a suspension of the water free organic medium which is not hydrophilic and does not have a tendency to absorb moisture. A preferred formula for the borating of Dumet wire is, for example, one which contains 120 grams of sodium borate (anhydrous), .5 gram of Cu_2O , 200 ccs. of amyl acetate and 100 ccs. of lacquer containing approximately .9 gram of anhydrous 1000 second nitrocellulose per 100 ccs. of high purity amyl acetate. This solution to give the best results is ball-milled over night, that is, for a period of about 12 hours after which the suspension gives best results after having been diluted with two litres of amyl acetate. When operating with this solution, it has been found that the heat required for borating to take place is 900 degrees C. The rate of coating is about 16 feet per minute. This permits the wire to be heated at 900 degrees C. for 4 seconds and allows it to be cooled in air for 20 seconds. The process requires the use of voltages of less than 100 volts during which the borate moves and adheres to the wire at low electrical potential. For the coating of .0162 Dumet wire, the voltage required at the beginning is about 60 volts which is gradually increased to 90 volts when 10,000 feet of wire have passed through the suspension.

This method has been found to be successful and satisfactory for production of even coatings with other vitreous materials besides borates namely with glass frit of types G12, G1 borax glass. The composition for G12 glass is approximately as follows: 56.7% of SiO_2 , 3.32% of Na_2CO_3 , 7.9% of K_2O , 0.6% of Ca , 28.4% of PbO , 1.3% of R_2O_3 . G1 glass has the following approximate compositions of: 20.6% Pb , 62.2% of SiO_2 , 6.84% of Na_2CO_3 , 6.45% of K_2O and 1.05% of R_2O_3 . There is, of course, nothing novel in the fact that non-conducting materials such as glass frit, aluminum oxide, silica, any of the anhydrous silicates or any other vitrifiable material can be deposited electrophoretically. The novel feature in the composition lies in the inclusion of a metallic oxide which permits the omission of a preoxidation treatment as well as means to speed up the electrophoresis while yet obtaining satisfactory good adherent coatings of the vitreous material.

Although copper oxide is perhaps the most use-

ful of the metallic addition agents to the suspension in view of the large use of copper clad wire in making glass to metal seals, other metallic oxides can also be used to advantage particularly when the base material is to be coated a metal other than copper. Examples of such oxides are chromic oxide Cr_2O_3 , tungstic oxide WO_3 , cobaltic oxide, iron oxide and aluminum oxide.

Other examples of preferred bath formulations in which such oxides are used are, for example, as follows:

- I. 25 gms. of #775 Pyrex glass (powdered)
25 ml. amyl acetate
5 ml. of lacquer containing approximately 3.33 g. of anhydrous 60-80 second nitrocellulose per 100 ml. of high purity amyl acetate
.5 gm. tungstic oxide (WO_3)
1 gm. sodium borate
- II. 200 gms. pulverized G-1 glass
250 ml. amyl acetate
50 ml. of lacquer (same as in I)
10 gms. green anhydrous chromic oxide, Cr_2O_3

The amount of oxide activator added to the electrophoretic bath may, of course, vary over wide limits. Increasing the amount of the oxide in the bath in relation to the total solid material tends to increase the speed at which the electrophoretic deposition will take place. However, if too great amounts are used, there will be a tendency for the deposit to become non-adherent and flaky. For this reason, it has been found preferable when depositing from baths containing cuprous oxide, for example, to limit the cuprous oxide to .04% to .08% of the total solid material. On the other hand, the amount of tungstic oxide which may be added without deleteriously affecting the coating is as much as 2% of the total solids. With chromic oxide, the metal oxide can be further increased to as much as 5% without deleteriously affecting the adhesive properties of the coating.

It is, of course, understood that while the process of this invention makes it possible to coat either single or composite metals without previously oxidizing the metal surface to be coated, the fact that such metal surface may have controlled oxidation is not detrimental and will not have a deleterious effect on the finished product.

While the above description and drawings submitted herewith disclose preferred and practical embodiments of the coating method of this invention, it will be understood by those skilled in the art that the specific details shown and described are by way of illustration and are not to be construed as limiting the scope of the invention.

What is claimed is:

1. An electrophoretic bath for coating unoxidized copper wire with a borate coating preliminary to using it in making a seal to glass consisting essentially of a suspension of a mixture of sodium borate and powdered cuprous oxide in an anhydrous non-hydrophilic organic liquid of low electrical conductivity.

2. In the electrophoretic method of coating unoxidized copper wire with a borate coating preliminary to using it in making a seal to glass, the steps comprising passing the copper wire through a suspension of a mixture consisting essentially of sodium borate and powdered cuprous oxide in a non-aqueous, non-hydro-

philic organic medium, maintaining an electric potential between said metal and a cathode through said suspension and thereby causing the mixture of sodium borate and cuprous oxide to coat the copper wire, withdrawing the copper wire from the suspension and passing the coated copper wire through a heated area wherein the sodium borate is caused to flow evenly over the surface of the copper wire.

RUSSELL E. PALMATEER.

10

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,922,221	Steenbeck et al.	Aug. 15, 1933
2,213,969	Ruben	Sept. 10, 1940
2,321,439	Verwey et al.	June 8, 1943
2,421,652	Robinson et al.	June 3, 1947