

PATENT SPECIFICATION

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(54) A METHOD FOR ELECTRO COATING METAL SURFACES WITH CARBON

(71) We, HITACHI LTD., a Japanese Body Corporate of 5-1, 1-chome, Marunouchi, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to an improved method for electrocoating carbon on the surface of a metal substrate or a metallized substrate. In a preferred embodiment it relates to parts of an electron tube having a black carbon coating on their surfaces and a method for the production thereof. The resulting carbon coated parts of electron tubes such as anodes, grids or shadow masks, cause little generation of gases, have excellent heat radiation efficiency, have extremely small secondary electron emission ratios and do not lose their adhesiveness even at a high temperature (such as 1,000°C).

It is known to coat a metal surface with carbon by applying a suspension of carbon using water glass as a binder by brushing or spraying. However, the adhesiveness between the metal surface and carbon depends greatly upon the characteristic of the water glass. For example, when the concentration of water glass is high, the adhesiveness is good, but since the surface of the carbon particles is protected by the water glass, the surface of the carbon layer cannot sufficiently exhibit the effect which it originally possesses. On the other hand, when the concentration of water glass is low, the adhesiveness between the metal surface and the carbon layer is poor and the carbon layer is apt to separate from the metal surface.

The present invention makes it possible to form a strong coating of carbon on a surface of a metal substrate without

damaging the optical, thermal and electrical characteristics which a carbon surface originally possesses. The process may be used to form a carbon coating layer in a uniform thickness on moulded metal materials having complicated shapes, such as parts of electron tubes.

The process of the present invention involves the formation of a carbon film on a metal substrate by the cataphoretic electrodeposition method (hereinafter referred to as the electrodeposition method). Organic resins contained in said carbon film are decomposed and removed by a subsequent heat treatment.

More specifically, the present invention provides a method for coating carbon on a surface of a metal or a metallized body, which method comprises electrodepositing a film on said surface from an electrodepositing liquid which is an aqueous dispersion comprising 0.4 to 12% by weight, based on the weight of the liquid, of carbon particles and 1 to 18% by weight, based on the weight of the liquid, of at least one water soluble electrodepositable organic resin. In order to remove gas-releasing components, the electrodeposited film is then subjected to a heat-treatment at 300° to 1000°C in order to decompose the resin.

The invention is illustrated in more detail by the accompanying drawings in which:

Figure 1 is a flow-sheet illustrating one embodiment of the process of the invention;

Figure 2 is a graph comparing secondary electron emission ratio to primary electron voltage of an iron plate coated with carbon by the process of the invention and that of an iron plate having no carbon coating;

Figure 3 is a cross sectional view of a part of an electrode for an electron tube coated by the process of the invention; and

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Figure 4 is a flow-sheet illustrating the production of parts of an electron tube in accordance with the present invention.

The metal substrate to which the method of the present invention is applicable can be, for example, a metal plate such as an iron, nickel, stainless steel, titanium copper or aluminium plate, a chromium plated, zinc plated or nickel plated metal substrate or a metallized non-metallic material. The choice of substrate depends on the intended use thereof; for example, when thermal resistance is required, the oxidation and reduction reactivity and cementation of the surface of the metal substrates should be taken into account.

The electrodepositing liquid used in the process of the invention is obtained by adding at least one water soluble electrodepositable resin as a vehicle to carbon or graphite and dispersing it in an aqueous medium. The water soluble electrodepositable resins may be any such resin conventionally used in the paint industry such as an alkyd resin, an acrylic resin, a phenol resin or a melamine resin. These resins may be used singly or in mixtures. The electrodepositing liquid comprises 0.4—12% by weight of carbon and 1—18% by weight of vehicle; when the compositions are outside these ranges, it is difficult to achieve satisfactory thickness, uniformity, adhesion strength and electrodepositing time.

Suitable electrodeposit conditions are as follows: a deposition voltage of 30—250 V (DC) and deposition time of 1/10 second to 5 minutes, preferably less than 2 minutes.

The thickness of the electrodeposited film depends on factors such as the composition of the electrodepositing liquid, the electrodeposit voltage and the electrodeposit time; the preferred thickness is in the range of 3μ — 70μ .

