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METHOD OF OBTAINING EMISSIVE COATINGS

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This invention relates to devices, particularly electronic tubes, which have filaments or other bodies provided with a coating or coatings of highly emissive substances. More specifically the invention is for an improved method of obtaining such coatings which are fine-grained, dense and uniform.

Heretofore, a method, commonly employed for obtaining such coatings, of barium, for example, is to use a solid barium compound, such as an azide and to bring it to such a temperature that the compound is decomposed and the barium which is driven off is deposited on the cold filament or other body which is to be coated. As distinguished from the foregoing, in the present invention materials are employed which are in the gaseous form and which are decomposed by heating, as for example by coming into contact with a heated filament which may or may not be the body upon which the coating is to be deposited. The temperature of decomposition of the gaseous compound which is used is preferably lower than the temperature of the volatilization of the constituent element of the gas such as barium, which is to provide the coating. By heating the filament above the temperature of decomposition of the compound, but not so high as the vaporization temperature of the substance to be deposited, the filament will decompose the gas, but nevertheless permit the barium or other emissive material to be deposited thereon. As suitable gaseous compounds for the foregoing purposes may be mentioned organometallic compounds of the alkali-earth metals such as many alkyls, and also alkylhalides of the aliphatic or aromatic group, aryls, etc. Also there may be used some of the acetates, naphtholates or amides as well as corresponding compounds and substitution products with various members of the paraffines and olefines which can be obtained by substitution of hydrogen, by substitution of metals, or by addition of the alkali-earth metals to carbon compounds which utilize a double valency bond of the carbon or to free organic radicals.

In order to more clearly explain the invention reference is made to the following description of one form of apparatus suitable for carrying out the invention taken in connection with the accompanying drawing, in which

Fig. 1 is an elevation partly in section and partly in perspective of apparatus for coating the filaments of electronic tubes.

The reference character 11 indicates a closed chamber having a removable portion 11a which is held in place by the spring clips 11b whereby

the interior is rendered readily accessible. This chamber may be provided with a plurality of exhaust tubes 12 leading into a common exhaust pipe 13 having connections as indicated at 14 to an exhaust pump and to vaporization apparatus for supplying a gas or gases of the character described above, the said pump, etc. not being shown in the drawing.

Several devices such as radio tubes 15, 16 and 17, to be treated in accordance with the present invention are shown connected with the exhaust tubes 12. The following description will be confined to the structure of one tube only and related parts, but it is obvious that the described features may be duplicated in as many different exhausting stations as is desirable.

A filament 18 is shown positioned substantially axially of the tube 15 and has supports 19 and 20 at each end thereof which are connected to leading-in wires 21 and 22. The leading-in wires 21 and 22 may be connected to terminals 23 and 24 carried through the walls of the chamber 11 and connected in turn to a battery 25. Surrounding the filament 18 there may be provided a grid 26 which as shown is in the form of a helix of wire and is carried by the supporting member 27 which is connected to a leading-in wire 28 which may be connected to a terminal 29 passing through the wall of the chamber 11. An anode or plate 30 is positioned around the grid 26 and the filament 18 and may be in the form of a cylindrical sleeve either with or without a longitudinal slit running throughout its length. A leading-in wire 31 connects the plate to a terminal 32 passing through the wall of the chamber 11. A battery is shown at 33 which has its positive terminal connected to the terminal 32 and its negative terminal connected to the terminal 23. A high frequency coil 34 is shown surrounding the tube 15 and has its terminals carried through a suitable bushing 35 to the outside of a chamber 11 and is connected with some suitable source of high frequency current not shown.

In operation the exhaust pump is first used to remove the gases within the tube in the usual way and then a suitable gas is admitted, this gas being of the character described above, such, for example, as an alkylhalide of barium. Upon raising the gas to a suitable temperature it is decomposed and the barium is deposited. The different provisions made for raising the temperature of the gas have somewhat different effects and will therefore be described separately. The filament 18 upon which it is desired to secure a deposit or coating of barium or other suitable

emissive substance may itself be heated by current from the battery 25. In this case it is desirable to bring the temperature of the filament to a temperature sufficiently high to effect decomposition of the gas and to free the barium, but not to a temperature above the vaporization temperature of barium. As the gas comes in contact with the heated filament it is decomposed and the barium deposited immediately thereon in a smooth, dense and uniform coating. Or, the temperature of the chamber 11 as a whole may be brought to a high temperature by any suitable means not shown and thereby the glass of the tube 15 is heated and in turn heats the gas within. In this case the barium is deposited more or less on all parts, but as it is only the filament which is operated at an incandescent temperature it is only on the filament that the coatings are effective in increasing the emissivity. Another method of producing the necessary heating is by means of the high frequency coil 34 which produces by inductive action current within the tube 15. By a suitable selection of the gaseous pressure within the tube 15 the induced current may be in the form of an electrodeless gaseous discharge. Or by a suitable arrangement of the filament the current may be induced therein. The arrangement shown in the drawing produces a certain amount of current in the plate or anode 30. If the plate is provided with the longitudinal slit as described hereinbefore, there will also be currents induced in the grid 26. When the heating is done by the grid or plate or any other body adjacent to the filament it is desirable that the temperature of such heated body be brought to a higher value than the vaporization temperature of the barium so that there will be little or no tendency for barium to condense thereon, but the barium will be chiefly deposited on the filament. If the plate is not provided with a longitudinal slit the tendency to act as a magnetic shield for the parts within the cylinder is so great that practically no currents are set up in such parts. The heating of certain parts adjacent to the filament may also be carried out by means of currents introduced into the tube conductively instead of inductively. The grid, or supporting member thereof, may be so connected that heating currents raise its temperature to the proper point to decompose the gas within the tube. While several different means have been shown and described for heating and bringing the temperature of the gas to a decomposition point it is to be distinctly understood that all the different means are not necessarily employed simultaneously but that one means only may be sufficient and preferable for a given set of conditions. The use of the battery 33 which is so connected that the filament is negative or acts as a cathode assists in drawing the positive ions to the filament and increases the rate of deposition on the filament.

