May 26, 1936. J. R. WILSON ET AL 2,041,802

ELECTRON EMITTER

Filed June 30, 1933

FIG. 1

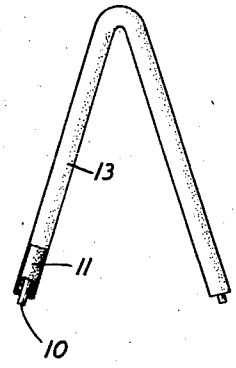


FIG. 2

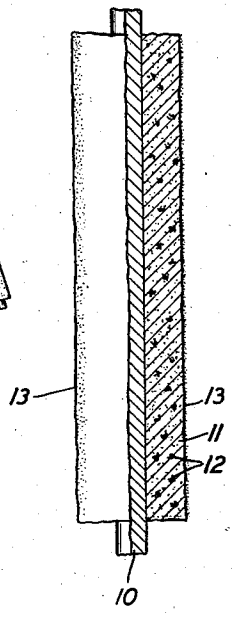


FIG. 3

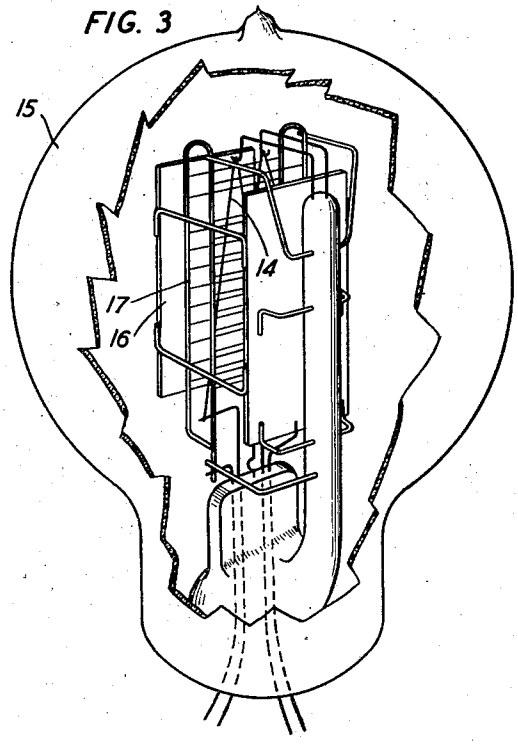
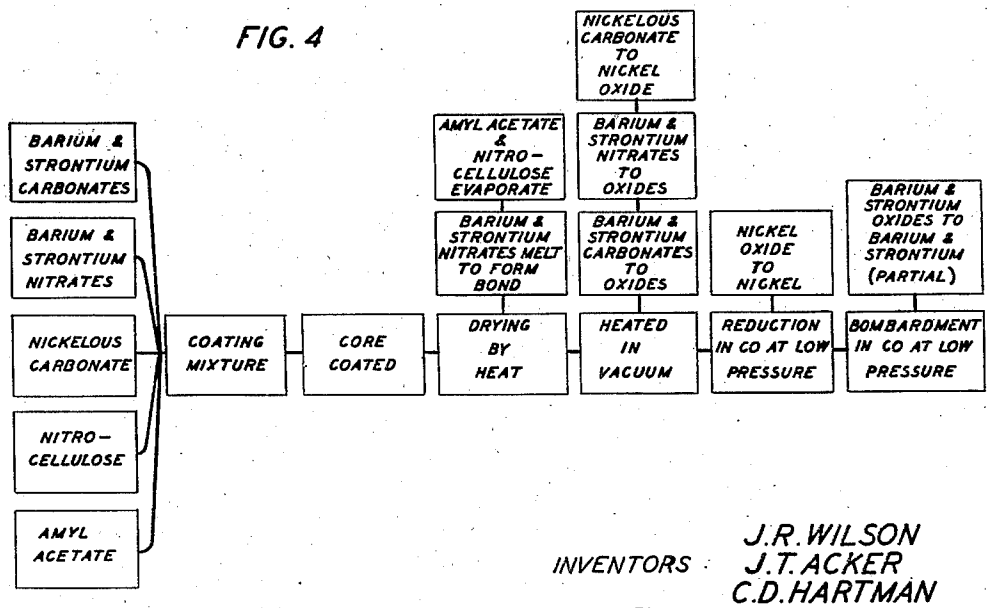


FIG. 4



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UNITED STATES PATENT OFFICE

2,041,802

ELECTRON EMITTER

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11 Claims. (Cl. 250—27.5)

This invention relates to electron emitters and more particularly to electron emitting cathodes of the coated type used in thermionic discharge and space discharge devices.

