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J. E. HARRIS

THERMIONIC CATHODE AND METHOD OF MAKING THE SAME

Filed Oct. 12, 1920

Fig. 1.

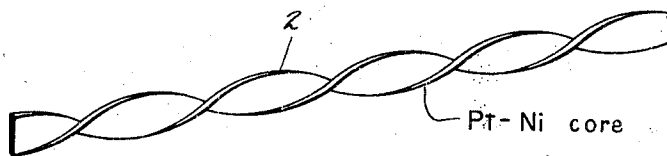
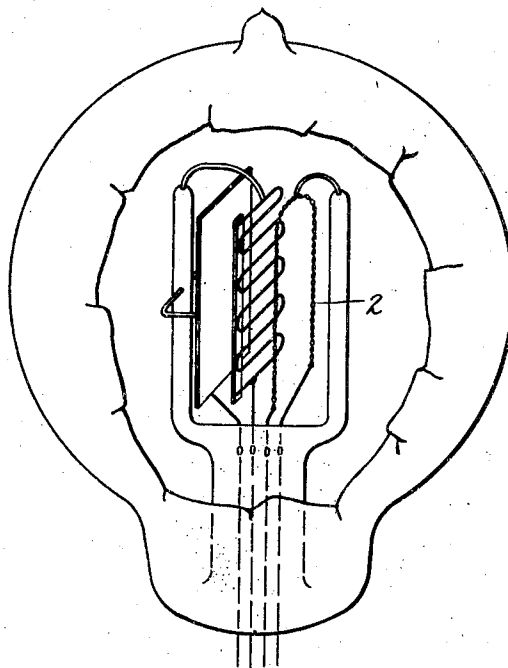


Fig. 2.



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by *W. E. Beatty* Atty.

UNITED STATES PATENT OFFICE.

JAMES E. HARRIS, OF EAST ORANGE, NEW JERSEY, ASSIGNOR TO WESTERN ELECTRIC COMPANY, INCORPORATED, OF NEW YORK, N. Y., A CORPORATION OF NEW YORK.

THERMIONIC CATHODE AND METHOD OF MAKING THE SAME.

Application filed October 12, 1920. Serial No. 416,386.

To all whom it may concern:

Be it known that I, JAMES E. HARRIS, a citizen of the United States, residing at East Orange, in the county of Essex, State of New Jersey, have invented new and useful Improvements in Thermionic Cathodes and Methods of Making the Same, of which the following is a full, clear, concise, and exact description.

This invention relates to electron emitting cathodes such as are used in vacuum tubes, and in a broad aspect relates to alloys. Its object is to provide an electron emitting cathode having high electron emitting activity. The invention comprises such a cathode having a core and a thermionically active coating therefor, the core containing a refractory and preferably malleable metal of low volatility such as platinum or palladium, and a metal such as nickel or cobalt. Nickel and cobalt for example, are characterized by the fact that upon being baked with an oxide of an alkaline earth metal in air they react with oxygen and the oxide much more readily than does platinum to form a compound which breaks down to the original constituents when heated in a vacuum. After about sixteen hours of operation in a vacuum tube, a cathode filament having the platinum-nickel core and a coating therefor comprising oxides of alkaline earth metals has an electron emitting activity considerably higher than that of a filament consisting of a platinum core and a coating therefor of said oxides.

The invention also comprises a method of making the cathode by coating the platinum-nickel core with oxides of alkaline earth metals, and further, comprises the core and an alloy containing the metals used for the core. The preferable coating materials and the preferable manner of applying them are set forth in detail below.

In the accompanying drawing, Fig. 1 represents in enlarged form a portion of a filamentary conductor which is suitable for use as an electron emitting cathode when constituted in accordance with this invention. Fig. 2 illustrates the use of such a filament in a thermionic repeater of the audion type.

A cathode is designated "2" in each figure and is shown as a twisted ribbon or filament

having, for example, a width of about .3 of a millimeter and the thickness of about .05 of a millimeter.

Filaments comprising metallic cores coated with oxides of alkaline earth metals are well-known. One example of such a filament is disclosed in U. S. patent to Nicolson and Hull, No. 1,209,324, December 19, 1916, "electron emitting cathode and the process of manufacturing the same." It has been discovered that filaments having greatly increased electron emitting activity can be produced by making the core of an alloy containing the metals specified above.

