United States Patent

Girard

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[54] METHOD OF ELECTRODEPOSITING VITREOUS COATINGS ATOP A MULTIAPERTURED SUBSTRATE

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[52] **U.S. Cl.** **204/181**

[51] **Int. Cl.** **B01k 5/02,** C23b 13/00

[58] **Field of Search** 204/181

[56] **References Cited**

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[57] **ABSTRACT**

Pinhole-free vitreous enamel coatings are electrophoretically deposited without frothing atop a multi-apertured substrate from an aqueous slurry of vitreous enamel and inert refractory particles by the inclusion of ammonium alginate or gelatine in the slurry in quantities less than 0.3 percent by weight of the water vehicle. Desirably a low ash producing organic film-forming binder, such as an acrylic emulsion, also is included in the bath in quantities less than 0.3 percent by weight water vehicle to enhance the toughness of the deposited film while the presence of minor quantities of an ionic wetting agent serves to enhance the plating characteristics of the bath.

6 Claims, 4 Drawing Figures

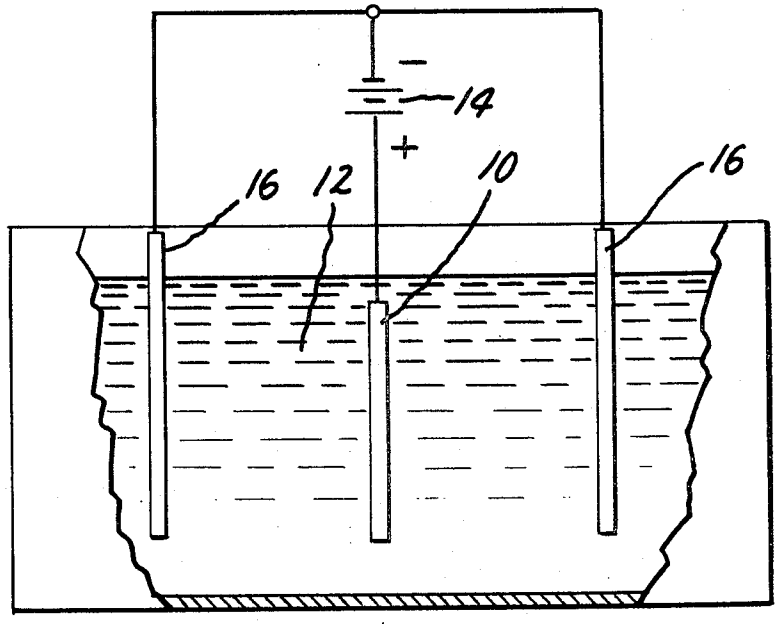


Fig. 1.

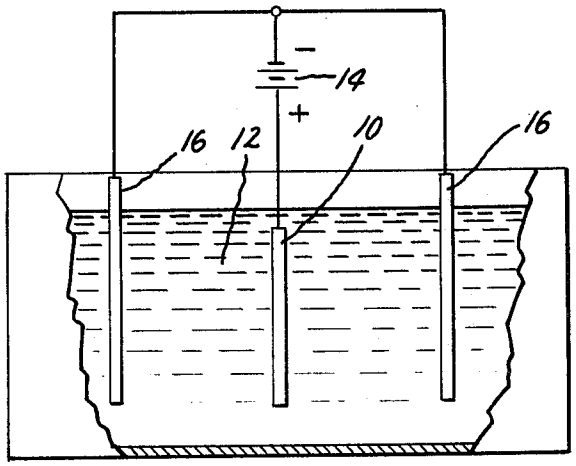


Fig. 2.

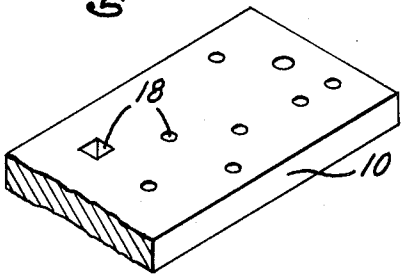


Fig. 3.

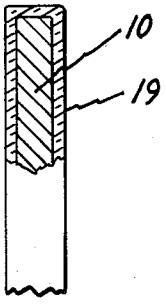
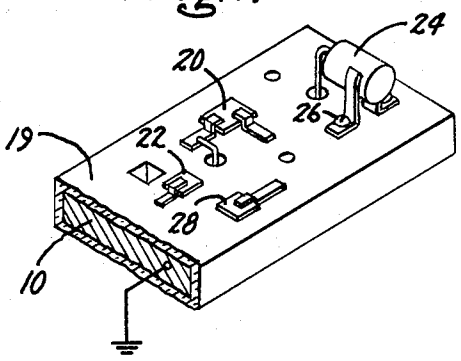


Fig. 4.



