

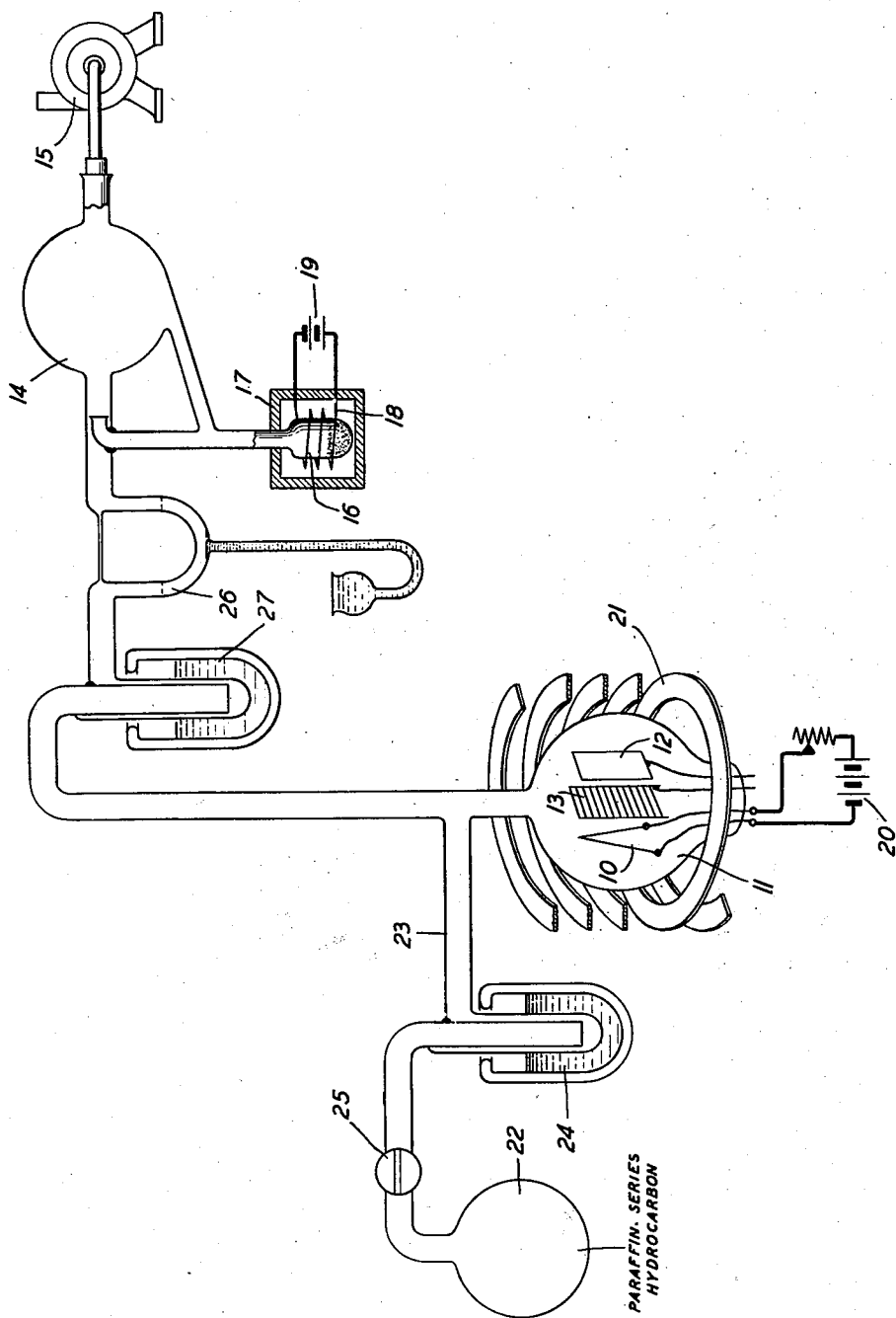
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ACTIVATION PROCESS FOR ELECTRON EMITTERS

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ACTIVATION PROCESS FOR ELECTRON
EMITTERS

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This invention relates to an activation process for electron emitters and more particularly to thermionic cathodes of the oxide-coated type used in vacuum and gas-filled discharge devices.