The well known dull emitter or oxide coated cathode has been, for a number of years, produced in two characteristic types, known as the "uncombined" type and the "combined" type.

The "uncombined" cathode comprises a metallic carrier or core of platinum, platinum alloy, nickel or nickel alloy coated with barium and strontium compounds of the type which can be easily decomposed by heat to the oxides. When this cathode is mounted in an enclosing vessel with the usual cooperating electrodes of an electron discharge device, the vessel evacuated, and the cathode heated, the compounds decompose to the oxides of barium and strontium with no chemical combination with the metallic carrier or core. This type of cathode has the white appearance of the oxides of barium and strontium.

The "combined" cathode comprises a metallic carrier or core of platinum, platinum alloy, nickel or nickel alloy coated with barium and strontium compounds of the type which can be easily decomposed by heat to the oxides. The coated carrier or core is heated in air to a high temperature, approximately 1100° C., which causes (1) the barium and strontium compounds to decompose to the oxides and (2) a portion of the barium and strontium oxides, the oxygen of the air and a portion of the material of the carrier or core to combine chemically to form complex compounds on the surface of the core which are dark grey or black in appearance. When this type of cathode is mounted in an enclosing vessel with the usual cooperating electrodes of an electron discharge device, the vessel evacuated, and the cathode heated, the complex compounds decompose to give the oxides of barium and strontium and finely divided core material. This cathode retains its dark appearance due to the finely divided core material dispersed throughout the barium and strontium oxides. Upon further treatment under appropriate conditions in the evacuated vessel both types of cathodes can be made thermionically active by the formation of small amounts of alkaline earth metals, notably barium. The thermionic characteristics of these cathodes depend largely upon these small amounts of alkaline earth metals in association with the matrix of oxides and, in the case of the "combined" type, also in association with the finely divided metal from the core.

In the case of the "uncombined" cathode thermionic activation results from the ordinary processes of outgassing the cathode and heating the anode and other cooperating electrodes by induced high frequency currents. In the case of the "combined" cathode thermionic activation is attendant upon a bombardment process in which the anode and other cooperating electrodes are maintained at a positive potential in order to draw space current in a gas at low pressure. The resulting bombardment of electrons and ionized gas on the electrodes causes heating and outgassing of the parts and simultaneously enhances the supply of thermionically active material in the cathode.

Thermionic devices using these types of cathodes are subject to loss of thermionic activity with use due to the loss of active material, i. e; barium metal, from the surface of the coating. The adequacy with which this surface is maintained or replenished with active material from a reserve supply in the coating matrix determines the emission activity of the cathode and the length of its useful life.

In this connection it should be noted that the "combined" cathode has in the past exhibited a superior characteristic of long life and this fact has been attributed to the presence of finely divided core material in the oxide coating which acts as a reservoir for active material. The "combined" cathode, however, has not been applicable to many uses due to limitations of coating and activation techniques. The "combined" cathode technique described above involves the heterogeneous reaction between the core surface, oxygen of the air and the solid barium and strontium oxides and the subsequent diffusion of the complex compounds, from the surface of the core to within the body of the remaining oxides. This process is also a function of the time and temperature of treatment and is difficult to control, hence the amount and state of dispersion of finely divided core material in the coating matrix after activation varies within wide limits. Moreover, the composition of the core material predetermines the kind and the amount of finely divided core material in the activated cathode, hence the process is limited in application. Furthermore the coating technique is not readily applicable to all shapes and sizes of desired cathodes. The method of activating this type of cathode is difficult to control, time consuming and inapplicable in many cases, notably in vacuum tubes employing a multiplicity of control electrodes and in vacuum tubes employing the equi-potential type of cathode.

