June 19, 1923. 1,459,400

C. D. HOCKER

ELECTRON EMITTING CATHODE AND PROCESS OF MAKING THE SAME

Filed Nov. 17, 1916

Fig. 1.

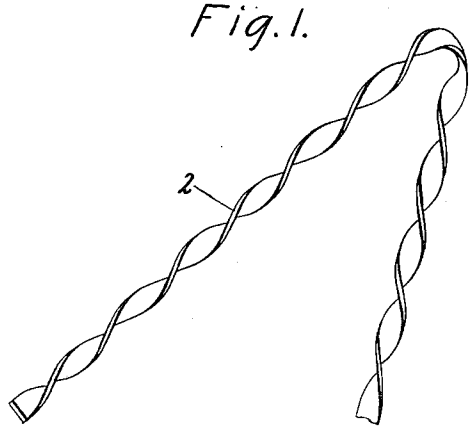
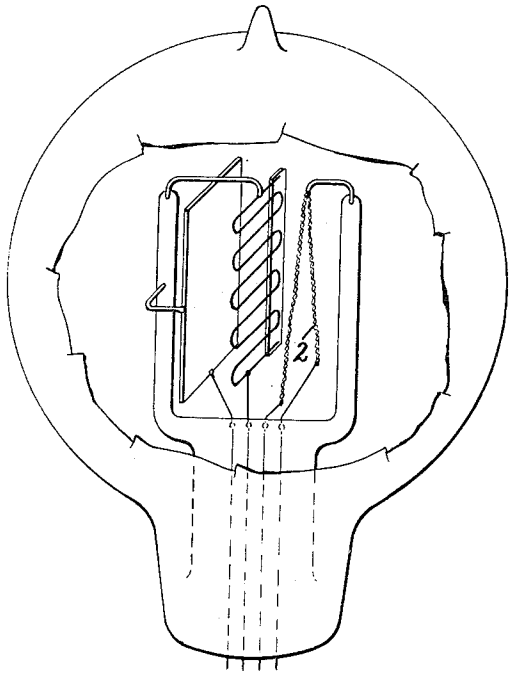



Fig. 2.

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Patented June 19, 1923. 1,459,400

# UNITED STATES PATENT OFFICE.

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## ELECTRON-EMITTING CATHODE AND PROCESS OF MAKING THE SAME.

Application filed November 17, 1916. Serial No. 131,858.

*To all whom it may concern:*

Be it known that I, CARL D. HOCKER, a citizen of the United States, residing at East Orange, in the county of Essex and State of New Jersey, have invented certain new and useful Improvements in Electron-Emitting Cathodes and Processes of Making the Same, of which the following is a full, clear, concise, and exact description.

This invention relates to electron emitting cathodes, and the process of making the same, and has for an object to improve the characteristics of such cathodes in any one or more of the following particulars:

A.—To make the thermionically active coating adhere more firmly to the electrode or filament by mechanically binding the active coating materials to the filament.

B.—To increase the electron emission at any given temperature.

C.—To lengthen the life of the filament at any given temperature.

This is accomplished by adding another substance such as a noble metal to the coating before it is applied. By noble metal is included compounds of a noble metal from which the noble metal may be produced by heating a compound thereof; for instance, gold, silver and platinum may be produced by heating gold oxide, silver oxide and ammonium chloro-platinate, respectively. Among the noble metals may be mentioned silver, gold and platinum, and the presence of one of these metals in the filament coating has been found to give the desired result. Whether the noble metal will serve to mechanically bind the coating to the filament, whether it increases the electron emission or length of life, or any combination of these, depends upon the noble metal used as well as upon the particular thermionically active substance or substances of which the coat is composed. The particular substance used in the coat, and the properties of the filament that are thereby improved will be later described.

The use of a material in the coating which serves to mechanically bind the coat to the filament has two distinct advantages: First, it makes it possible to apply any coating in an adherent form; second, it permits the application of coats composed of a mixture of substances in definite proportions—a definiteness which cannot be insured when these substances have to be alternately applied in layers as previous filaments have been made.

Fig. 1 of the drawing shows a twisted filament, electrode or cathode made according to the invention; and Fig. 2 shows an evacuated vessel having a filament such as shown in Fig. 1.

It is proposed to use a filament core of platinum or one of platinum alloyed with other metals of the platinum group, i. e., iridium, rhodium, palladium, osmium, ruthenium. Oxides or other compounds of the alkaline earth group, either singly or in combination, comprise a portion of the thermionically active coat to which is added one of the noble metals or a compound thereof, such as an oxide of platinum, gold or silver.