5 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 metal 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.

55 In the case of the "uncombined" cathode ther-

mionic activation results from the ordinary processes of outgassing the cathode and heating the anode and other cooperating electrodes, for example, 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 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 emissive 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 of 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 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 amount of finely divided core material in the activated cathode, hence the process is limited in application.

The changes in thermionic activity with time which occur in this type of emitter depend largely upon operating conditions, such as temperature, anode potential and heating current supplied to and space current drawn from the emitter. But the effect of these operating conditions will depend greatly on the chemical and physical composition of the coating. The operating temperature will control such factors as the rate of evaporation of

alkaline earth metal from the surface, and its replenishment by the diffusion of more alkaline earth metal from the lower layers of the oxide matrix. Other operating conditions will control such factors as gas evolution and cleanup and their concomitants of poisoning and positive ion bombardment. The initial condition of the active surface depends, of course, upon its preparation and involves such vital factors as the total quantity of alkaline earth metal in the oxide matrix and the state of division and aggregation of the various components of the oxide matrix.

Although the instantaneous activity of the cathode is doubtlessly associated with the configuration of the extreme surface, and transient variations in activity should be associated with changes in this configuration, the end of the useful life of an oxide-coated cathode or emitter is very probably due, except for mechanical failure, to the gradual depletion of the reservoir of alkaline earth metal within the oxide matrix. To this end, any features should be of advantage which tend to increase the initial quantity of alkaline earth metal, to promote the retention of this free metal within the oxide matrix or to effect an optimum surface configuration for the highest thermionic efficiency.

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

Another object of the invention is to increase the thermionic efficiency of oxide-coated emitters.

A further object of the invention is to provide a more reproducible and more easily controllable activation process by the straightforward use of chemical reactions in or with the oxide coating.

In accordance with this invention an oxide-coated electron emitter is prepared by coating a suitable core or carrier with alkaline earth salts or compounds such as carbonates, hydroxides, or nitrates held in suspension or solution in an organic vehicle or water. The coating is decomposed by heating to form the oxides. The emitter is then glowed at reduced pressure in an atmosphere of a hydrocarbon gas or vapor, such as methane. The extent of reduction and the quantity of alkaline earth metal produced by this method of activation can definitely be determined by the time and temperature of the filament glowing and the gas pressure.

The reduction method of this invention may also be employed for activating a complex matrix or coating on a suitable core in which a finely divided free metal of the eighth group of the periodic table of the elements is dispersed through the barium and strontium oxides. In this form of the invention the free metal of the eighth group is partially or wholly reduced prior to the introduction of the carbonaceous reducing agent into the activation process. Since the reduction of the barium and strontium oxides to free metal is directly accomplished chemically, the free metal is dispersed throughout the oxide coating and may be adsorbed upon or alloyed with the free metal of the eighth group, such as nickel, which serves as a large depository surface for the free barium. The coating, therefore, is a matrix of barium and strontium oxides, finely divided free nickel dispersed throughout the oxides, and free metallic barium and strontium adsorbed on the geometrical surface and also upon the surfaces of the various particles of oxides and free metal in the matrix as well as very possibly alloyed with the particles of free nickel.

The process of activation of this invention may be employed to produce a composite thermionic

emitter involving other materials than alkaline earth metals and an eighth group metal. Such an emitter would involve an active metal, a finely divided metal of lower vapor pressure on which the active metal is adsorbed or with which it is alloyed, and an oxide of the active metal or a mixture of oxides containing the oxide of the active metal. For instance the emitter may have a composite coating consisting of a matrix of free thorium, free molybdenum and thorium oxide. Similarly rare earth metals may constitute the active metal of the matrix and be employed with tin or any other suitable free metal less volatile than the active metal. Of course the oxides of the rare earth metals are also included in the matrix, and are the source of the active metal prepared by the activation process of this invention.