When a platinum-nickel core coated with a carbonate of an alkaline earth metal is baked in air (as described below) nickel oxide is formed and an oxide of the alkaline earth metal is formed, and then a compound containing nickel and the oxide of the alkaline earth metal is formed. In the subsequent baking operation (as described below) during the pumping out of the vacuum tube the compound breaks down, yielding oxygen and nickel and the oxide of the alkaline earth metal so that the coating then left on the core comprises the alkaline earth oxide in intimate contact with finely divided nickel. When the platinum-nickel core coated with the oxide of the alkaline earth metal is baked in air the nickel oxidizes much more readily than the platinum and although reaction takes place between the coating material and nickel very little reaction takes place between the platinum and the coating materials. After the cathode filament comprising the platinum-nickel core and the coating therefor containing oxides of alkaline earth metals in intimate contact with finely divided nickel has been held at its normal operating temperature, in the vacuum tube, for about sixteen hours, it has an electron emitting activity about double that of a filament consisting of a platinum core and a coating therefor of oxides of alkaline earth metals in intimate contact with finely divided platinum.

Proportions of 95% platinum and 5% nickel give the most satisfactory alloy when due consideration is given to the malleability desirable in order that the alloy may be

worked into wire, the degree of activity of the finished cathode and the burn out life and especially the activity life of the cathode. Probably the low limit of the platinum content and also of the nickel content for a satisfactory core is determined principally by the rate of volatilization or burning out of the cathode when in use in vacuum tubes. Pure platinum burns out more rapidly than platinum alloyed with small quantities of nickel; but nickel is very volatile and too much nickel alloyed with the platinum will decrease the burn out life of the cathode. When the nickel content of the core is increased to more than about 15%, the rate of burning out of the cathode becomes higher than that of a platinum core filament; and when the nickel content of the core is decreased to less than 2%, the rate of burning out of the cathode becomes of the order of that of a platinum core filament. Moreover, a nickel content of about 2% (or more) of the core material is desirable in order to make the coating material adhere strongly to the core. However, the scope of my invention is not to be regarded as limited to any stated proportions of constituents, since primarily the object of the invention is to produce a cathode having a high electron-emitting activity.

A preferable method of making the alloy core is the invention of Mr. Howard T. Reeve and is claimed in an application in his name, Serial No. 416,464, filed October 12, 1920, "methods of making cores for cathodes of vacuum tubes," assigned to the assignee of this application. The method will now be set forth in detail in connection with the description of the process of making the cathode of this invention.

The constituents of which the alloy is to consist are thoroughly mixed in the form of finely powdered metals in the desired proportions, for example 95% platinum and 5% nickel. The mixture is pressed in a steel die to form a coherent ingot of convenient size and shape. For an ingot weighing about 25 grams, a convenient form is a cylinder $\frac{3}{8}$ of an inch in diameter. The pressure used on the die may be exerted manually, but preferably a pressure of at least several tons per square inch, such as can be conveniently obtained from a hydraulic press or the like, should be used. The ingot is next fused or sintered, in a vacuum or in an inert gas. This fusing or sintering may be done by putting the ingot in a small refractory crucible of alundum, magnesia or the like, the crucible being placed in a vacuum furnace of any suitable type. A type which has been used with good results has an evacuated space connected with any good oil pump capable of producing a vacuum of .001 mm. of mercury, this space containing a helical heating coil

of graphite, tungsten, molybdenum, or the like, which surrounds the crucible. The coil is heated by the passage of a large, low voltage electric current from the secondary winding of a step-down transformer. The vacuum chamber preferably has a transparent top so that the temperature of the ingot may be observed with an optical pyrometer. Since the melting point of nickel is about 1450° C. and that of platinum is about 1750° C., the temperature used for sintering or fusing the ingot is in the neighborhood of 1500° C. to 1800° C. The duration of the fusing or sintering operation should be as short as possible, in order that the amount of nickel vaporized shall be as small as possible. The duration will depend upon the size of the ingot. With a 25 gram ingot in the form of a cylinder $\frac{3}{8}$ of an inch in diameter, fusing or sintering in the crucible would be for only a few minutes.

Another way in which the sintering temperature may be obtained is by clamping the ingot between two electrodes in a bell-jar, exhausting the air from the jar, and passing a heating current through the ingot, increasing the current until a sintering temperature of about 1500° C., as observed with an optical pyrometer for example, is reached, and then cutting the current off. Where the ingot is heated in this manner, the duration of the sintering will be only momentary and will be only from about a quarter to a tenth as long as where the ingot is fused or sintered in a crucible in a furnace as referred to above.

