May 14, 1957 J. E. BEGGS 2,792,273

OXIDE COATED NICKEL CATHODE AND METHOD OF ACTIVATION

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Fig. 1.

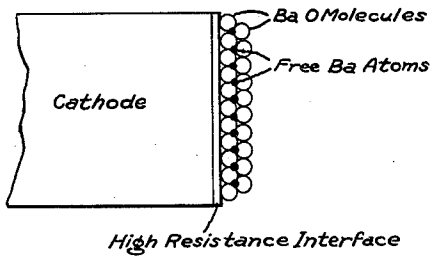


Fig. 2.

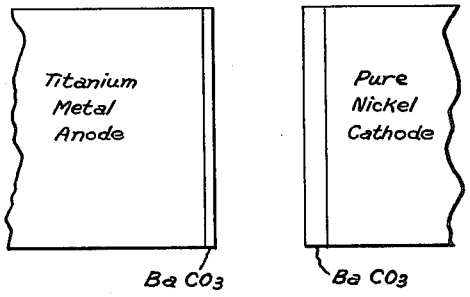
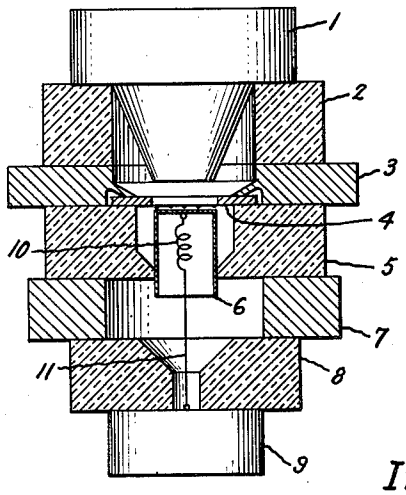


Fig. 3.



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OXIDE COATED NICKEL CATHODE AND METHOD OF ACTIVATION

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5 Claims. (Cl. 316—20)

This invention relates to oxide coated nickel cathodes and a method for activating an oxide coated nickel cathode.

A conventional form of thermionic emitting cathode consists of a nickel base which is coated with an alkali earth metal oxide such as barium oxide. Before such a coated cathode can be used as an electron emitter it must be activated. A concept of activation is that before such a cathode can be used as an emitter there must be free atoms of an alkali earth metal present in the oxide coating. One method of obtaining free atoms is to introduce impurities such as magnesium, aluminum or silicon into the nickel to make the base relatively active and to aid in reducing a portion of the oxide coating and thereby release free metal atoms. This method has the advantages of easy and nearly complete activation and high initial emission and the inherent disadvantages of an interface which develops between the nickel base and the activated oxide coating, and a characteristic slump in emission during the life of the cathode. This interface has a relatively high resistance and therefore, a portion of the anode to cathode voltage drop will occur across this high resistance interface thereby reducing the electron emission from the activated oxide coating on the cathode.

A cathode may also be formed of pure nickel coated with barium oxide. This type of cathode has the inherent advantages of no interface and relatively stable emission characteristics during the life of the cathode. However, a cathode of this type is relatively difficult to activate, since nickel is a relatively poor reducing agent, and has low initial emission.

Since nickel without a high resistance interface makes an ideal cathode base, it is particularly desirable that a method be found which will permit activation of an oxide coated substantially pure nickel cathode.

It is therefore an object of my invention to provide an activated oxide coated pure nickel cathode without a high resistance interface between the cathode base and the oxide coating.

Another object of my invention is to provide a method of producing an oxide coated pure nickel cathode which has relatively stable emission characteristics during its life, is easy to activate fully, and has high initial values of emission current.

A further object of my invention is to provide a method of activating an oxide coated pure nickel base cathode without the use of additional reducing agents in the cathode structure and which is easily activated.

An additional object of my invention is to provide a method of activating an oxide coated cathode without the formation of gas or other contaminates during the activation process.

In accordance with the method of my invention a pure nickel cathode is coated with a compound of an alkali earth metal such as barium carbonate. The cathode is heated to a temperature of approximately 1000° C.

which converts the barium carbonate to barium oxide. A substantially pure form of the alkali earth metal is then evaporated onto the cathode surface to form an activated oxide coated nickel cathode.