In the process of the invention, the coated substrate is subjected to a heat treatment in order to decompose the resin. The furnace used for the heat treatment may contain an oxidizing or an inert atmosphere, but for a high temperature treatment, an inert atmosphere is preferred. The duration of the heat treatment depends on the temperature; for example the heat treating time may be one hour when the heat treating temperature is about 350°C while about 5 minutes is sufficient when the temperature is 800°C . Under these conditions, the organic resins are substantially completely decomposed. In order to achieve this, a temperature of at least 300°C is required even for resins having low heat decomposition temperatures such as acrylic resins. The maximum temperature is governed by the fact that finely powdered carbon or

graphite which has good dispersibility is oxidised and decomposed at a temperature of higher than $1,000^{\circ}\text{C}$. A conveyor furnace can also be used, but when the travelling speed of the conveyor is high, the rate of temperature elevation is too high, the organic resin in the film is rapidly heat decomposed and the carbon layer is apt to separate from the metal plate. The heating rate must therefore be carefully controlled. Similar considerations must also be given to the cooling rate. When the cooling rate is too high and the density of the carbon layer is high, the difference between the thermal expansion coefficient of the metal substrate and that of the carbon layer is considerable and this causes separation of the carbon layer. It has been found that for the best results the heating and cooling rates are preferably lower than $70^{\circ}\text{C}/\text{min}$.

Figure 2 shows one of the effects obtained by the method of the present invention. The graph provides a comparison of the secondary electron emission ratio to primary electron voltage of an iron plate deposited with carbon in accordance with the present invention and an iron plate having no carbon coating. As is clear from Figure 2, the carbon deposited plate A of the present invention exhibits secondary electron emission ratio to each primary electron voltage which is about 50% lower than that of the plate B having no carbon layer.

Figure 3 is a cross sectional view of a color selection electrode which is one embodiment of an electrode part obtained by the method of the present invention. In this Figure 3, 1 is an opening through which a number of electron beam passing holes 2 are excavated, 3 is a skirt part, and 4 is a carbon layer deposited on the whole surface of said opening 1 and skirt part 3.

Figure 4 is a flowsheet for the production of parts of an electron tube in accordance with the present invention. According to one embodiment for the production of electron tube parts as shown in Figure 4, the surface of a material having a shape suitable for the manufacture of an electron tube part and made of an electrodepositable material such as iron plate or stainless steel, is degreased with trichloroethylene for rustproofing and cleaned with a surface active agent. Then, the portions to be welded are masked so as not to be electrodeposited and the surface is subjected to surface conditioning by pretreatment. The treated material is then dipped in an electrodepositing liquid obtained by mixing 0.5—4% by weight of carbon powders, 1—15% by weight of a water soluble organic resin binder and water and electrodeposit is carried out by applying a DC voltage of 60—200 V for 3

minutes to form an electrodeposited film comprising a mixture of carbon powders and the binder on the surface of the material. This film is then baked at 130—180°C for 30 minutes to heat-cure the film to render it hard.

The resulting material having the electrodeposited film on its surface is then molded into the shape of an electron tube part by cutting and pressing. The drawability and pressability are generally excellent and the film does not generally separate from the substrate.

Furthermore, after removal of cutting oil and metal dusts which adhere to the electrodeposited film in molding, the film can be subjected to the heat treatment to cause heat decomposition of the binder, thereby eliminating it.

The present invention therefore makes it possible to obtain electron tube parts having a carbon layer on their surface which has a uniform thickness and a strong adhesion power even when the thickness is greater than that of a conventional electrodeposited film.

The invention is illustrated by the following Examples.

Example 1

Using an electrodepositing liquid comprising 3% by weight of carbon powder (average particle size 35 μ), 18% by weight of alkyd resin and 79% by weight of water, electrodeposition was carried out on a degreased and pretreated iron plate (surface area about 80 cm^2) for 40 seconds under a voltage of DC 100 V and then the film was subjected to washing with water, washing with solvent, air blow and hot air drying. Then, the electrodeposited film was heat treated in an electric furnace at 400°C for 30 minutes to obtain an extremely strong jet-black carbon film of 20 μ in thickness. When said iron plate was in the form of a shadow mask, the same carbon film as obtained above was also formed thereon.

Example 2

Using an electrodepositing liquid comprising 12% by weight of carbon powder (average particle size 0.2 μ), 2% by weight of acrylic resin and 86% by weight of water, electrodeposition was carried out on a degreased titanium plate (surface area about 80 cm^2) for 5 minutes under a voltage of DC 30 V and then the electrodeposited film was subjected to washing with water, washing with solvent, air blow and hot air drying. The electrodeposited film was heat treated in a reducing furnace at 700°C for 10 minutes to obtain a carbon film having an irregular surface of 5 μ in thickness. When said titanium plate was in the form of

an anode, the same carbon film as obtained above was also formed thereon.

Example 3

Using an electrodepositing liquid comprising 4% by weight of graphite paste (Aquadag [Registered Trade Mark]), 9% by weight of phenol resin and 87% by weight of water, electrodeposition was carried out on a nickel plated and degreased copper plate (surface area 400 cm^2) for 10 seconds under a voltage of DC 200 V and the electrodeposited film was subjected to washing with water, washing with solvent and air blow. The resulting electrodeposited film was then heat treated in a furnace of oxidizing atmosphere at 450°C for 30 minutes to obtain a carbon film having a smooth surface of 12 μ in thickness. When said nickel plated copper plate was in the form of an anode, the same carbon film as obtained above was also formed thereon.

