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D. V. EDWARDS ET AL

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EMISSIVE CATHODE

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Fig. 1.

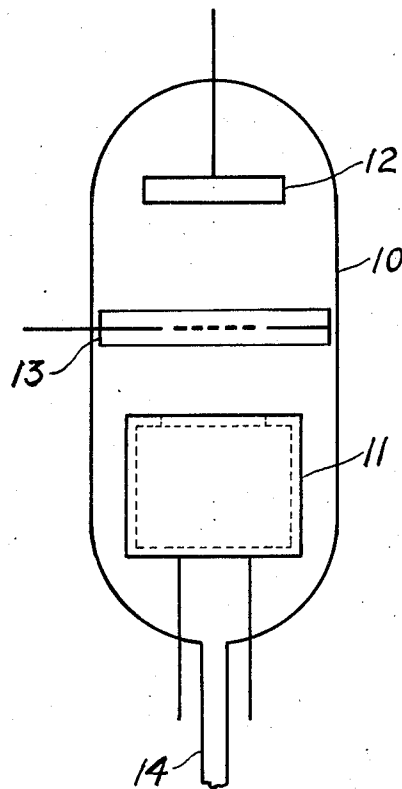
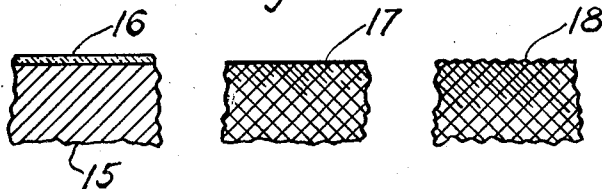


Fig. 2.



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EMISSIVE CATHODE

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20 Claims. (Cl. 250—27.5)

This invention relates to electron emissive cathodes and method of preparing the same, the present application being a continuation in part of our Patent No. 1,985,855, issued December 25, 1934. The present invention relates particularly to an improved method for forming a soluble emissive compound and dissolving the same in a cathode core, and to an improved cathode of this "dissolved" type.

The object of the invention is to produce readily a strong, stable emitting surface which will not distill barium vapor, especially under the severe conditions encountered in grid-controlled gaseous discharge tubes.

According to the process described in the patent above mentioned several of the steps are performed before the cathode is assembled in a tube and preferably in a draught of air or in the presence of oxygen. The said process contemplated oxidizing the cathode core, thus taking part of the core for forming a compound soluble therein, in the event such compound is formed on the core.

According to the present invention the surface to be made emissive is coated with a mixture comprising a compound of a highly electropositive metal and a compound of a base or core metal, said compounds being suitable, upon heating, for forming the desired soluble emissive compound, which latter compound is formed in the tube and dissolved in the core while the tube is on the pump. Preferably an excess of the base metal compound is used, which excess is subsequently reduced to metal. The resulting cathode, when cool, comprises the core metal with the emissive compound dissolved therein and preferably with an excess of emissive compound distributed throughout, the latter containing crystals of reduced base metal.

One embodiment of the invention has been selected for the following description which should be read in connection with the accompanying drawing, in which

Fig. 1 represents, diagrammatically, a discharge tube containing a cathode according to the invention; and

Fig. 2 represents, in section, enlarged portions of the surface of said cathode in several stages of its treatment.

In Fig. 1 the usual envelope is indicated at 10 and contains a cathode 11, the emissive surface of which ordinarily is its inner surface or other surfaces disposed within the cathode such as are provided by vanes or filaments. The usual methods for heating such surfaces may be employed.

The envelope also contains one or more cooperating electrodes such as anode 12 and control grid 13. A tubular extension 14 is provided for exhausting the tube or for admitting gas, as desired.

To make the desired surface of cathode 11 emissive it is first coated with a mixture comprising a highly electropositive metal compound, preferably one or more alkaline earth carbonates, and a base metal compound, preferably an oxide of the metal which forms the cathode surface. The proportions we use are such as to supply at least one atom of base metal for every atom of alkaline earth metal, or the base metal oxide may be in excess. In Fig. 2 a portion of the cathode surface or core metal is shown at 15 and the said mixture thereon at 16. The coating mixture may be prepared in the form of a water paste or suspension and applied to the surface to be made emissive, or carriers other than water may be used, such as collodion or paraffin. A specific coating comprises, for instance, a mixture of equal parts by weight of barium carbonate BaCO_3 and nickel sesquioxide Ni_2O_3 mixed with sufficient water to form a paste which is painted on the desired cathode surface, preferably of nickel. This mixture gives an excess of nickel in the form of nickel monoxide NiO , over barium in the form of barium oxide BaO . Even a large excess of NiO is permissible. If desired, the monoxide may be used at the start instead of the sesquioxide.

The coated cathode is then dried and mounted in tube 10 with the other electrodes and the tube is evacuated by connecting it at 14 to a suitable vacuum pump. While the pumping continues the cathode is heated whereby the barium carbonate changes to barium oxide with evolution of carbon dioxide, the nickel sesquioxide is reduced to nickel monoxide with evolution of oxygen, and the barium oxide combines with the nickel monoxide to form a compound which melts and dissolves in the core metal. Some of the excess nickel monoxide is soluble in metallic nickel and also disappears into the core. To complete the reaction the temperature of the cathode surface should be raised to 1150°C . or higher and the reaction is quite rapid when the temperature is maintained above 1200°C . If portions of the coating should peel due to unequal expansion, no damage is done because such portions will dissolve into the core at their points of contact if the temperature is maintained high enough.