In making a cathode according to the invention, filament 2 of platinum which may be twisted as shown in Figs. 1 and 2, is suspended from spaced electrodes which are connected to a suitable source of electricity. The coating mixture is made into a fluid or plastic condition by mixing with a suitable fluid medium such as water. A trough filled with the coating mixture thus formed is moved longitudinally along the filament while the filament dips into the coating mixture. The coat is then dried or baked on the filament by heating the same to a suitable temperature. A convenient way of baking the coat is to pass an electric current through the filament. When the first coat is baked the filament is allowed to cool and a second coat is applied and baked. This process of applying a coat and baking the same is repeated four or five times, for example, or until a coat of suitable thickness has been provided. A filament thus treated is then baked for a suitable length of time at a temperature which depends upon the material used. Specific values of the temperatures and length of time for baking are given below. As to specific types of filaments and their characteristics, it has been found that the presence of platinum in the coat increases the length of life of a filament and mechanically binds the active coating to the filament. A filament having platinum in the coat may be made by using equal molecular parts of barium oxide and strontium oxide, to which mixture is added a molecular part of platinum equal to the sum of the molecular parts of the oxides. Metallic platinum is not used, but it is proposed

to use a suitable compound thereof such as ammonium chloro-platinate $(NH_4)_2\ PtCl_6$ which is easily converted to metallic platinum on ignition. These ingredients are mixed with water and applied as a paste to the wire being coated. Three to five coats should be applied to the filament which should be finally baked in air at a temperature of about 1,000 degrees centigrade for about two hours.

The life of the filament can be still further increased by adding calcium oxide to the coating mixture. For instance, equal molecular parts of barium oxide, strontium oxide and calcium oxide may be mixed with three molecular parts of platinum in the form of ammonium chloro-platinate. This filament is given the same treatment as the one described in the preceding paragraph. The subject matter of this paragraph is described and claimed in the application of Harris Serial No. 139,532, filed December 29, 1916, for electron emitting cathodes and process of manufacturing the same.

A filament having an electron emission which is higher at a given temperature than the filaments described above, may be provided by adding gold in the form of gold oxide to the coating material instead of adding platinum in the form of ammonium chloro-platinate. The table given below indicates the proportions of the various ingredients which have been found to give good results.

*Gold in the coat.*

(Molecular parts.)

| BaO. | SrO. | CaO. | Au. |
|---|---|---|---|
| ⅓ | ⅓ | ⅓ | 1 |
| ..... | 1 | ..... | 1 |

The filaments having gold in the coat must, after coating, be finally baked only a short time, for example, about five to ten minutes, and at a low temperature, for example, about 600 to 700 degrees centigrade.

Filaments having silver in the coat have an activity at a given temperature which is very much better than other known types of filaments. Such a filament will not stand to be run at high temperatures without burning out. However, they will supply all of the space current required of other types of filaments now in use without being operated at a temperature high enough to endanger their life. All of the filaments below described having silver in the coat appear to last indefinitely when run at the minimum filament current (i. e. lowest temperature) necessary to give the electron emission required of filaments now in use.

The following table gives the proportions of the various ingredients including silver which may be used in the coating mixture. The compound of silver used was the oxide $Ag_2O$.

*Filaments with silver in the coat.*

(Molecular parts.)

| BaO. | SrO. | CaO. | Ag. |
|---|---|---|---|
| ½ | ½ | ..... | 2 |
| ⅓ | ⅓ | ⅓ | 1 |
| ⅓ | ⅓ | ⅓ | 2 |
| ..... | 1 | ..... | 1 |
| 1 | ..... | ..... | 1 |

The filaments having silver in the coat must be baked only a few minutes, that is, about five to ten minutes, and at a low temperature, for instance, at 600 to 700 degrees centigrade. This is to fix the coating or to make it adhere to the filament core. Then this filament is mounted in a tube which is exhausted by any suitable means to produce a high vacuum. An electric current is passed through the filament to heat the same to a temperature sufficient to volatilize all or substantially all of the silver. The volatilized silver sublimes and forms a coating on the inside of the vacuum tube. The filament may then be removed from this tube and mounted in another tube, in which it is to be used as an electron source or the volatilization of the silver may take place in a tube of the form shown in Fig. 2, in which the filament is permanently mounted as the presence of the silver coating on the sides of the tube does not interfere with the operation of the tube as a thermionic device.