With the above ideas in mind, this invention is concerned with an electron emitter of the coated type which is not subject to the limitations of fabrication, activation and application of the "combined" type and which has characteristics of life and thermionic emission superior to those of the present so-called "combined" and "uncombined" types.

An object of this invention is to increase the operating life of oxide coated electron emitters.

Another object of this invention is to obtain saturation efficiency of emission from oxide coated emitters with low power consumption.

A further object of this invention is to obtain optimum dispersion of active material in the coating matrix of the emitter.

In accordance with this invention any refractory metal suitable for a cathode may be used as the carrier or core on which the coating is formed or deposited. A coating mixture is prepared which comprises compounds of alkaline earth metals and a compound of a metal or compounds of metals of the eighth group of the periodic system of chemical elements suspended with a binder in a suitable suspending medium. A binder is added to promote the ease of handling the cathode during the fabrication of the electron device. The binder decomposes or disappears during the subsequent heat operations. This mixture is coated or sprayed onto the carrier or core. The coated carrier or core is then heated at a low temperature to evaporate the suspending medium and cause the binder to function but not at a sufficiently high temperature to cause chemical combination between the mixture and the carrier or core material. The coated carrier or core is then mounted in an enclosing vessel with the usual cooperating electrodes of an electron discharge device. The vessel is then evacuated and the cathode heated so that the compounds are decomposed to oxides. The oxide of the metal of the eighth group, which is now finely dispersed throughout the coating, is reduced in situ by means of a reducing gas whereby the metal is uniformly dispersed throughout the oxides of alkaline earth metals in a definite amount and in a definite state of dispersion. Upon electron bombardment in carbon monoxide, a portion of the alkaline earth oxides is reduced to alkaline earth metal which diffuses in and through the matrix of alkaline earth oxides and the free metal of the eighth group where it is deposited on or alloyed with the constituents of the matrix. It can be seen that by this invention, a definite and reproducible cathode of the coated type can be produced which has the optimum characteristics of thermionic activity and long life.

As a specific example of the invention, a triadic composition of barium and strontium carbonates and nickelous carbonate is mixed with a suitable organic binder, such as nitrocellulose, and a suitable organic solvent, such as amyl acetate, which gives a suspension of the proper viscosity for readily coating or spraying the type of carrier or core on which the coating is to be formed. The coated carrier is then heated at a low temperature to remove the solvent. The cathode is then mounted in a vessel and processed as outlined above to make a thermionically active cathode.

In another specific application of the invention barium and strontium nitrates are added to the above mixture to form a low temperature fusible bond for the carbonates. In this case the coated carrier is then treated at a low temperature to remove the solvent and then at a higher temperature to fuse the nitrates. These temperatures, however, are not high enough to cause chemical combination with the carrier or core material.

In a further specific application of the invention, a mixture of barium and strontium carbonates and nickelous carbonate is suspended in a solution of water and barium and strontium nitrates which gives a suspension of the proper viscosity for readily coating or spraying the type of carrier or core on which the coating is to be formed. The coated carrier is then heated at a low temperature to evaporate the water and then at a higher temperature to fuse the nitrates. These temperatures, however, are not high enough to cause chemical combination with the carrier or core material. The cathode is then mounted in a vessel and processed as outlined above to make a thermionically active cathode.

This invention will be more clearly understood from the following detailed description in connection with the accompanying drawing.

Fig. 1 illustrates a coated filament made in accordance with this invention.

Fig. 2 is an enlarged view of a portion of the filament shown in Fig. 1 with a quarter sector cut away and shown in cross-section to illustrate the complex matrix of this invention.

Fig. 3 illustrates a discharge device of the three electrode type embodying an emitter made in accordance with this invention and

Fig. 4 is a diagrammatic arrangement showing the various steps of the coating and transformation process of one form of the invention.