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METHOD OF ELECTRODEPOSITING VITREOUS COATINGS ATOP A MULTIAPERTURED SUBSTRATE

This application relates to a method of electro-phoretically depositing electrically insulating vitreous coatings atop a metallic substrate and in particular to electrophoretic deposition techniques utilizing an ionic colloidal material selected from the group consisting of ammonium alginate and gelatine to plate out simultaneously with the enamel thereby isolating the metallic substrate from contact with the aqueous vehicle.

For mass fabrication of electrical devices such as radio receivers, it often is desirable to screen print the electrical components forming the radio receiver atop an electrically insulated metallic substrate which subsequently serves as the radio receiver chassis. To permit the passage of wiring through the chassis and the structural mounting of components not amenable to thick or thin film deposition, the substrate to be coated customarily is provided with in excess of approximately 100 various dimensioned apertures often as small as 1/16-inch diameter. Complete coating of the small aperture sidewalls with a vitreous insulator by conventional dip coating techniques however is uncertain requiring the utilization of superior coverage techniques, such as electrophoretic plating, to assure a pinhole-free electrically insulating coat over the complete substrate. During electrophoretic deposition employing an enamel frit aqueous slurry, electrolysis at the plating electrodes often tends to produce frothing in the slurry negating deposition of a continuous vitreous enamel coating.

It is therefore an object of this invention to provide a method of electrophoretically depositing a vitreous enamel coating from an aqueous slurry without significant frothing.

It is also an object of this invention to provide a method of electrophoretically depositing pinhole-free vitreous coatings atop a metallic substrate.

It is still a further object of this invention to provide a method of electrophoretically plating vitreous enamel coatings not limited by the thickness of the deposited coating.

These and other objects of this invention primarily are achieved by the formation of the vitreous enamel coating utilizing a bath containing 20 to 60 percent vitreous particles suspended in a water vehicle along with an ionic colloidal material selected from the group consisting of ammonium alginate and gelatine in quantities less than 0.3 percent by weight of the water vehicle to codeposit with the vitreous particles sealing the substrate from the water vehicle to inhibit frothing. For additional toughness in the film without blistering upon subsequent firing, an organic film-forming binder selected from the group consisting of an acrylic and a cellulose also can be added to the bath in quantities below 0.5 percent by weight of the water vehicle. The substrate then is immersed in the bath and an electrical potential is applied to the substrate to electrophoretically plate vitreous particles atop the substrate whereupon the coated substrate is fired at a temperature above 600°C to mature the deposited particles to a pinhole-free coating less than 10 mils thick. Particularly advantageous deposition characteristics are obtained when the bath also includes an ionic wetting agent to enhance the charge of the chosen ionic colloidal material within the bath.

These and various other objects, features and advantages of the invention will be better understood from the following description taken in connection with the accompanying drawings in which:

FIG. **1** is a sectional view of an electrophoretic bath during plating of a multi-apertured substrate;

FIG. **2** is an isometric view of the substrate to be plated;

FIG. **3** is an enlarged sectional view illustrating the plating of the enamel particles atop the substrate; and

FIG. **4** is an isometric view illustrating utilization of the enamel coated substrate to accept deposition of electronic components thereon.

The electrophoretic deposition of a vitreous enamel coating atop a multi-apertured substrate **10** is illustrated in FIG. **1** and generally comprises the immersion of the previously cleaned, e.g., by conventional pickling or sandblasting, substrate within

an aqueous bath **12** containing 20 to 60 percent vitreous enamel particles in a dimension between 400 and −325 mesh along with a small quantity of an ionic colloidal material chosen from the group consisting of ammonium alginate and gelatine in quantities less than 0.3 percent by weight of the water within bath **12**. Generally the enamel chosen for bath **12** contains less than 6 percent by weight sodium oxide, lithium oxide and mixtures thereof to assure good electrical characteristics in the deposited enamel coating. Bath **12** also can contain small quantities of a low ash organic film forming binder, such as an acrylic or a cellulose (as will be more fully discussed hereinafter), to enhance the toughness of the deposited coating as well as minor quantities of a commercially available ionic wetting agent, such as Tergitol sold by Rohm and Haas. In conventional fashion substrate **10** is connected to the positive terminal of D.C. voltage source **14** while two inactive cathodes, identified by reference numeral **16**, disposed on opposite sides of substrate are connected to the negative terminal of the voltage source.