The pressures maintained by the pump during the fusing or sintering have been from .01 to .001 of a millimeter of mercury, though probably a vacuum of only a few millimeters would suffice. However, the higher the vacuum, the better will be the results, since the sintering in a vacuum or in an inert gas prevents oxidation of the nickel. Of course, as is indicated above, the fusing or sintering may be done in an induction furnace or in any suitable vacuum furnace.

When the ingot has been fused or sintered, it is forged to get it into the form of a rod and then the rod is swaged into wire, which is drawn through diamond dies or the like to the required size, all of this forging, swaging and drawing being cold working. Hot working is not advisable for if the platinum nickel alloy were worked hot the nickel would be oxidized and as a consequence the material or work, would become very brittle. The material is annealed at frequent intervals during all of this forging, swaging and drawing. Great care must be taken that the working at any stage is not pushed too far, without annealing, else the material, or work, is likely to be

come so brittle that it will crack. The method of annealing depends on the stage of the working, that is, on the dimensions, especially the length of the work. In general, the larger the diameter, the higher the annealing temperature. The temperature should be between about 1100° C. and the fusing temperature, which latter temperature, is in the neighborhood of 1700° C.

Regarding the duration of the heating for annealing, it is only necessary to bring the work up to the annealing temperature and then let it cool off. The method of heating for annealing should preferably be such as will guard against oxidation of the nickel. When the working is in the first stages, for instance when the work is in the form of an ingot of the size referred to above, the work may well be heated to the annealing temperature in the oxy-hydrogen flame, and preferably cooled in a reducing, hydrogen flame (the supply of gas from the oxygen tank being shut off) until the ingot is below red heat, when it is withdrawn from the flame and quenched in water. When the work has increased considerably in length, the method preferred consists in clamping the work between electrodes, in a vacuum, and passing an electric current through it to give the required temperature, which as is indicated above, is in the lower part of the range from 1100° C. to 1600° C. In any case, if the work becomes oxidized, the oxide can be broken down by heating the work in a vacuum for a few minutes at a temperature of about 1000° C.

The wire made from the ingot as described above is suitable for use as a core for coated cathodes of the type referred to above. However, the wire is preferably cold rolled into ribbon form having, for example, a width of .3 of a millimeter and a thickness of .05 of a millimeter and the ribbon coiled and pulled out into the twisted filamentary form common for thermionic cathodes, and shown, for example, in United States patent to Nicolson and Hull, referred to above.

A filament having high activity can be made by coating the core described above with an oxide of any alkaline earth metal by applying a coating of the carbonate or hydroxide of the metal to the core, heating the coated core in air for about 5 to 20 minutes at about 1200° C., by passing current through it, and later heating it in a vacuum for several minutes at about 1000° C. by passing a current through it, during the pumping of the vacuum tube. However, a more durable filament, and one having uniformity of electron-emitting activity over a longer period, is made by applying coatings of strontium carbonate and barium carbonate to the platinum-nickel core by a method somewhat similar to that disclosed for applying such coatings to a platinum core in

the application of Carl D. Hocker, Serial No. 252,689, filed September 5, 1918, "process of manufacturing electron emitting cathodes," assigned to the assignee of this application. Preferably, a total of about 16 coats of the carbonates should be applied. The coating material is embodied or suspended in a solid carrier which may be of waxy material such as paraffin, by stirring together the desired quantity of strontium carbonate and barium carbonate into the same batch of molten paraffin, until the mixture has cooled and then forming the mixture into rods or pieces of other convenient shape. Preferably, the relative amounts of the ingredients are 2½ grams of barium carbonate, 7½ grams of strontium carbonate, and 100 grams of paraffin. To apply each coat, the solid rod containing the carbonates is passed along the length of the core, the core being heated in the usual way (that is, by passing a current through it) to a temperature sufficiently high to melt the paraffin, so that the coating material will be deposited on the core. After the application of each coating, current should be passed through the strip to flash it momentarily to a red heat which serves to burn off the paraffin, reducing the alkaline earth compound to an oxide which adheres closely to the filament. During the coating process, the filament may be held by any suitable supports. After the last coat has been applied to the core, the filament is baked in air for about 5 to 20 minutes at a temperature of about 1200° C. The filament is, of course, later heated in a vacuum for several minutes at a temperature of about 1000° C., during the pumping of the vacuum tube. After the filament has had its normal operating current passed through it for about 16 hours, in the vacuum tube, it has an electron-emitting activity about twice as great as that of a filament made by similarly coating a platinum core.