In accordance with one aspect of this invention, the objects previously set forth are accomplished by forming a matrix on the cathode core or surface 10 which includes alkaline earth oxides 11, such as barium and strontium, a metal of the eighth group 12, such as nickel, in a free state and crystalline form, dispersed throughout the oxides, and free metallic barium or barium and strontium 13 in the matrix and on the surface thereof.

The metal 12 distributed through the oxides, primarily is introduced in the coating as a compound and serves as a depository surface for free barium in the coating or on the surface thereof and the barium either is alloyed with or is adsorbed on the nickel particles. In effect, the free nickel is covered with a skin layer or film of metallic barium. In view of the large number of particles in the oxide coating and their dispersed positions between the particles of oxides, it is evident that a large amount of free barium is always in reserve in the coating and this barium is supplied by diffusion to the surface to replace the film of barium depleted during operation of the emitter.

The adequacy with which this surface is maintained or resupplied from a reserve supply in the coating matrix determines the emissive activity of the emitter and the length of life or duration of time the emitter may be considered as emitting a copious supply of electrons. The amount of surface barium and the concentration thereof will depend upon and be in equilibrium with the volume concentration of barium and nickel within the matrix.

Another advantage of the dispersion of nickel throughout the matrix is the elimination of bright spots in the emitter. This is chiefly due to the separation or dispersion of the free nickel in the oxides whereby fusion of the nickel is avoided.

While nickel has been specified as a preferable metal for association with the alkaline earth

oxide, other metals of the eighth group, singly or in combinations, may prove equally as good, such as iron, cobalt, palladium or platinum or nickel-platinum, etc. Furthermore, the invention is not limited to the inclusion of alkaline earth oxides or metals with the other metallic element since the alkaline earth metals and oxides may be replaced by alkali metals, rare earth metals, and their oxides, or other thermionically active substances.

It should be realized that when an electron emitter is mentioned in this specification it is intended that the emitter may be employed in a variety of forms depending on the purpose for which it is to be used. For instance an incandescent or directly heated emitter may be the common form of a filamentary conductor. An indirectly heated type may be an equipotential surface. And a cold emitter or cathode may be a metallic electrode which is rendered active by a suitable potential in combination with a conducting gas or vapor.

In order to secure the advantages of this invention and to realize the long life of the emitter, the following description is given to illustrate more clearly how the invention may be practiced, but it is to be understood that the proportions are merely suggestive and the invention is not to be bound thereby.

A filamentary emitter 10, such as a fine wire or ribbon core of nickel, platinum, or alloy thereof is preferably preglowed in a vacuum oven to remove deleterious matter and occluded gases and then subjected to an annealing temperature treatment in an atmosphere of hydrogen. The treated wire or ribbon may be coated or provided with any number of layers by dipping or spraying with a suspension of a coating mixture which may be prepared as follows:

	Grams
Barium carbonate	255
Strontium carbonate	300
Barium nitrate	50
Strontium nitrate	100
Nickelous carbonate	40

The vehicle used for such a suspension may be water of the proper proportions to give a wet mixture of the viscosity to suit the type of core to be coated. Instead of water the vehicle may be an organic binder, such as cellulose nitrate dissolved in amyl acetate. The mixture should be continually agitated during the coating of the filmentary core to secure a uniform distribution and to prevent settling of the nitrates or carbonates. Nickelous carbonate is recommended because this compound is stable at ordinary temperatures, but at the elevated temperatures used in discharge devices, it is easily reduced to the oxide and metal. Furthermore, it is readily obtained in pure form and requires no extraordinary precautions in handling. Under proper conditions many other nickel salts or compounds or compounds or salts of the other metals in the eighth group of the periodic system which can be easily reduced to an oxide or metal may be used.

By varying the amount of nickelous carbonate in the original mixture, filaments can be produced having different black body constants thereby making it possible to produce filaments with any desired power characteristic in shapes and sizes hitherto impossible. In the above mixture the ratio of nickelous carbonate to barium and strontium carbonates is substantially 1 to 18.