The invention will be more clearly understood from the following detailed description in connection with the accompanying drawing which illustrates an arrangement of suitable apparatus for accomplishing the results of this invention.

Referring to the drawing, an electron emitter 10 is arranged in an enclosing vessel 11 with suitable cooperating electrodes such as an anode or plate 12 and a grid or control electrode 13. The emitter 10 which is of the oxide-coated type may consist of a suitable core material, such as nickel, platinum, or an alloy thereof, having a coating of barium and strontium carbonates or other compounds which have been coated on the emitter or filament from a solution or suspension of carbonates in water or an organic vehicle with or without a suitable binding material such as nitrates of alkaline earth metals. The vessel is connected to a suitable evacuating system including a mercury aspirator pump 14 backed by a mechanical pump 15. The mercury aspirator pump is provided with the usual reservoir of mercury 16 enclosed in a chamber 17 for confining the heat generated by a heating element 18 surrounding the mercury reservoir. The heating element may be supplied with current from a suitable source, such as a battery 19. The emitter 10 is shown in the form of a filamentary conductor adapted to be heated to incandescence by a suitable battery 20, but it is to be understood that the invention is not limited to the particular form of the emitter since the emitter may assume other configurations such as an equi-potential surface or a cold surface which emits electrons under the influence of a positive ion discharge. The electrodes within the vessel 11 may also be denuded of gas by surrounding the device with a high frequency induction coil 21 to induce current in the electrodes to heat them to sufficient temperature to drive out the gases. It is, of course, understood that with the use of a high frequency coil the electrodes should preferably be of cylindrical form to be easily raised to the desired denuding temperature. The plate and grid may also be connected together to a source of positive potential to cause heating of the plate and grid by electron bombardment from the filament to denude the plate and grid of gases which are drawn out by the pumps. A reservoir 22 containing a hydrocarbon of the paraffin series, such as methane, is connected to the vessel 11, to inject a supply of the reducing gas into the vessel 11 to activate the coating on the emitter 10. The supply of the gas is passed through a communicating tubing 23 and a liquid air trap 24 is inserted between the reservoir 22 and the vessel 11. A suitable cut-off valve 25 is provided in the out-

let of the reservoir 22 to cut off the supply of the gas when not required.

In order to set forth the advantages of the improved activating process of this invention a specific pumping routine will be explained whereby the results of this invention may be realized. The vessel 11 with the coated emitter 10 and the other electrodes is sealed to the pumping station including the aspirator pump and the oil pump and executed to less than 10^{-4} millimeters of mercury. After this pressure is attained in the vessel 11 a baking oven is placed around the vessel to heat the vessel to a temperature just below the softening point of the glass of the vessel. The emitter 10 is then heated to a glowing temperature to decompose the carbonates to oxides and during this treatment the emitter is out-gassed by gradually increasing the heating current until the gas evolution ceases. The plate and grid are then heated, preferably by induced high frequency current, by the coil 21 to an incandescent temperature. This is continued for five minutes and during the last minute the filament is again out-gassed. During these various steps the pumps are continually withdrawing the gases evolved by the electrodes and when a working vacuum is obtained, the electrodes are allowed to cool and a valve 25 is opened and the hydrocarbon gas, such as methane, is flowed through the station and the vessel 11. The flow of methane gas is throttled just ahead of the aspirator pump 14 by a partial mercury cut-off 26 to promote a more uniform pressure of the order of .01 millimeter of mercury throughout the exhaust system. A liquid air trap 27 is also included in the system between the vessel 11 and the cut-off 26. During this treatment the filament is glowed for a short time at approximately 50% above the operating current.

