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UNITED STATES PATENT OFFICE

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METHOD OF COATING THERMIONIC CATHODES

No Drawing. Application filed August 22, 1928. Serial No. 301,443.

My invention relates to thermionic discharge devices and more particularly to an improved method of coating the filaments of such devices with an alkaline-earth oxide.

An object of my invention is to provide a simple and efficient method of producing oxide-coated electron-emitting filaments for utilization in space discharge devices, such as vacuum tubes.

Another object of my invention is to provide an improved method for the production of filaments or ribbons comprising a foundation metal having a firmly adherent, stable coating of a compound which is adapted to be converted to an oxide, or mixture of oxides, with high electron-emission characteristics.

A further object of my invention is to provide a method for the production of oxide-coated filaments which comprises coating the foundation metal of the filament with an aqueous solution of an alkaline earth salt that may be decomposed at a comparatively low temperature without producing an oxidizing effect, heating the coated filaments in an atmosphere of carbon dioxide to form an alkaline earth carbonate, and then converting the carbonate to the oxide during the final evacuation of the tube.

It is well known that when filamentary material is coated with an alkaline earth oxide, the electron emissivity of such material is greatly increased. Various methods have been employed for applying the oxide coating, such as by coating the filament with a mixture of barium and strontium carbonates and an organic binder or by applying successive layers of an alkaline earth carbonate and an organic binder and later converting the carbonates to the oxides.

A very desirable method of producing oxide-coated filaments and one which has produced satisfactory results is described in my copending application, Serial No. 590,777, filed on September 27, 1922 Patent 1,695,899. This method consists in applying successive coatings of an aqueous solution of barium and strontium nitrates to the filament. Each successive coating is heated to ignition temperature in an atmosphere of carbon dioxide which converts the nitrates into the carbonates. The carbonate-coated filament is then placed in the electron tube and the carbonates decomposed, leaving a firmly adherent coating of an electron-emitting oxide, or a mixture of oxides, on the filament.

The above specified method has been found satisfactory when the foundation metal of the filament is composed of a material that is difficult to oxidize, such as platinum or an alloy of platinum, but when attempts were made to utilize this method to apply an oxide coating to a filament having an easily oxidizable foundation metal, such as nickel, tungsten, copper or alloys of these metals, it was found that the oxidizing atmosphere produced by the decomposition of the nitrates has the tendency to oxidize the foundation metal. The resulting filament, therefore, consisted of a partially oxidized foundation metal having an oxide coating which did not give satisfactory emission.

I have made the discovery that if one or more of the trinitrides of the alkaline earth metals are utilized in place of the nitrates that the foundation metal will not be oxidized and an oxide-coated filament will be produced that will give satisfactory emission even when an easily oxidizable foundation metal is employed.

In practicing my invention, the filament or conductor to be coated is first thoroughly cleansed in the usual manner, such as by heating to incandescence in a neutral or non-oxidizing atmosphere, such as in hydrogen or nitrogen, to remove accumulated dirt and dust and is then dipped in, or passed through, a solution of one or more of the alkaline earth trinitrides. The nitride-coated filament is passed through a furnace filled with carbon dioxide or the filament may be heated by electric energy in a carbon dioxide atmosphere, as described in my copending application to which reference has previously been made. I prefer, however, to pass the wire or ribbon through the aqueous solution and to dry the applied coating in an electric tube furnace which is energized by a suitable source of electricity and in which an atmosphere of carbon dioxide is maintained. I have found

that a temperature of about 200° C. is sufficient to convert the nitrides into the carbonates. This operation may be repeated as many times as necessary to obtain a coating having the requisite thickness.

The final step in the process occurs when the coated filament is embodied in a thermionic device. In manufacturing thermionic tubes, it is the usual practice during the evacuation of the tube to heat the several elements to a high temperature to drive out the occluded gas. It is during this heat treatment that the carbonates are converted into the oxides.

Although an aqueous solution of any one or a mixture of two or more of the alkaline earth trinitrides may be employed, I prefer to utilize a concentrated solution containing a mixture of about 60% of barium trinitride and 40% of strontium trinitride per liter of water. The number of coats employed will, of course, vary according to particular requirements. I have found that when from 40 to 80 coats were applied to a one mil tungsten wire, good electron emission was obtained.

While I have described a preferred embodiment of my invention, it will be understood that various modifications will be apparent to those skilled in the art without departing from the spirit thereof. I desire, therefore, that only such limitations shall be imposed on my invention as are required by the prior art and the appended claims.

I claim as my invention:

1. The process of treating a conductive element which comprises coating said element with an aqueous solution of trinitride of an alkaline earth metal and subsequently heating said element to the decomposition temperature of the trinitride in an atmosphere of carbon dioxide.

2. The process of treating a conductive element which comprises coating said element with an aqueous solution of the trinitrides of metals of the alkaline earth group and subsequently heating said element to the decomposition temperature of the trinitride in an atmosphere of carbon dioxide.

3. The process of treating a conductive element which comprises coating said element with an aqueous solution of barium and strontium trinitrides and subsequently heating said element in an atmosphere of carbon dioxide to a sufficient temperature to convert the trinitrides to carbonates.

4. The process of manufacturing a coated filament which comprises depositing thereon successive coatings of an aqueous solution of a trinitride of a metal of the alkaline earth group, subjecting each coating to the decomposition temperature of the trinitride in an atmosphere of carbon dioxide and finally heating the coated filament to convert the carbonates to the oxides.

5. The process of manufacturing an electron-emitting element which comprises depositing successive coatings of an aqueous solution of barium and strontium trinitrides upon a foundation metal, heating the coated foundation metal in an atmosphere of carbon dioxide subsequent to each coating to convert the trinitrides to the carbonates, and finally heating the coated foundation metal to convert the carbonates to oxides.

6. The process of manufacturing an electron-emitting element which comprises depositing successive coatings of an aqueous solution of one or more of the trinitrides of the metals of the alkaline earth group upon a foundation metal, heating the coated foundation metal in an atmosphere of carbon dioxide to a sufficient temperature to convert the trinitrides into the carbonates, and subsequently mounting said coated foundation metal in an electron tube and converting said carbonates to oxides during the treating process of the tube.

7. In the process of preparing an oxide coated filament, the steps which comprise successively coating a foundation metal with an aqueous solution of one or more of the alkaline earth metal trinitrides and heating the coated foundation metal in an atmosphere of carbon dioxide subsequent to each coating to convert the trinitrides to the carbonates.

8. In the process of coating an easily oxidizable foundation metal with an oxide coating, the steps which comprise depositing successive coatings of an aqueous solution of barium and strontium trinitrides, on a foundation metal, heating the coated foundation metal subsequent to each coating in an atmosphere of carbon dioxide to convert the trinitrides to the carbonates, and converting the carbonates to the oxides during the evacuation of the tube.

In testimony whereof, I have hereunto subscribed my name this 14th day of August, 1928.

LEON McCULLOCH.