After the filament is coated it is heated only to a low temperature to drive off the suspension vehicle. The coated filament 14 is then heated in an inert atmosphere up to 675° C. to fuse the barium and strontium nitrates and form a flux or bond between the core and the coating material. At this temperature, no chemical combination with the core material occurs. The coated filament 14 may be mounted in a vessel 15 with its cooperating electrodes, such as an anode 16 and grid 17 as shown in Fig. 3. The vessel is then connected to an evacuating system including the usual baking oven enclosing a header which is connected to a mercury aspirator pump backed with a mechanical oil pump. A liquid air trap may be inserted in the system. The vessel 15 is baked for a suitable length of time to remove water vapor and other gases given off at low temperatures from the vessel after which a suitable low pressure can be obtained in the vessel by means of the vacuum pumps. The emitter is then glowed at the proper temperature in vacuum, to decompose the nickelous carbonate to nickel oxide. The plate and grid of the device are heated to a temperature just below the point where evaporation of nickel would darken the vessel. This heating may be accomplished by bombardment or by heating the plate and grid by induced high frequency current. This heat treatment is continued for five minutes. During this process the emitter is outgassed by heating to a temperature whereby the barium and strontium carbonates and nitrates are decomposed to the oxides. After the above transformations have occurred in the matrix, and a high degree of vacuum obtained in the device, the emitter is activated by bombardment in carbon monoxide at a low pressure and simultaneously heating the emitter for about ten minutes at approximately a 50 per cent increase in the normal operating current. During this activating treatment the nickel oxide is reduced to free nickel and some of the barium oxide is reduced to free barium and this free barium is adsorbed on the surface of the emitter while the remainder of the barium is alloyed with or is adsorbed on the free nickel dispersed throughout the coating matrix.

The initial incorporation of the nickel in the form of a compound results in the final product of a finely divided depository for the free barium in the matrix, to serve as a reservoir for replenishing the barium on the surface of the emitter which is gradually depleted during operation. The free nickel in the oxide matrix tends to increase the initial quantity of free barium since the barium is readily alloyed with or adsorbed by the nickel. The free nickel also promotes the retention of the barium within the coating matrix and tends to effect an optimum surface configuration for the highest thermionic efficiency of the emitter.

While the emitter of this invention may be activated by the method heretofore described, other advantageous results may be obtained by activating the emitter in accordance with the process disclosed in a Patent No. 2,019,504 issued November 5, 1935, to C. H. Prescott, Jr. In this application the coated emitter is activated by glowing the emitter in an atmosphere of a hydrocarbon gas or vapor, such as methane, at reduced pressure. In this process the hydrocarbon reacts with the barium and strontium oxides to produce free barium and strontium in and upon the oxide matrix. In this process, which is known as chemical activation, the free metal is dispersed throughout the

oxide matrix and is adsorbed upon or alloyed with the free nickel which serves as a large depository for the barium. When the chemical activation process is used in connection with the complex matrix emitter of this invention, the activating gas is removed by further pumping of the device to a low pressure and then the device is sealed off the header of the pumping station.

The primary consideration in the production of an emitter of high thermionic efficiency in accordance with this invention is to obtain an optimum dispersion of finely divided free metal or metals throughout the coating matrix, and in fact, the total radiant emissivity of the emitter corresponds roughly to the degree of metal dispersion. In the coating matrix of this invention, the ratio of free metal, such as nickel, to barium and strontium oxides is approximately 1 to 24. This ratio has been found to give the optimum thermionic emission and life. It is of course understood that this ratio may be varied when certain other factors become more controlling than optimum emission and life.

What is claimed is:

1. A coating composition for the production of thermionically active emitters comprising carbonates of barium and strontium, nickelous carbonate, and a binder material.

2. A coating composition for the production of thermionically active emitters comprising carbonates of barium and strontium, nitrates of barium and strontium, a carbonate of nickel, and a fluid binder of nitro-cellulose in amyl acetate.