Example 4

Using the same electrodepositing liquid as used in Example 3, electrodeposition was carried out on the cleaned and pretreated surface of an iron plate photoetching part (surface area about 750 cm^2) for 30 seconds under a voltage of 100 V. The resulting electrodeposited film was then washed with water and subjected to air blowing and then was heat treated in an N_2 gas atmosphere in which N_2 gas was passed at a rate of 300 l/min at 550°C for 30 minutes to obtain a strong carbon film of 14 μ in thickness. When said iron plate was in the form of a shadow mask, the same carbon film as obtained above was also obtained thereon.

Example 5

Using an electrodepositing liquid comprising 10% by weight of maleinized oil resin, 2% by weight of carbon and 88% by weight of water, electrodeposition was carried out on an iron plate (surface area 1200 cm^2) subjected to degreasing, cleaning, masking and pretreatment at DC of 50 V for 30 seconds. The electrodeposited film was subjected to baking at 170°C for 20 minutes and the plate was molded into an electrode. The surface of this electrode stained by the molding was degreased and then was heat treated at 450°C for 10 minutes to obtain the electrode coated with a carbon film of 5 μ in thickness having the similar properties to those mentioned above.

WHAT WE CLAIM IS:—

1. A method for coating carbon on a surface of a metal or a metallized body, which method comprises electrodepositing a film on said



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minutes to form an electrodeposited film comprising a mixture of carbon powders and the binder on the surface of the material. This film is then baked at 130—180°C for 30 minutes to heat-cure the film to render it hard.

The resulting material having the electrodeposited film on its surface is then molded into the shape of an electron tube part by cutting and pressing. The drawability and pressability are generally excellent and the film does not generally separate from the substrate.

Furthermore, after removal of cutting oil and metal dusts which adhere to the electrodeposited film in molding, the film can be subjected to the heat treatment to cause heat decomposition of the binder, thereby eliminating it.

The present invention therefore makes it possible to obtain electron tube parts having a carbon layer on their surface which has a uniform thickness and a strong adhesion power even when the thickness is greater than that of a conventional electrodeposited film.

The invention is illustrated by the following Examples.

Example 1

Using an electrodepositing liquid comprising 3% by weight of carbon powder (average particle size 35 μ), 18% by weight of alkyd resin and 79% by weight of water, electrodeposition was carried out on a degreased and pretreated iron plate (surface area about 80 cm^2) for 40 seconds under a voltage of DC 100 V and then the film was subjected to washing with water, washing with solvent, air blow and hot air drying. Then, the electrodeposited film was heat treated in an electric furnace at 400°C for 30 minutes to obtain an extremely strong jet-black carbon film of 20 μ in thickness. When said iron plate was in the form of a shadow mask, the same carbon film as obtained above was also formed thereon.

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Example 5

Using an electrodepositing liquid comprising 10% by weight of maleinized oil resin, 2% by weight of carbon and 88% by weight of water, electrodeposition was carried out on an iron plate (surface area 1200 cm^2) subjected to degreasing, cleaning, masking and pretreatment at DC of 50 V for 30 seconds. The electrodeposited film was subjected to baking at 170°C for 20 minutes and the plate was molded into an electrode. The surface of this electrode stained by the molding was degreased and then was heat treated at 450°C for 10 minutes to obtain the electrode coated with a carbon film of 5 μ in thickness having the similar properties to those mentioned above.

WHAT WE CLAIM IS:—

1. A method for coating carbon on a surface of a metal or a metallized body, which method comprises electrodepositing a film on said

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- 4 surface from an electrodepositing liquid which is an aqueous dispersion comprising 0.4 to 12% by weight, based on the weight of the liquid, of carbon particles and 1 to 18% by weight, based on the weight of the liquid, of at least one water soluble electrodepositable organic resin, and heat-treating the electrodeposited film at a temperature of 300° to 1000°C to decompose the resin.
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- 10 2. A method according to claim 1 wherein said water soluble organic resin is an alkyd resin, acrylic resin, phenol resin or melamine resin.
- 15 3. A method according to claim 1 or 2 wherein the electrodeposition is carried out at a voltage of 30—250 V. (DC), for 1/10 second to 5 minutes.
- 20 4. A method according to any one of the preceding claims wherein the electrodeposited film is 3 to 70 μ thick.

5. A method according to any one of the preceding claims wherein the surface to be coated with carbon is a surface of an electron tube part.

6. A method according to any one of claims 1 to 4 wherein the resulting coated metal or metallized body is moulded into an electron tube part.

7. A method according to claim 1 substantially as hereinbefore described.

8. A coated surface obtained by a method as claimed in any one of the preceding claims.

9. An electron tube part obtained by a method as claimed in claim 5 or 6.

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