Substrate **10** is illustrated in FIG. **2** and generally comprises a metallic sheet of, for example, enameling iron, i.e., iron containing less than 0.2 percent carbon, having normally in excess of 100 apertures **18** of various dimension and geometric configuration passing therethrough. Typically substrate **10** is less than 35 mils thick and contains apertures ranging between one-sixteenth inch and three-eighths inch at aperture center dependent upon the desired usage for the aperture, i.e., whether the aperture is to serve for mechanically mounting components to the substrate or to permit electrical wiring to pass therethrough. Desirably, the edges of the apertures are rounded to a radius one-half the thickness of the substrate to minimize the effects of tension in the enamel during subsequent firing of the coated substrate.

An anionic colloidal material selected from the group consisting of ammonium alginate or a gelatine, e.g., Knox gelatine or Zein, is included in the bath in quantities less than 0.3 percent by weight of the water vehicle to codeposit with the enamel thereby sealing the substrate from the water vehicle to inhibit frothing due to electrolysis. The conductivity of the colloidal material, however, permits continued plating of the enamel atop the substrate. Ammonium alginate is preferred as the colloidal material of the bath because ammonium alginate in quantities less than 0.3 percent by weight water vehicle produces relatively smooth plating of the enamel coating upon the substrate without frothing and forms an enamel coating exhibiting superior resistance to water washing. While vitreous enamel baths containing commercially available gelatines exhibit plating characteristics comparable to baths containing ammonium alginate, the enamel coating deposited from a gelatine containing bath is slightly more sensitive to water washing and slightly more bubbles are produced during plating. Vitreous enamel coatings deposited from baths containing up to 0.3 percent by weight of gums such as gum arabic, gum tragacant or gum karaya as the anionic constituent however either exhibit poor strength, rough plating, froth formation or lack of adhesion to the substrate upon water washing dependent upon the particular gum employed in the bath. In general, inclusion of ammonium alginate or a gelatine in the bath in quantities in excess of 0.3 percent by weight of the water vehicle tends to produce blistering in the enamel coating when subsequently fired.

It is postulated that the immunity from frothing of an electrophoretic bath containing ammonium alginate or a gelatine is obtained by a sufficient voltage drop across the plated colloidal material to impede electrolysis of the water vehicle. Electrolysis however may occur at substrate **10** with the colloidal material minimizing the size of the generated gas bubbles to inhibit observable frothing at the surface.

Although good deposition of a vitreous enamel coating is achievable utilizing only ammonium alginate or gelatine in the bath in quantities below 0.3 percent of the water vehicle, desirably an organic film-forming binder having an acrylic or cellulose base also is added to the bath in quantities less than

0.3 percent by weight of the water vehicle to increase the toughness of the deposited coating. The binder employed in bath **12** should produce an ash residue less than (preferably below one-half) the ash residue produced upon firing ammonium alginate with acrylic based emulsions available from Rohm and Haas under the trade designations E269, E450 and WS24 being highly suitably for utilization in this invention. Cellulose based materials such as methyl cellulose, ethyl cellulose and carboxymethylcellulose, also can be employed as the film forming binder of the vitreous enamel bath although a commercially available ionic wetting agent, such as Tergitol, often is required in small quantities, e.g., less than 0.1 percent by weight water vehicle, to produce an anionic charge upon non-ionic film forming binders such as carboxymethylcellulose. In general, the deposition characteristics of all baths of the invention are improved by the addition of minor quantities of an ionic wetting agent to the bath notwithstanding the fact that the bath may contain only anionic ingredients. Desirably, the film forming binder (if employed) is present in the bath in quantities between approximately 70 and 90 percent by weight of the ionic colloidal material in the bath.