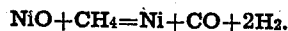
In this activating process free barium is prepared by direct chemical reduction. The methane gas decomposes and deposits carbon upon and in the emitter coating which subsequently reacts with the barium and strontium oxides. It is possible that the methane gas may react directly with the alkaline earth oxide, but the results are quite the same in both cases and the overall reaction would be: $\text{BaO} + \text{CH}_4 = \text{Ba} + \text{CO} + 2\text{H}_2$ and $\text{SrO} + \text{CH}_4 = \text{Sr} + \text{CO} + 2\text{H}_2$. The possible intermediate reaction would be: $\text{CH}_4 = \text{C} + 2\text{H}_2$ and $\text{BaO} + \text{C} = \text{Ba} + \text{CO}$ and $\text{SrO} + \text{C} = \text{Sr} + \text{CO}$.

The vessel 11 is then thoroughly re-evacuated and the filament glowed for a few minutes at or above the temperature used during the period that the filament is subjected to the methane treatment, to finally out-gas the filament and stabilize the activity. The vessel 11 is then sealed off the pump. The thermionic activity of the emitter 10 develops during the carbonization or activating step and as the device is aged under normal operating conditions it exhibits a high degree of thermionic activity and prolonged life.

A distinct advantage of this activating process is the control of the activation by means of the degree of carbonization which is definitely determined by the time and temperature of the filament glowing and the pressure of the activating gas. Methane gas is preferred since it is the only hydrocarbon which will not condense in liquid air. It may be possible to use other hydrocarbons, for instance, acetylene gas, but in this instance it will be necessary to remove the liquid air traps during the carbonization process. Likewise, other carbon-producing substances which will chemically react with the barium and

strontium oxides of the emitter may be used to reduce the oxides to free metal and thereby activate the filament.

The activating process of this invention may also be applied to a complex emitter such as disclosed in the application of J. R. Wilson—J. C. Acker—C. D. Hartman, Serial No. 678,426, filed June 30, 1933. In this application a metal of the eighth group of the periodic table, for instance, nickel, is dispersed throughout the oxide coating and when the emitter is activated in accordance with the carbonization process of this invention the reduction treatment not only reduces the barium and strontium oxides, but also positively reduces any remaining nickel oxide or nickel compounds which have not previously been reduced. The chemical reaction for the reduction of nickel oxide would be as follows:



A particular advantage of this invention in the use of a hydrocarbon rather than some other reducing agent is that the oxides of carbon are gaseous and no foreign materials are introduced by its use. Another advantage is that the full reducing effect of a gaseous hydrocarbon may be obtained, since its use may be deferred until the carbonates, the most convenient alkaline earth materials for coating, and decomposed to the oxides.

Because of the positive nature of the activating process by carbon reduction it is possible to build up a large initial amount of active material, namely, free barium, in the oxide matrix of the emitter and this supply of free barium is conducive to long life for the emitter. By control of the surface configuration of the emitter which is determined by the composition of the matrix as a whole, it is possible to obtain a high thermionic efficiency for this type of emitter. This high thermionic efficiency may be used to increase the range of temperature saturation in a discharge device, in which range the space current is independent of filament temperature. In other words, with the improved emitter of this invention it is possible to obtain more current at the same temperature, or the same current at lower temperature than with other types of oxide coated emitters. It is also possible to get an optimum dispersion of both the eighth group metal and the alkaline earth metal throughout the structure of the coating matrix in the emitter of the above mentioned application.

What is claimed is:

1. The method of activating an alkaline earth oxide-coated cathode which comprises enclosing the cathode in a vessel, evacuating said vessel to a high degree, introducing a material yielding free carbon upon thermal decomposition, heating said cathode, and completing the activation by chemically combining the free carbon with the alkaline earth oxides coated on the cathode to form free alkaline earth metal in and on the coating.