A better understanding of my invention may be had by reference to the drawing in which Fig. 1 is an illustrative drawing of a conventional oxide coated cathode; Fig. 2 is an illustrative drawing of the anode and cathode structure of an electron tube; and Fig. 3 is a miniature triode tube with a cathode which has been activated in accordance with the method of my invention.

Fig. 1 of the drawing illustrates the results of a conventional method of activating a cathode. For example, it may be assumed that the cathode of Fig. 1 is nickel having a small amount of impurity such as silicon. On this nickel cathode is applied a slurry of alkali earth metal carbonates. A commonly used mixture consists of approximately equal percentages of strontium carbonate, and barium carbonate with a small percentage of calcium carbonate. The cathode is then heated to a temperature at which the carbonates are converted to oxides and at which a portion of the barium oxide is reduced forming free barium and a barium ortho-silicate (Ba_2SiO_4) which forms as an interface between the metal of the cathode and the activated oxides. The free barium activates the cathode so that, when heated, electrons will be emitted and the cathode may be used in a conventional thermionic electron tube. The barium activates the cathode rather than the strontium or calcium since it is relatively most active and therefore reduced at a low temperature while the strontium and calcium remain in oxide form. Free calcium and strontium will also activate a cathode and may be obtained by heating a cathode to a higher temperature.

Referring now to Fig. 2, there will be described the method of activating a pure nickel cathode in accordance with the method of my invention. In Fig. 2 there is illustrated an anode of a metal of the titanium group. For the purposes of this specification, a metal of the titanium group is any metal in the IV*a* group of a standard chemical periodic table. Metals in this group include titanium, zirconium, hafnium and thorium. The titanium anode is coated with a thin layer of barium carbonate ($BaCO_3$) and the pure nickel cathode is coated with a relatively thicker layer of barium carbonate or with a mixture of barium, strontium and calcium carbonates. The anode and cathode are then heated and held briefly at a temperature of approximately 800° C. At this temperature the carbonates are converted into oxides. The anode and cathode are then raised to a temperature of approximately 1000° C. and held at this temperature until the complete process of activation has taken place. At 1000° C. the barium oxide on the anode is rapidly reduced by the titanium. The oxygen is absorbed by the titanium leaving the titanium anode clean and bright and the barium is evaporated and deposited on the oxide coated cathode. In this manner free barium atoms are introduced into the oxide coated cathode and the cathode is activated without the necessity of any reducing agents being present in the initial coating of carbonates or in the nickel.

The carbonates may be prepared for application in any conventional manner. For example, powdered carbonates can be suspended in an amyl-acetate solution and then allowed to settle. In this manner, fine particles may be obtained, which when mixed with a nitro-cellulose binder, are easily applied to the anode and cathode surfaces. This method of preparation eliminates many impurities which may be introduced if the carbonates are prepared by conventional ball-milling processes. Such impurities can appreciably increase the rate of activation of the cathode but tend to form a high resistance interface.

Referring to Fig. 3 of the drawing, there will now be described an application of my method for activating an oxide coated nickel cathode in accordance with my invention. Fig. 3 shows a titanium anode **1**, a ceramic spacer **2**, a grid connector **3**, a fine wire grid structure **4**, a ceramic spacer **5**, a pure nickel cathode **6**, a cathode connector **7**, a ceramic spacer **8** and a heater connector **9**. Nickel cathode **6** is formed from a piece of nickel foil and has attached to the underside thereof a heater **10** which is connected to heater connector **9** by lead **11**. Cathode connector **7** is electrically connected to cathode **6** by a conductive film which is formed on the lower surface of ceramic spacer **5**. The active face of titanium anode **1** is coated with a thin layer of barium carbonate which is approximately 0.1 mil thick. It is not necessary to apply an even coating to the anode since the barium carbonate diffuses over the anode surface when heated. A small amount at one point is generally sufficient. The nickel cathode is coated with a layer of barium carbonate or a mixture of barium, strontium and calcium carbonates from 0.5 to 2 mil thick. The carbonates may be applied in a nitro-cellulose binder which will easily adhere to the anode and cathode tube elements. The tube elements are then stacked in the illustrated order with shims of nickel foil between each of the titanium and ceramic members. The tube elements are held in contact with the nickel shims and placed in a chamber which is evacuated. By means of conventional induction heating equipment, the temperature of the tube elements is brought up to a temperature of approximately 800° C. and held for a short period of time, i. e. in the neighborhood of 1 to 2 minutes, until all of the carbonates have been converted to oxides. The temperature of the tube elements is then raised to approximately 1000° C. At this temperature the barium oxide on the titanium anode is rapidly reduced. In the reduction process the oxygen is absorbed by the titanium and the barium is evaporated onto the surface of cathode **6**. Pure nickel is a poor reducing agent and therefore even at this high temperature no appreciable portion of the oxides on the nickel cathode are reduced and since no reducing agents are used, no interface is formed. At a temperature of approximately 1000° C. the nickel shims form a eutectic liquidus with the titanium and when the tube is subsequently cooled the liquidus solidifies into a titanium-nickel alloy thereby completing and sealing the tube structure. In this manner, a completed tube with an activated cathode, is formed in one operation. The method of tube construction utilizing metal shims to bond tube parts together is more completely described and is claimed in my copending application Serial No. 464,126 filed October 22, 1954 and assigned to the assignee of this invention.