The evolved carbon dioxide and oxygen are removed by the pump. When the sesquioxide is used in the applied coating it may be that the

oxygen is released in a very active or nascent condition and thus assists in the reaction. When all of the gas has been evolved, the surface thus treated should have a smooth, metallic appearance, slightly tarnished. This condition is indicated at 17 in Fig. 2, and the color is grayish due to the excess NiO on the surface.

To the best of our knowledge the nickel-barium compound thus formed and dissolved in the core is barium nickelate $\text{BaO} \cdot \text{NiO}$.

The tube is disconnected from the pump and hydrogen admitted at atmospheric pressure or possibly at two or three pounds per square inch higher pressure in case a faster reaction is desired. The cathode is then heated whereupon the hydrogen diffuses throughout the core and reduces the excess dissolved NiO to metallic nickel. A temperature of 300°C . is satisfactory but the reaction may be hastened by using a higher temperature. No action seems to take place between the barium nickelate and the hydrogen.

The tube is then re-evacuated and degased in the usual manner after which the cathode surface (in the example above described) is rendered highly emissive by reason of the barium nickelate dissolved in its nickel core. This condition is indicated at 18 in Fig. 2 which represents a smaller portion of the cathode than 17, with greater enlargement in order to illustrate the spongy nature of the emissive surface obtained as above described. To the eye the finished cathode surface looks like frosted nickel. It has a spongy nature which can be detected under a microscope. Under a high power microscope this sponge appears to be composed of crystals of nickel in a matrix of barium nickelate, the relatively large particles of the latter being distributed through the core. The core metal appears to be saturated with nickelate and a large excess of the latter is found at the spongy surface. One theory is that this excess may be soluble in the nickel core at operating temperature, and precipitates out each time the filament cools, or it may be simply a reserve supply maintaining the core in a saturated condition and replacing nickelate lost by overloading or during the manufacturing process.

Two advantages of the present cathodes over those described in our Patent No. 1,985,855, above mentioned, are therefore, the spongy character of the cathode surface which increases the effective emissive surface many fold and also helps to increase the electrical conductivity of the emissive surface; and the ability to make filaments with a much higher ratio of barium nickelate to core metal.

The final conditioning of our cathode may be hastened by filling the tube with inert gas and bombarding the cathode while it is heated to about 1000°C .

Instead of the above described hydrogen treatment an alternative method for reducing the excess NiO is to continue the vacuum pumping with the cathode heated to about 1200°C . However, this method is slow due to the time required for the oxygen to diffuse to the surface, whereas the hydrogen quickly reduces the NiO throughout the core. Hydrocarbon vapors may be used as the reducing agent in place of hydrogen.

We have reason to believe that any compound of one of the alkaline-earth metals with oxygen and one of the metals of the iron group may be substituted for the compound of nickel, barium and oxygen above mentioned, the temperatures

and time of treatment being modified accordingly. Thus the dissolved emissive compound may be an alkaline earth ferrate or cobaltate and we have found that base metals adjacent to the iron group in the atomic series of elements may be used and similar results obtained therewith. For instance, we have found that barium manganate and barium cuprate may be used. Barium chromate is only slightly soluble and may be used at relatively high operating temperatures. Barium cuprate is soluble in copper as well as in metals of the iron group. It volatilizes at a lower temperature than barium nickelate, hence barium cuprate filaments must be operated at a relatively low temperature. The class of base metals therefore includes chromium, manganese, iron, cobalt, nickel and copper, which have consecutive atomic numbers from 24 to 29, inclusive. All of these metals are heavy metals in the first long period in the periodic system and possibly some heavy metals in the second long period may be used, such as molybdenum which has atomic number 42.

It should be understood that the core may be composed in whole or in part of nickel or another metal in which the desired emissive compound is soluble, so long as the core surface is composed of such a metal to a depth sufficient to constitute a reservoir of emissive compound to meet the required life of the cathode. The portion of the cathode body below this depth may contain a more refractory metal or possibly a refractory substance other than a metal.

Cathodes prepared as above described are extremely stable, are not easily poisoned, do not sputter easily, do not form hot spots and do not gas. They may be operated safely at several hundred degrees centigrade higher temperature than ordinary barium oxide coated filaments with less evaporation of active material on to nearby electrodes.

The electrical conductivity of barium nickelate and also of the other compounds of the class described herein is very high and comparable to that of metals. This is important in that heavy emission currents are conducted to the surface without sufficient potential drop in the emissive material to cause dissociation by electrolysis, and probably accounts for the great stability of said compounds. Another reason for their stability is probably that, if there is any decomposition by heat, the products thereof are non-volatile at operating temperatures and recombine. With the usual oxide coatings the products of decomposition are volatile and decomposition proceeds slowly at temperatures at which such coatings are emissive.