One of the important advantages of the alloy of this invention is that it may consist of pure metals such as platinum and nickel so that its composition can be controlled by chemical analysis, whereas with the platinum core now in common use containing platinum mixed with varying amounts of iridium and rhodium, a satisfactory analysis is a most difficult matter.

The nickel in the platinum-nickel core produces a desirable increase in the ohmic resistance of the core, as do the iridium and rhodium in the platinum core now in common use containing those metals. However, the iridium and rhodium may of course also be incorporated in the mixture of powdered platinum and nickel used in making the core of this invention, for further increasing the resistance, without departing from the invention.

One important advantage of this invention is that whereas with a filament having a platinum core it is necessary to bake the oxide coating on for about two hours, with the nickel filament about 5 to 20 minutes suffices. The reason for this difference is probably that the oxidation of the core metal which must occur before the coating material reacts with the core metal, takes place much more quickly in the case where the core contains nickel, than where the oxidation of platinum must take place, since nickel oxidizes much more rapidly than platinum.

It should be understood that where platinum and nickel are referred to herein, without mention of their equivalents, such references are to be regarded as also including equivalents of the platinum, for instance, palladium, osmium, rhodium, iridium and ruthenium, or equivalents of the nickel, for instance, cobalt.

What is claimed is:

1. An electron emitting material, comprising an alloy containing a refractory metal and a metal in the nickel-cobalt group, said alloy having the property of yielding when coated with an oxide of an alkaline earth metal and baked in air and then in a vacuum, a coating having an electron-emitting activity considerably greater than that of a coating made by similarly treating platinum.

2. A cathode containing a core formed from an alloy comprising a metal of the platinum group and a metal which upon being baked with an oxide of an alkaline earth metal in air reacts with oxygen and the oxide of the alkaline earth metal to form a compound that breaks down to the original constituents when heated in a vacuum, said alloy having the property of yielding, when coated with an oxide of an alkaline earth metal and baked in air and then in a vacuum, a coating having an electron-emitting activity considerably greater than that of a coating made by similarly treating platinum.

3. An electron-emitting cathode comprising an alloy containing platinum and at least 2 per cent of nickel, and a coating containing thermionically active material, said cathode having an electron-emitting activity considerably greater than that of a platinum filament coated with alkaline earth metal oxides.

4. An electron-emitting cathode comprising an alloy containing approximately 95% platinum and 5% nickel.

5. A cathode containing a core formed from an alloy comprising platinum and a metal of the nickel-cobalt group which upon being baked with an oxide of an alkaline earth metal in air reacts with oxygen and the oxide of the alkaline earth metal to

form a compound which breaks down to the original constituents when heated in a vacuum, said alloy having the property of yielding, when coated with an oxide of an alkaline earth metal and baked in air and then in a vacuum, a coating having an electron-emitting activity considerably greater than that of a coating made by similarly treating platinum.

6. An electron-emitting element having a core comprising a refractory metal and a metal of the nickel-cobalt group which upon being baked with an oxide of an alkaline earth metal in air, reacts with oxygen and the oxide of the alkaline earth metal to a materially greater extent than said refractory metal to form a compound which breaks down to the original constituents on being heated in a vacuum, said element having a coating for the core comprising an oxide of an alkaline earth metal.

7. The process of making an electron-emitting cathode which comprises baking a filament containing platinum and nickel with an oxide of an alkaline earth metal in the presence of oxygen.

8. The process of making an electron-emitting cathode which includes baking a core containing platinum and nickel with an alkaline earth metal in the presence of oxygen for a short period to form a compound containing nickel and said alkaline earth metal and later baking the core and the compound in the absence of oxidizing conditions to cause said compound to break down into nickel, oxygen and an oxide of said alkaline earth metal.

9. The process of making an electron-emitting cathode which includes baking a core containing platinum and nickel with oxides of barium and strontium in the presence of oxygen for about five to twenty minutes at a temperature of about 1200° C., and later baking the coated core in the absence of oxidizing conditions at a temperature of about 1000° C. for a period of several minutes.