3. The method of producing a thermionically active emitter which comprises coating a core suitable for an emitter with compounds of alkaline earth metals and a compound of metals of the eighth group, fourth series, of the periodic system, subjecting said core to a heat treatment to decompose the alkaline earth and eighth group compounds to oxides, and reducing the eighth group metal oxide to metal in vacuum.

4. The method of producing thermionically active emitters which comprises coating a core suitable for an emitter with compounds of alkaline earth metals of low and high fusing points and a compound of a metal of the eighth group, fourth series, subjecting said core to a preliminary heating to fuse said alkaline earth compounds of low fusing point, heating said core in a vacuum to convert the eighth group metal compound to oxide, heating said core in vacuum to decompose said high fusing point alkaline earth compounds to oxides, and reducing said eighth group metal oxide to metal with carbon monoxide in a vacuum.

5. The method of producing thermionically active emitters which comprises coating a core suitable for an emitter with nitrates and carbonates of alkaline earth metals and a carbonate of the eighth group of the periodic system, subjecting said core to a preliminary heating to fuse the nitrates of alkaline earth metals, heating said core in vacuum to decompose the alkaline earth compounds and eighth group carbonate to oxides, and reducing the eighth group metal oxide to metal with carbon monoxide in a vacuum.

6. The method of producing a thermionically active emitter which comprises coating a core suitable for an emitter with barium, strontium and nickelous carbonates, decomposing the nickelous carbonate to nickel oxide, decomposing the barium and strontium carbonates to oxides, and reducing the nickel oxide to nickel in the presence of carbon monoxide.

7. The method of producing a thermionically active emitter which comprises coating a core suitable for an emitter with barium, strontium and nickelous carbonates, decomposing the nickelous carbonate to nickel oxide, decomposing the barium and strontium carbonates to oxides, reducing the nickel oxide to free nickel in an atmosphere of carbon monoxide, reducing barium oxide to metallic barium in the same atmosphere, and associating the metallic barium with the nickel.

8. The method of forming layers on a filamentary core with a coating suspension of barium, strontium and nickelous carbonates which comprises agitating the coating suspension during application to maintain a relative proportion of nickelous carbonate to barium and strontium carbonates, dispersing the nickelous carbonate throughout the layers of barium and strontium carbonates, decomposing the nickelous carbonate to oxide in the absence of decomposition of the barium and strontium carbonates, decomposing the barium and strontium carbonates to oxides, converting the nickel oxide to metallic nickel to the exclusion of reduction of barium and strontium oxides, and subsequently reducing part of the barium and strontium oxides.

9. The method of coating an electron emitter with a coating suspension of barium and strontium nitrates and barium, strontium and nickelous carbonates which comprises agitating the coating suspension during application to maintain a relative proportion of nickelous carbonate to barium and strontium carbonates, heating the coated emitter at a low temperature in air to fuse the barium and strontium nitrates, heating the emitter to convert the nickelous carbonate to nickel oxide, heating in vacuum to change the barium and strontium carbonates to barium and strontium oxides, heating the emitter in a reducing atmosphere of carbon monoxide at a low pressure to reduce the nickel oxide to free nickel, and heating the emitter in the same atmosphere to a higher temperature to reduce some of the barium oxide to free barium which is associated with the free nickel.

10. The method of forming electron emitters which comprises coating a core with different compounds of alkaline earth metals having high and low melting points and a compound of a metal of the eighth group of the periodic system, heating the coated cathode at a low temperature to fuse the low melting point compounds of alkaline earth metals, heating the core in vacuum to a higher temperature to convert the eighth group compound to oxide, heating the core in vacuum to a higher temperature to decompose the high melting point alkaline earth compounds to oxides, and reducing the eighth group oxide to metal with the aid of a reducing gas in vacuum.

11. A cathode comprising a core metal, an uncombined coating matrix having combined characteristics on said core metal, said matrix consisting of barium and strontium oxides, finely divided particles of nickel dispersed throughout the oxides, a reservoir supply of free barium absorbed on said nickel particles, and an atomic layer of barium on the surface of said matrix.

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