Reference is made throughout the specification to "platinum" filaments and to filaments having a "platinum" core, by which is meant a filament composed chiefly of platinum even though the filament core contains small amounts of other substances, such as iridium, which is found in commercial platinum, and the claims which recite "a filament containing platinum" or the like, are to be construed as meaning that the filament contains at least platinum, and not that the filament contains platinum to the exclusion of other metals or substances. This construction is to be given the word "containing" wherever used in the claims.

What is claimed is:

1. The process of manufacturing an electron emitting cathode which consists in applying to an electric conductor a coating containing a metal of the alkaline earth group and a noble metal.

2. The process of manufacturing an electron emitting cathode which consists in applying to an electric conductor a coating containing a metal of the alkaline earth group and a noble metal, and baking said coating.

3. The process of manufacturing an electron emitting cathode which consists in applying to an electric conductor a coating con-

taining barium, strontium and a noble metal, and baking said coating.

4. The process of manufacturing an electron emitting cathode which consists in applying to an electric conductor a coating containing a noble metal and a thermionically active metal, and baking said coating.

5. The process of manufacturing an electron emitting cathode which consists in applying to an electric conductor a coating containing silver and a metal of the alkaline earth group, and baking said coating.

6. The process of manufacturing an electron emitting cathode which consists in applying to an electric conductor a coating containing silver, barium and strontium, and baking said coating.

7. The process of manufacturing an electron emitting cathode which consists in applying to a filament containing platinum, a coating containing silver and a metal of the alkaline group, and baking said coating.

8. The process of manufacturing an electron emitting cathode which consists in applying to a filament containing platinum, a coating containing silver, barium and strontium.

9. The process of manufacturing an electron emitting cathode which consists in preparing a coating by mixing a substance containing a metal of the alkaline earth group with a substance containing a noble metal, applying said coating to an electric conductor, and baking said coating.

10. The process of manufacturing an electron emitting cathode which consists in preparing a coating by mixing a substance containing a metal of the alkaline earth group with a substance containing a noble metal, applying said coating to an electric conductor, baking said coating, applying another of said coatings, and in baking said coatings.

11. The process of manufacturing an electron emitting cathode which consists in coating an electric conductor with a coating comprising a fluid medium, an oxide of a noble metal and a substance containing a metal of the alkaline earth group, baking said coating, and in repeating the steps of coating and baking to provide a coat of a desired thickness.

12. The process of manufacturing an electron emitting cathode which consists in applying to an electric conductor a coating containing a metal of the alkaline earth group and a noble metal, in baking said coating, and removing the noble metal from the coating.

13. The process of manufacturing an electron emitting cathode which consists in applying to an electric conductor a coating containing a metal of the alkaline earth group and a volatilizable noble metal, and in baking said coating at a temperature sufficient to volatilize the noble metal in said coating.

14. The process of manufacturing an electron emitting cathode which consists in applying to an electric conductor a coating containing a metal of the alkaline earth group and a volatilizable noble metal, in initially baking said coating to fix the same on said conductor, and in finally heating said coating in vacuo to a temperature sufficient to volatilize the noble metal from said coating.

15. An electron emitting cathode comprising an electrode containing a noble metal, said electrode having a coating containing a different noble metal and a metal of the alkaline earth group.

16. An electron emitting cathode comprising an electrode containing a noble metal, said electrode having a coating containing an oxide of a different noble metal and metallic oxides of the alkaline earth group.

17. An electron emitting cathode comprising an electrode having a coating containing silver and a metal of the alkaline earth group.

18. An electron emitting cathode comprising a platinum electrode having a coating containing silver and a metal of the alkaline earth group.

19. An electron emitting cathode comprising an electrode containing silver, barium and strontium.

20. An electron-emitting cathode having a multi-layer coating, each of said layers containg a metal of the alkaline earth group and a noble metal.

21. The process of manufacturing an electron emitting filament which comprises coating a metallic core with an alkaline earth oxide, treating said filament with a volatilizable noble metal, and in removing said noble metal from said filament.

22. The process of manufacturing an electron emitting filament which comprises coating a metallic core with an alkaline earth oxide, treating said filament with a noble metal at a temperature below the volatilization point of said noble metal, and then heating said filament to a temperature above the volatilization point of said noble metal.

23. The process of manufacturing an electron emitting filament which comprises coating a metallic core with an alkaline earth oxide, treating said filament with silver at a temperature below the volatilization point of silver, and then heating said filament to a temperature above the volatilization point of silver.

In witness whereof, I hereunto subscribe my name this 16th day of November, A. D., 1916.

CARL D. HOCKER.