We claim:

1. The method of preparing an electron emissive cathode which comprises coating a nickel core with a mixture comprising alkaline earth carbonate and an oxide of nickel, heating said coating under reduced pressure to at least 1150°C degrees centigrade whereby it decomposes and forms a compound which is soluble in the core, and dissolving said compound in the core under said reduced pressure.

2. The method according to claim 1 in which the coating contains an excess of nickel oxide over that required to form the soluble compound, dissolving some of said excess in the core together with the said compound, and then reducing the nickel oxide to metallic nickel by heating the cathode in a hydrogen atmosphere.

3. The method of making an electron emissive

surface which comprises coating a nickel surface with a mixture of barium carbonate and nickel oxide, heating the same above 1150 degrees centigrade under reduced pressure, then heating in a hydrogen atmosphere, and re-evacuating.

4. The method of making an electron emissive surface which comprises coating a metal surface with a mixture comprising a compound of a highly electropositive metal which will yield an oxide thereof and a compound of a base metal which will yield an oxide thereof with evolution of oxygen, said base metal being selected from the group comprising chromium, manganese, iron, cobalt, nickel, copper and molybdenum, heating said coating to a temperature sufficient to decompose said compounds yielding the oxides and forming therefrom a compound which is soluble in the metal which provides the said surface, and dissolving the last-mentioned compound in the last-mentioned metal.

5. The method of preparing an emissive cathode which comprises coating a nickel core with a mixture comprising a compound of barium and an oxide of nickel, heating said coating under reduced pressure to convert the barium compound to barium oxide, continuing said heating to above 1150 degrees centigrade until said barium and nickel oxides form a compound which dissolves in the nickel of the core, and reducing any excess of nickel oxide to metallic nickel.

6. The method of preparing an emissive cathode which comprises coating a metal core with a mixture of an alkaline-earth metal compound and a compound of a metal of the iron group, the latter compound being adapted to evolve oxygen, forming from said coating a compound containing the said metals and oxygen, and dissolving the last-mentioned compound in the metal of the core.

7. A partly prepared cathode comprising a nickel core having dissolved therein barium nickelate and nickel monoxide.

8. A partly prepared cathode comprising a metal core having dissolved in the metal of said core a compound of one of the heavy metals of the first long period in the periodic system with an alkaline-earth metal and oxygen, and also dissolved in said core metal an oxide of said heavy metal.

9. An electron emissive cathode comprising a nickel core with barium nickelate dissolved therein and having additional barium nickelate forming a spongy surface therefor.

10. An electron emissive cathode comprising a base metal core selected from among the iron group metals and metals adjacent thereto in the atomic series of elements, an electron emissive compound dissolved in said core, said compound comprising one of said base metals, an alkaline earth metal and oxygen, and an undissolved amount of said compound distributed through the core when it is in a cold state.

11. A cathode as defined in claim 10 in which

said undissolved amount of emissive compound contains in suspension crystals of said base metal.

12. An electron emissive cathode comprising a core of one of the metals having atomic numbers from 24 to 29, inclusive, and an electron emissive compound dissolved in said core, said compound comprising one of the heavy metals adjacent to the iron group in the atomic series of elements, an alkaline earth metal and oxygen.

13. An electron emissive cathode comprising a core of one of the metals having atomic numbers from 24 to 29, inclusive, and an electron emissive compound dissolved in said core, said compound comprising one of the metals chromium, manganese, copper and molybdenum, an alkaline earth metal and oxygen.

14. An electron emissive cathode comprising a core of one of the metals adjacent to the iron group in the atomic series of elements and an electron emissive compound dissolved in said core, said compound comprising one of the metals having atomic numbers from 24 to 29, inclusive, an alkaline earth metal and oxygen.

15. An electron emissive cathode comprising a core of one of the metals adjacent to the iron group in the atomic series of elements and an electron emissive compound dissolved in said core, said compound comprising one of the metals chromium, manganese, copper and molybdenum, an alkaline earth metal and oxygen.

16. An electron emissive cathode comprising a core of one of the metals having atomic numbers from 24 to 29, inclusive, with an alkaline earth cuprate dissolved therein.

17. An electron emissive cathode comprising a core of one of the metals having atomic numbers from 24 to 29, inclusive, with an alkaline earth chromate dissolved therein.

18. An electron-emissive cathode comprising a base metal core the metal of which has an electron-emissive compound dissolved therein, said compound having an electrical conductivity comparable to that of the core metal, and an additional amount of said compound at the surface of the core in its cold state.

19. The steps in the preparation of an emissive cathode which comprise coating a metal core with a mixture of a highly electropositive metal compound and a compound of the core metal, the proportions of said compounds in the mixture being such as to provide more atoms of core metal than of electropositive metal in the respective compounds, mounting said cathode in a tube, and heating the cathode while exhausting the tube until the coating decomposes and forms a compound which disappears into the solid core metal.

20. An electron emissive cathode comprising a nickel core with barium nickelate dissolved therein and having a spongy surface consisting chiefly of barium nickelate and forming a matrix containing crystals of nickel.

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