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3,004,816

HYDROGEN BREAKDOWN OF CATHODES

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2 Sheets-Sheet 1

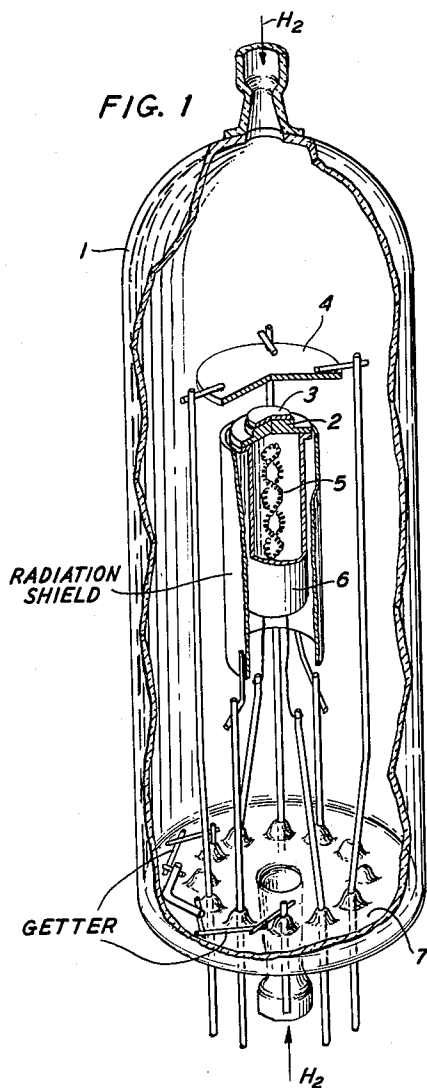


FIG. 1

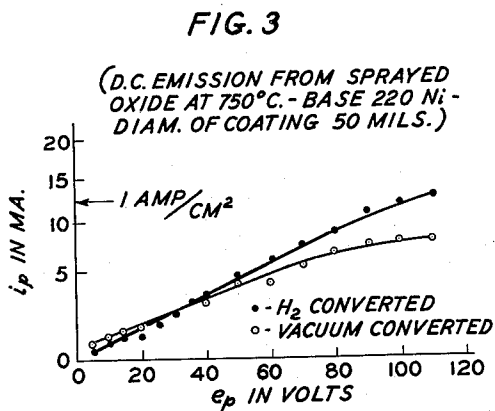


FIG. 3

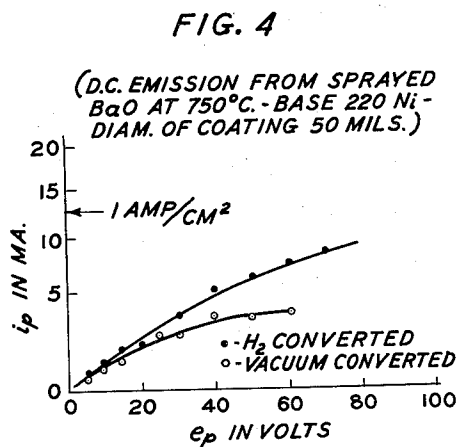


FIG. 4

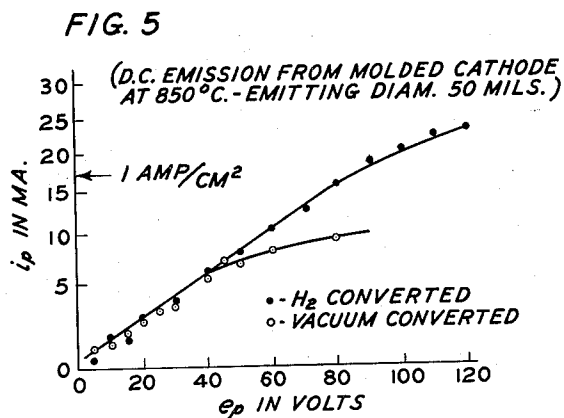


FIG. 5

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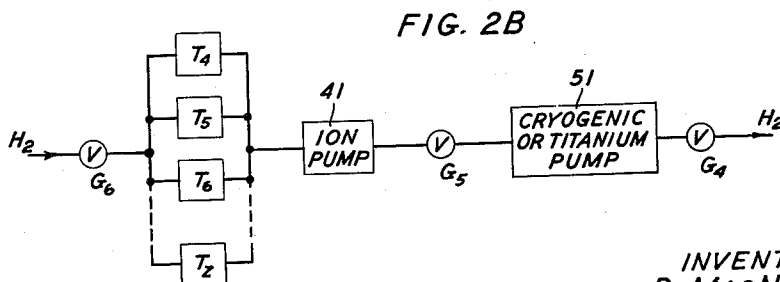
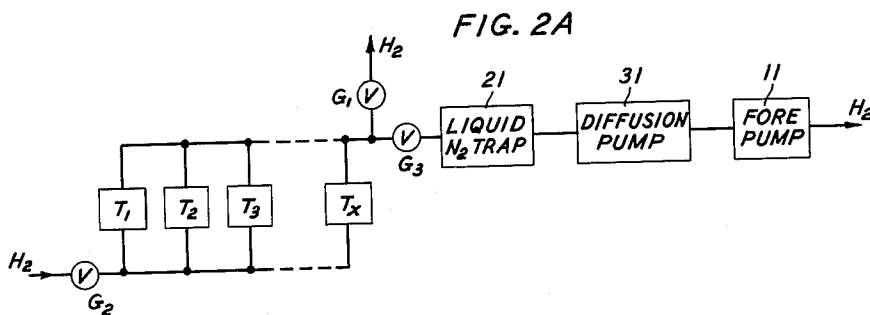
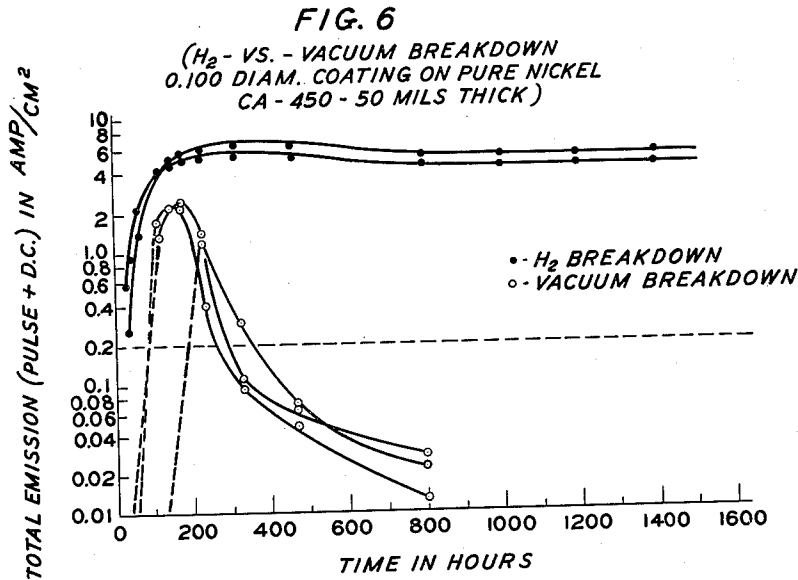
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HYDROGEN BREAKDOWN OF CATHODES

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HYDROGEN BREAKDOWN OF CATHODES

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3 Claims. (Cl. 316-8)

This invention relates to a method for processing the cathode emissive surfaces of thermionic tubes.

There are two fundamental types of cathode structure in commercial use at this time, each of which may be processed in accordance with the method set forth herein. The first of these, and the most conventional (sprayed oxide), typically consists of a nickel base having a coating of an alkaline earth metal oxide generally including barium oxide. A second type of structure, described in United States Patent 2,543,439 (molded or sintered cathode), includes a molded element which is made of a pressed and fired mixture generally of nickel powder together with a compound of the same alkaline earth metal.

Cathodes which contain the alkaline earth carbonates are normally processed by converting the carbonates to the oxides in a vacuum at temperatures ranging from 850-1100° C. During this conversion the environment within the enclosing envelope is predominantly oxidizing and due to the close spaced geometry of many of our present-day structures this oxidizing ambient can easily attack not only the cathode base but also other electrode elements such as beam formers, grids, accelerators and even anodes to the detriment of overall performance.