2. The method of activating a cathode coated with alkaline earth oxides which comprises enclosing the cathode in an evacuated vessel, introducing a reducing hydrocarbon gas into the vessel, and heating the cathode to effect direct chemical action between the oxides and the reducing gas.

3. The method of activating an oxide-coated cathode which comprises subjecting a cathode having a coating including barium and strontium oxides to an atmosphere of a hydrocarbon gas of

the paraffin series at reduced pressure, and heating the cathode to produce free carbon which reacts chemically with the barium and strontium oxides to form free barium and strontium.

5 4. The method of activating oxide-coated cathodes of the barium and strontium oxides type which comprises subjecting the cathode to an atmosphere of methane gas at reduced pressure, and producing direct chemical reaction between
10 the methane gas and the barium and strontium oxides to reduce the oxides to free barium and strontium.

5. The method of activating an oxide-coated cathode having free nickel dispersed throughout
15 barium and strontium oxides which comprises subjecting the cathode in vacuum to an atmosphere of a hydrocarbon gas of the paraffin series, heating said cathode, producing chemically free carbon, converting some of the barium oxide to
20 free barium, and depositing said barium upon the free nickel dispersed in said oxides.

6. The method of activating a cathode coated with alkaline earth compounds having a compound of the eighth group of the periodic table
25 of the elements dispersed throughout the alkaline earth compounds which comprises inserting the cathode in an enclosing vessel, decomposing the compounds to oxides, evacuating the vessel to a high degree, reducing the eighth group oxide to
30 free metal, injecting methane gas in said vessel, and heating said cathode to a temperature considerably above normal for a definite time interval to chemically reduce some of the oxides present in the coating.

7. The method of activating a cathode coated with alkaline earth compounds having a compound of the eighth group of the periodic table
35 dispersed throughout the alkaline earth compounds which comprises inserting the cathode in an enclosing vessel, evacuating the vessel to a high degree, decomposing the compounds to oxides, reducing the eighth group oxide to free
40 metal, injecting methane gas in said vessel, heating said cathode to a temperature considerably above normal for a definite time interval to chemically
45 reduce some of the oxides present in the coating, and heating the cathode at a higher temperature to stabilize the emission properties of the coated cathode.

8. The method of activating a cathode having a coating including barium and strontium oxides which comprises inserting the cathode in a vessel, evacuating the vessel, heating the cathode to
5 the out-gassing temperature, injecting a supply of methane gas in the vessel at low pressure, simultaneously heating the cathode above the out-gassing temperature, removing the gas, evacuating the vessel to a higher degree, heating the cathode
10 to stabilize the activity of the coating, and sealing the vessel.

9. The method of activating a cathode having a coating including barium and strontium oxides which comprises inserting the cathode in a vessel, evacuating the vessel, out-gassing the cathode by
15 heating, injecting methane gas into the vessel to a pressure of the order of 0.01 millimeter of mercury, heating the cathode at approximately 50% above the operating current, re-evacuating the vessel, and glowing the cathode to stabilize the
20 activity of the cathode.

10. The method of producing a thermionically active cathode having a complex coating matrix including an active metal, a finely divided metal
25 of lower vapor pressure and an oxide of the active metal which comprises inserting the cathode in a vessel, evacuating the vessel, out-gassing the cathode, and injecting a hydrocarbon gas of the paraffin series into said vessel at a low pressure
30 to activate the cathode by reducing some of the oxide to active metal and associate the active metal with the metal of lower vapor pressure.

11. The method of producing an active cathode having a complex coating matrix including an active metal, a finely divided metal of lower
35 vapor pressure and an oxide of the active metal which comprises, enclosing the cathode in a vessel, evacuating the vessel, out-gassing the cathode, introducing methane gas into the vessel at a low pressure to produce the active metal by
40 reduction of some of the oxide and depositing the active metal on the metal of lower vapor pressure and the surface of the cathode, re-evacuating the vessel, and stabilizing the activity of the cathode
45 by heating in vacuum.

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