The process of reducing the barium oxide on the titanium anode may be described by the reaction, $2BaO+Ti \rightarrow TiO_2+2Ba$. At 1000° C., the TiO_2 is dissolved by the titanium leaving the surface clean and bright. In this fashion free barium is obtained which may be utilized to activate the barium oxide on the cathode and no gases are liberated. The evaporated barium also acts as a getter of any stray gases. The cathode structure when activated consists essentially of barium oxide molecules or a mixture of alkali earth metal oxide molecules such as barium, strontium and calcium oxide with interspersed barium atoms. Barium oxide as well as mixtures of alkali earth metal oxides can be activated with a very small quantity of free barium present. For example, a cathode may be considered to be activated if approximately 1 atom of barium is present for every 100 oxide molecules. Oxide coated cathodes may be activated by evaporating substantially pure forms of other alkali earth metals; however, barium is particularly suited because it is very active and can be evaporated at a relatively low temperature.

While I have described the method and structure of my invention in relation to a particular embodiment, it will be apparent to those skilled in the art that various changes and modifications may be made without departing from the invention in its broader aspects, and that the appended claims are intended to cover all such changes and modification as fall within the true scope and spirit of the invention.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of activating the electron emitting surface of an electron tube which includes an anode made from metal from the titanium group, a substantially pure nickel cathode providing a passive support, comprising coating the said anode and said passive support with at least one alkali earth metal carbonate, heating the anode and cathode to an elevated temperature in vacuum to decompose said carbonate to alkali earth metal oxide, further heating the anode and cathode to a higher temperature to cause said alkali earth oxide on the anode to be reduced and the alkali earth metal evaporated from the anode onto the coated support to activate said oxide coating thereon.

2. The method of claim 1 wherein the alkali earth metal carbonate is converted to oxide at a temperature of approximately 800° C., and the evaporated alkali earth metal is barium which is evaporated onto and activates the cathode at a temperature of approximately 1000° C.

3. The method of activating a thermionic cathode including a passive metal support and a layer of an alkaline earth metal compound thereon which comprises supporting said cathode within an envelope including an electrode member having a surface of a metal selected from the titanium group exposed to the interior thereof, evacuating the envelope and heating said electrode member to a temperature sufficient to reduce alkaline earth metal compound thereon and evaporate pure alkaline earth metal onto the layer of alkaline earth metal compound on said cathode.

4. The method of activating a thermionic cathode including a passive metal support and a layer of an alkaline earth metal compound thereon which comprises supporting said cathode within an envelope including an electrode member having a surface of a metal selected from the titanium group exposed to the interior thereof, evacuating the envelope and heating said member to a temperature of approximately 1000° C. to reduce the alkaline earth metal compound thereon and evaporate pure alkaline earth metal onto the layer of alkaline earth metal compound on said cathode.

5. The method of activating a thermionic cathode including a passive metal support and a layer of an alkaline earth metal compound thereon which comprises supporting said cathode within an envelope including an electrode member having a surface of a metal selected from the titanium group exposed to the interior thereof, applying a layer of alkaline earth metal compound to said electrode member, evacuating the envelope and heating said electrode and said coated passive metal member to a temperature sufficient to reduce the alkaline earth metal compound on said electrode member and evaporate pure alkaline earth metal onto the layer of alkaline earth metal compound on said cathode.

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