Minor amounts of a conventional suspending agent, such as a starch, also may be employed in the bath to augment the inherent suspension of the enamel particles therein. Similarly, in accordance with the teachings of my patent application Ser. No. 885,236 filed Dec. 12, 1969 and entitled "Enameled Metal Substrates and Method of Forming", inert materials, such as silicon dioxide or aluminum oxide, non-reactive with the enamel particles at the enamel firing temperature and having a melting temperature above the enamel firing temperature desirably are added to the bath in quantities between 10 and 35 percent by weight of the enamel particles to enhance the enamel viscosity during subsequent firing. Silicon dioxide particles of a dimension between 400 and −325 mesh also can be entirely substituted for the enamel particles of bath **12** when a glass coating (rather than an enamel coating) is desired atop substrate **10**. Bath **12**, however, desirably is free from electrolytes tending to produce conductivity therein to assure the deposition of the anionic colloidal materials upon the substrate in relatively large proportions at the initiation of electrophoretic deposition.

Voltage source **14** employed for the electrophoretic deposition normally is within a range from 1 to 120 volts (and preferably 30 to 60 volts) to produce a densely compact enamel coating on the substrate without electrolysis at the electrodes in sufficient quantities to produce frothing. Deposition of the enamel atop the substrate is continued until a coating less than 20 mils, and preferably between 12 to 13 mils, is formed thereon. Because the anionic particles deposited from the bath are sufficiently conductive to permit continued deposition of the enamel coating without an appreciable thickness limitation, the deposited enamel coating **19** is slightly thicker at the edges of the substrate (as illustrated in FIG. **3**) whereat the magnetic field is concentrated during electrophoretic deposition. The excessive edge building-up however is less than 20 percent, e.g., 1 mil excess for a 5-mil coating, and can be tolerated for screen printing.

After electrophoretic deposition of vitreous enamel coating **19** atop substrate **10**, the substrate is removed from the bath, rinsed in water to remove surface residue and placed in a furnace where the substrate is fired at a temperature typically between 790° and 830°C for a period of approximately 2 to 5 minutes to mature the enamel and form an electrically insulating coating less than 10 mils thick atop the substrate. To accept screen printing of electrical components thereon, the substrate preferably has a vitreous enamel coating between 6 and 7 mils thick subsequent to firing with at least a 5 mil coating at the edges. Because the enamel bath generally is not self-limiting, the excess build-up at the edges counteracts (to a limited extent) surface tension drawing of the enamel during firing tending to remove enamel from the edges of the substrate.

Those radio receiver components adaptable to screen printing, e.g., thin film resistors and screen printed capacitors identified by reference numerals **20** and **22** in FIG. **4**, then can be deposited directly atop the pinhole-free enamel coating while structural components not lending themselves to vacuum or thin film deposition, e.g., tunable condenser **24**, etc., are mechanically mounted to the substrate by soldering or other suitable fastening devices, such as bolts **26**. The insulating quality of the coating also permits utilization of the coating as a capacitor dielectric by screen printing a suitable electrode, e.g., a palladium-silver electrode **28**, atop the enamel with underlying substrate **10** being employed as the counter-electrode.

A more complete understanding of the novel features of this invention may be obtained from the following specific examples of electrophoretic deposition baths suitable for plating substrate **10**.

EXAMPLE 1

An electrophoretic bath is prepared by mixing 30 parts by weight of ground coat enamel frit with 100 parts by weight water to which are added 10 parts by weight silicon dioxide, 0.1 parts by weight of ammonium alginate and 0.1 parts by weight of acrylic polymer WS24 sold by Rohm and Haas. A sulfonated carboxylated anionic wetting agent commercially available under the tradename Tergitol from Rohm and Haas also is added to the bath in quantities of approximately 0.05 parts by weight and the ingredients are ball milled to −200 mesh. A 1 ½ × 2 inch × 30 mil enamel iron substrate having in excess of 100 apertures then is inserted into the bath formed by the thoroughly mixed ingredients between two platinum electrodes and 30 volts D.C. is applied between the platinum electrodes and the enamel iron substrate to pass a plating current of approximately 2.5 amperes through the bath. Plating of the enamel atop the substrate is continued until a 12 to 13 mil-thick coating is deposited thereon whereupon the substrate is removed from the bath, rinsed in water to remove the spongy surface of the enamel and fired at a temperature of 830°C for 3 ½ minutes to mature the enamel to a pinhole-free 6 mil-thick vitreous enamel layer. Resistor and capacitor components of a superheterodyne radio receiver then are deposited directly atop the enamel coated substrate.

