Patented Nov. 10, 1931 1,830,825

UNITED STATES PATENT OFFICE

HUGH S. COOPER AND MAURICE D. SARBEY, OF CLEVELAND, OHIO, ASSIGNORS TO KEMET LABORATORIES COMPANY, INC., A CORPORATION OF NEW YORK

CATHODE

No Drawing. Application filed November 20, 1928. Serial No. 320,743.

Our invention relates to electron-emitting cathodes and to processes for the manufacture thereof. It has for one of its objects a new process for producing electron-emitting cathodes which is applicable to a wider range of materials than previous processes and produces highly satisfactory cathodes by a more simple, inexpensive and convenient method than has previously been used. It has for a further object the production of a cathode of high emitting power from metals previously unadapted to high emission.

Cathodes for vacuum tubes are commonly constructed by applying a coating of the oxides of the alkaline earth metals to cathode structures made of such metals as platinum or nickel, usually in filament form, for increasing the electron-emitting power to a useful value. The coatings of alkaline earth metal oxides have customarily been applied by repeatedly coating the structure with thin layers of solutions, or suspensions, of appropriate materials in a carrying medium and then driving off the medium.

Our invention provides a new process for the application of the alkaline earth metal oxides to appropriate cathode structures, which may be filaments of metals such as platinum or nickel or may be structures of more refractory metals, by a simple immersion of the structure in an appropriate solution and a heating therein.

Other objects and details of our invention will be apparent from the following description.

In practicing our invention as a means for applying to a metal cathode a suitable coating of the mixed oxides of barium, strontium and calcium we may take an appropriate mixture of the desired oxides and agitate them with cold water, thereby obtaining a solution of the mixed hydroxides containing further portions in suspension. It may be noted that while the solubilities of the hydroxides of all three metals are relatively low, they are sufficient for our purpose. We then bubble carbon dioxide gas through the solution to convert the mixed hydroxides to the bicarbonates, which also show a small, but sufficient, solubility in water. We find it convenient to provide a small excess of the material which is kept suspended in the solution by the agitation of the gas bubbles, in order to maintain a saturated condition in the solution. Continuing the bubbling of gas, we then immerse within the solution the desired cathode structure, which may conveniently be a filament, and may be formed of the desired metal such as platinum, nickel, molybdenum, tantalum or tungsten or other suitable metal. We then pass an electric current through the cathode structure sufficient to raise it to a high temperature while immersed. The precipitation of the mixed oxides upon the cathode structure is in part, at least, produced by the heating of the solution of bicarbonates and the breaking down thereby of the bicarbonates into the normal carbonates, which are less soluble than the bicarbonates and are accordingly thrown out of the solution. In order to maintain as high a concentration of the bicarbonates as possible in the solution, we find it desirable to utilize cooling means for keeping the bulk of the solution at a low temperature.

The high temperature throws substantial portions of the dissolved bicarbonates of the alkali earth metals out of the solution upon the cathode structure. These materials apparently precipitate in part, at least, in the form of normal carbonates and are at once baked upon the wire in a homogeneously adherent form. The thickness of the coating formed depends upon the length of time that the heating is continued within the solution and upon the temperature to which the wire is heated. When a sufficiently heavy coating is obtained, the heating may be discontinued and the filament removed from the solution. As so prepared, the coating is extremely resistant to atmospheric effects which might tend to injure its electron-emitting properties, and the filament may be kept in this form without particular precautions for storage until it is needed for use.

The prepared filament may then be assembled with other electrode members in the usual way for the production of an electronic device, and mounted within a tube suitable for evacuation. During the evacuation, the

cathode is heated in the usual way to a sufficiently high temperature to break down the carbonates or hydroxides into oxides, and drive off the carbon dioxide and moisture.

A particularly advantageous feature of the process above described lies in the fact that the bicarbonates are precipitated by an elevation in temperature of the solution, being partially decomposed into the normal carbonates which are of lower solubility than the bicarbonates. This fact results in a particularly advantageous precipitation of the normal carbonates from the solution in the neighborhood of the heated wire, with an evolution of carbon dioxide. The precipitated materials collect upon the heated filaments.

The material thus thrown down is baked upon the wire in a homogeneously adherent form, which appears to be composed largely of the normal carbonates depending upon the temperature of the filament upon which they are precipitated. If the temperature is sufficiently high, they may, of course, be partially dissociated into the oxides, or because of the presence of water vapor, into hydroxides. However, the major portion of the deposit appears to remain in the form of the normal carbonates.

When so conducted the process of our invention produces a cathodic member composed of the desired metal, coated with oxides of one or more of the alkaline earth metals in such form as to have an excellent electron emission.

In general, our method of heating the cathode body while immersed in a bulk solution of the materials to be used as a coating, works particularly well with all those materials which are more soluble cold than hot, and which are therefore thrown out of solution by the local heating of the cathode and deposited upon the cathode.

Another good example of this class of materials is calcium hydroxide. We find that a solution of this material with an excess in suspension is excellently adapted to the practice of our process. In this case it is of course unnecessary to use carbon dioxide but it is desirable to keep the solution cool by suitable means so that the amount of hydroxide in solution may be a maximum, and so that the suspended material may pass into solution as the dissolved material is precipitated on the cathode body. The coated cathode is subsequently heated in vacuo as previously described to break down the hydroxide into oxide, and drive off moisture.

The process of our invention is thus particularly desirable for application of an electron-emitting coating to cathode structures of such materials as platinum or nickel since it produces highly satisfactory coating by a process which is simpler, more certain and less expensive than any previous process. The process is furthermore not limited to the common metals previously used, as has been found to be the case with the previous coatings, but is adapted to the production of excellent electron-emitting coatings upon other metals such as tungsten, molybdenum, etc. which have not previously been coated with satisfactory electron emissive coatings.

While we have disclosed several embodiments of the process of our invention as well as the product obtained thereby, it is capable of still other modifications therefrom without departure from the spirit thereof, and it is desired therefore that only such limitations shall be imposed upon the appended claims as are stated therein or required by the prior art.

We claim as our invention:

1. The process of producing an electron-emitting cathode which comprises preparing a solution of the bicarbonate of the alkaline earth metals, immersing a cathode structure therein and heating while therein to decompose the bicarbonate and precipitate on said cathode from the decomposed solution less soluble compounds of the alkaline earth metals.

2. The process of producing an electron-emitting cathode structure which comprises preparing a suspension of the mixed bicarbonates of the alkaline earth metals in a water solution thereof, bubbling carbon dioxide therethrough, cooling said solution, immersing therein a cathode structure and heating the cathode structure while therein.

3. The process of producing an electron-emitting cathode structure which comprises preparing a suspension of the mixed bicarbonates of the alkaline earth metals in a water solution thereof, bubbling carbon dioxide therethrough, cooling said solution, immersing therein a cathode structure, heating the cathode structure while therein and precipitating upon the cathode structure decomposition products of the dissolved and suspended materials.

4. The process of making an electron-emitting cathode which comprises immersing a metallic conductor in an aqueous solution containing the bicarbonate of an alkaline-earth metal, and passing electric current through the conductor to heat the same and deposit an alkaline earth metal compound on the conductor.

5. The process of making an electron-emitting cathode which comprises immersing a metallic conductor in an aqueous solution of an alkaline-earth metal bicarbonate, and passing electric current through the conductor to heat the same and deposit solid alkaline-earth metal compound on the conductor.

In testimony whereof, we affix our signatures.

HUGH S. COOPER.
MAURICE D. SARBEY.