10. The method of making an electron-emitting cathode which comprises coating a core containing platinum and nickel with material comprising an alkaline earth metal and baking the coated core in the presence of oxygen about five to twenty minutes to cause reaction between the core and the coating material.

11. An electron-emitting cathode containing platinum, nickel, barium oxide and strontium oxide.

12. An electron-emitting cathode comprising an alloy of platinum and nickel and also comprising an alkaline earth metal.

13. An electron-emitting cathode comprising a core containing platinum and nickel and a coating containing nickel.

14. An electron emitting cathode com-

prising a core containing platinum and nickel and a coating containing an alkaline earth metal.

15. An electron-emitting cathode comprising a core containing an alloy of platinum and nickel and having a coating containing barium and strontium.

16. An electron-emitting cathode comprising a core containing platinum and nickel and a coating containing nickel and an alkaline earth metal.

17. An electron-emitting cathode comprising a core containing an alloy of platinum and nickel and a coating containing nickel, barium and strontium.

18. An electron-emitting cathode comprising a core which volatilizes only at a high temperature and a coating containing nickel and an alkaline earth metal.

19. An electron-emitting cathode comprising an alloy containing a metal of the platinum group and a metal of the nickel-cobalt group, said alloy being less volatile than the second mentioned metal, and said cathode having a considerably higher electron-emitting activity than a platinum filament coated with oxides of alkaline earth metals.

20. An alloy comprising a metal of the platinum group and a metal which upon being baked with an oxide of an alkaline earth metal in air reacts with oxygen and said oxide much more readily than does platinum to form a compound that breaks down to the original constituents when heated in a vacuum.

21. An alloy comprising a metal of the platinum group and a metal which upon being baked with an oxide of an alkaline earth metal in air reacts with oxygen and said oxide to form a compound much more readily than does platinum.

22. An electron-emitting cathode core comprising platinum and a metal which upon being baked with an oxide of an alkaline earth metal in air reacts with oxygen and said oxide much more readily than does platinum, to form a compound that breaks down to the original constituents when heated in a vacuum.

23. An electron emitting cathode comprising an alloy containing a metal of the platinum group and a metal more volatile than said first metal, said alloy being coated with thermionically active material containing said more volatile metal.

24. An electron emitting cathode comprising an alloy containing a metal of the platinum group and a metal more volatile than said first metal, said alloy being coated with oxides of alkaline earth metals.

25. An electron emitting material comprising a core and a coating containing an

oxide of alkaline earth metal baked thereon, said core comprising a refractory metal alloyed with a metal of the nickel-cobalt group capable of forming an unstable compound by reaction with said coating, said material also containing a product formed by reaction between said second mentioned metal and said coating, and having an electron emissivity materially greater than platinum similarly coated and treated.

26. An electron emitting material comprising an alloy core and a coating containing an oxide of alkaline earth metals baked thereon, said alloy core comprising a refractory metal alloyed with a second metal, such as nickel, capable of forming an unstable compound by reaction with said oxide of alkaline earth metal, said material also containing said second metal in finely divided form in intimate contact with said oxide.

27. An electron emitting element comprising a core having a coating containing an oxide of alkaline earth metal, said coating comprising also a metal of the nickel-cobalt group.

28. An electron emitting element comprising a core having a coating containing an oxide of an alkaline earth metal, said core containing in preponderating amount a refractory metal which remains substantially inert toward oxides of alkaline earth metals at the operating temperature, said coating containing also a metal of the nickel-cobalt group.

29. An electron emitting element comprising a core of a refractory metal alloyed with a lesser amount of a metal, such as nickel, which volatilizes at a relatively lower temperature than said refractory metal, and a coating containing an oxide of an alkaline earth metal applied to said core, said refractory metal being substantially inactive chemically with respect to said oxide.

30. A filament comprising a core containing a metal of the platinum group alloyed with at least one of the two metals, nickel and cobalt, and a coating containing strontium and barium oxides, said filament having a degree of thermionic activity considerably greater than a platinum filament similarly coated and operated under similar conditions.

31. An electron emitting cathode comprising an alloy containing platinum and a maximum of 15 per cent of nickel, and a coating containing a thermionically active material, said cathode having an electron emitting activity considerably greater than that of a platinum filament similarly coated.

In witness whereof I hereunto subscribe my name this 9th day of October A. D., 1920.

JAMES E. HARRIS.