EXAMPLE 2

A bath is prepared containing 40 cc's of a 0.2 percent Ammonium Alginate solution in water, 15 drops of Rohm and Haas acrylic polymer emulsion E269, 1 drop Rohm and Haas Tergitol 08 Wetting Agent, 5.5 grams of enamel powder and 1.5 grams silicon dioxide and the materials are ball milled for 15 minutes to insure good dispersion of the constituents within the bath thus formed. A multi-apertured enamel iron substrate then is immersed as the anode within the bath and a potential of approximately **35** volts is applied between the substrate and two adjacent electrodes to produce a current flow of approximately 2.5 amperes at the substrate. The deposition of the enamel is continued to a thickness of approximately 13 mils whereupon the enamel is fired at a temperature of 830°C for 3.5 minutes to produce an electrically insulating coating of approximately 6.5 mils atop the substrate.

EXAMPLE 3

An electrophoretic bath is formed by thoroughly mixing the following constituents:

25 parts by weight ground coat enamel No. 2232 sold by Ferro Corp.
5 parts by weight magnesium oxide ground to −200 mesh
0.3 parts by weight gelatine sold by Knox Corp.
1/20 parts by weight Tergitol sold by Rohm and Haas
100 parts by weight water.

A 2 ½ × 1 ½ inches × 30 mil enamel iron substrate then is immersed in the bath between two inactive electrodes and a

30 volt D.C. power supply is connected between the substrate and electrodes to produce a current flow of approximately 2.5 amperes at the substrate. After an approximately 14 mil thick coating is deposited atop the substrate, the substrate is rinsed in water and fired at 830 °C for 3.5 minutes to mature the enamel to a coating approximately 6 mils thick. The substrate then can accept direct deposition of electrical components forming a radio receiver.

EXAMPLE 4

An electrophoretic bath is formed by thoroughly mixing the following constituents:

25 parts by weight ground coat enamel No. **2232** sold by Ferro Corp.
5 parts by weight silicon dioxide ground to −200 mesh
0.3 parts by weight ammonium alginate and
100 parts by weight water

whereupon an enamel iron substrate is immersed as an anode in the bath intermediate two inactive cathodes. A potential of 30 volts D.C. then is applied between the substrate and cathodes to initiate plating of the enamel, silicon dioxide and ammonium alginate atop the substrate and plating is continued until a 12 mil coating is formed thereon. After removal of the coated substrate from the bath, the substrate is rinsed in water and fired at 830°C for 3.5 minutes to form a pinhole-free enamel coating approximately 6 mils thick atop the substrate.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A method of electrophoretically depositing an electrically insulating vitreous coating atop a metallic substrate comprising immersing said substrate in an electrolytic bath containing between 20 and 60 percent by weight vitreous particles suspended in a water vehicle, said bath further containing an ionic colloidal material selected from the group consisting of ammonium alginate and gelatine in quantities less than 0.3 percent by weight of the water vehicle to seal the substrate from the water vehicle during plating of said vitreous particles thereon, applying an electrical potential to said immersed substrate to electrophoretically plate said vitreous particles atop said substrate and subsequently firing said coated substrate at a temperature in excess of 600°C to mature said deposited vitreous particles to a pinhole-free coating.

2. A method of electrophoretically depositing an electrically insulating vitreous coating according to claim **1** wherein said ionic colloidal material is ammonium alginate, said vitreous particles are enamel particles and said bath further contains inert refractory particles in quantities between 10 and 40 percent by weight of the enamel, said inert refractory particles being substantially non-reactive with said enamel particles at the enamel firing temperature and having a melting temperature above the firing temperature of said enamel to increase the viscosity of the enamel during firing.

3. A method of electrophoretically depositing an electrically insulating vitreous coating according to claim **2** wherein said bath further includes a low ash content organic film forming binder selected from the group consisting of an acrylic and a cellulose in quantities below 0.3 percent by weight of said water vehicle.

4. A method of electrophoretically depositing an electrically insulating vitreous coating according to claim **2** wherein said bath further includes an ionic wetting agent to enhance the charge of said ionic colloidal material within said bath.

5. A method of electrophoretically depositing an electrically insulating vitreous coating according to claim **4** wherein said bath further includes an acrylic film forming binder in quantities less than 0.3 percent by weight of said water vehicle.

6. A method of electrophoretically depositing an electrically insulating vitreous coating according to claim **1** wherein said vitreous particles are plated atop said substrate to a thickness less than 20 mils and said subsequent firing matures the particles to a pinhole-free coating less then 10 mils. thick.

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