In the foregoing description barium has been used as typical of emissive substances, but it is to be understood that other metals of the alkali-earth group such as strontium, may also be used as well as alkalis such as potassium, rubidium, or caesium, or mixtures thereof. For the purposes of this specification the general term "alkaline metal" includes all of the aforementioned metals, i. e., metals of both the alkali and alkali-earth groups. Deposition of two or more of such emissive substances may take place simultaneously, and also compounds of copper, nickel, etc. may be used to obtain a simultaneous coating of such

materials as form anhydrides of amphoteric compounds. Instead of depositing the amphoteric substance together with the emissive substance the surface of the filament may be prepared with a layer of such material as aluminum oxide or zirconium oxide or similar material. The combination of an emissive substance with an anhydride of an amphoteric compound provides a layer or coating which is very resistive to the disintegrating effect of a gaseous discharge. The surface of the filament may also be prepared for the reception of the coating by rendering it porous which can be accomplished by corrosion or etching, or oxidation and subsequent reduction, or by amalgamation and subsequent vaporization of the mercury. By thus preparing the surface the deposited material is enabled to penetrate deeper and in greater quantities and may form alloys.

One of the advantages of the foregoing method is that it is particularly adapted for use in connection with tubes in which the electrodes have been mounted and the tube has been evacuated and degassed. However, it is not so restricted in its application as the method is also adapted to be used in coating bodies which have not been mounted in position to be used as electrodes.

We claim:

1. The method of making an emissive cathode which consists in first rendering the surface of the metallic core porous and then heating the core in an atmosphere containing a gaseous compound of an alkaline metal to a temperature above the decomposition temperature of said compound and below the vaporization temperature of said metal from the core surface.

2. The method of making an emissive cathode which consists in first rendering the surface of the metallic core porous and in finely divided state, heating it in a vacuum, and then heating it in a gaseous atmosphere of an organic metallic compound of an alkaline earth metal to a temperature sufficient to decompose the organic metallic compound.

3. The method of making an emissive cathode which consists in first rendering the surface of the metallic core porous and in finely divided state, heating it in a vacuum, and then heating it in a gaseous atmosphere of an organic metallic compound of barium to a temperature sufficient to decompose the organic metallic compound and deposit barium on the core.

4. The method of making an emissive cathode which comprises the steps of first removing occluded gases from a metallic core and then heating the core in an atmosphere containing a gaseous compound of an alkaline metal to a temperature intermediate the decomposition temperature of said compound and the vaporization temperature, from the core surface, of the metallic constituent of said compound.

5. The method according to claim 4 with the additional step of maintaining the core cathodic to another electrode while the core is heated in the said atmosphere.

6. The method of making an emissive cathode which comprises the steps of coating a core with a metallic compound, removing the occluded gases from the coated core, and heating the core in an atmosphere containing a gaseous compound of an alkaline metal to a temperature above the decomposition temperature of said compound and below the vaporization temperature of said alkaline metal, the compound initially applied to the core being non-emissive relative to the alkaline

metal and capable of combining chemically with said metal to form a double-metal compound on the core.

7. The method of rendering a cathode emissive in a discharge tube containing a cathode core and another electrode intended to be non-emissive, which comprises the steps of de-gassing the core and said electrode, providing an atmosphere in said tube containing a gaseous compound of an alkaline metal, heating the latter electrode to a temperature above the vaporization temperature of the metallic element of said compound and simultaneously heating the core to a temperature intermediate the decomposition temperature of said compound and said vaporization temperature.

8. A method of coating a cathode for an electron discharge device which comprises introducing gaseous organic compounds of alkaline earth metals, decomposing these organic compounds, the alkaline earth metal yielded being deposited at the cathode forming a high emissive coating.

9. A method of coating a cathode for an electron discharge device which comprises introducing gaseous alkaline earth metal alkyl, decomposing this alkaline earth metal alkyl, the alkaline

earth metal yielded being deposited at the cathode forming a high emissive coating.

10. A method of coating a cathode for an electron discharge device which comprises introducing gaseous barium alkyl, decomposing this barium alkyl, the barium yielded being deposited at the cathode forming a high emissive coating.

11. The method of alloying an alkaline metal with a core metal which comprises making the surface of a metallic core porous, disposing said core in an atmosphere containing a gaseous compound of an alkaline metal, and decomposing said compound, the alkaline metal yielded being deposited in the pores of said core and alloyed therewith.

12. The method of alloying an alkaline metal with a core metal which comprises disposing and heating a metallic core in an atmosphere containing a gaseous compound of an alkaline metal and decomposing said compound at such temperature for the core that the alkaline metal yielded alloys therewith.

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