Heretofore, the processing of assembled tubes containing either sprayed oxide or molded cathodes has been done in two steps. The alkaline earth carbonates are first reduced to their respective oxides by vacuum heating and then the cathodes are activated by drawing current. In brief, a typical prior art breakdown procedure consists of sealing the element on a vacuum station which is evacuated to a pressure of the order of 10^{-7} millimeters of mercury. The cathode is then heated at a temperature of the order of 950° C. until the carbonates are broken down to the oxides. This heating procedure, which may take of the order of 5-30 minutes for an emitting layer thickness of approximately 1-4 mils, is terminated when substantially all of the carbonates are broken down. The breakdown point is indicated by a sudden drop in pressure within the chamber. The cathode is then heated to about 1000° C. and is held at this temperature for about 5 minutes. The temperature of the structure is dropped to about 850° C. where the total current is then measured by direct current or pulse measurement.

According to those methods employed in the prior art carbon dioxide is liberated at pressures which are usually sufficient to oxidize the cathode nickel base as well as other metallic surfaces in the cathode. Thus, during the conversion the atmosphere within the tube envelope is oxidizing and this oxidizing condition tends to degrade the overall performance of the electron emitter.

Normally, sprayed cathodes are converted in a matter of minutes although in some close spaced structures longer times may be necessary. However, when a molded cathode is being converted the breakdown period is generally of the order of 20-40 minutes which is caused by the large amounts of material employed, the higher densities of the pressed materials and the pore structure of this cathode. It has been determined that this same structure may be completely converted according to the method as set forth hereinbelow in a time period of the order of 5-15 minutes.

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In accordance with the present invention, cathodes which contain the alkaline earth carbonates are processed by converting the carbonates to the oxides in an atmosphere consisting essentially of hydrogen, a reducing atmosphere, although inert ingredients may be added for other reasons discussed. The utilization of a reducing atmosphere has been found to enhance the workable emission level of thermionic tubes converted according to conventional prior art techniques by a factor of as high as two. It has also been determined that cathodes can be converted at lower temperatures and as will be indicated hereinbelow, other beneficial effects may be derived from this processing.

The object of this invention will be more fully understood and others will become apparent from the description of the invention, which will be made with reference to the accompanying drawing, forming a part of the specification, and wherein:

FIG. 1 is a schematic front elevational view of a diode structure processed in accordance with the invention;

FIG. 2A is a diagram of a pump station employing fore and diffusion pumps in accordance with the processes herein;

FIG. 2B is a diagram of a pump station employing an ion pump and a cryogenic or titanium pump in accordance with the processes herein;

FIG. 3 on two-thirds power paper is a graphical representation of total emission in amperes per square centimeter against plate voltage in volts, showing emission levels obtained from both a vacuum and hydrogen converted barium-strontium-calcium oxide sprayed cathode on 220 grade nickel, a nickel of 99.00+ percent purity containing various activators such as silicon, titanium, aluminum, magnesium, calcium and manganese;

FIG. 4 on two-thirds power paper is a graphical representation of total emission in amperes per square centimeter against plate voltage in volts, showing emission levels obtained from both a vacuum and hydrogen converted barium oxide sprayed cathode on 220 grade nickel;

FIG. 5 on two-thirds power paper is a graphical representation of total emission in amperes per square centimeter against plate voltage in volts, showing emission levels obtained from both a vacuum and hydrogen converted barium-strontium oxide molded cathode; and

FIG. 6 on two-thirds power paper is a graphical representation of total emission in amperes per square centimeter against time in hours, showing the life data for cathode coatings on pure nickel for both a hydrogen and a vacuum treated thermionic tube.

A general outline of a method suitable for use in the manufacture of a thermionic tube in accordance with the method of this invention is set forth below. Certain operating parameters and ranges as well as the type of materials employed are indicated.

Any of the powdered emitting mixtures well known in the preparation of sprayed and molded cathodes may be employed. These materials contain a barium compound which will break down on a vacuum station to yield barium oxide. In general this compound is a carbonate. Such materials include the single carbonate material, barium carbonate; the double carbonate material, coprecipitated barium-strontium carbonate; and the triple carbonate material, coprecipitated barium-strontium-calcium carbonate. In general, it has been found that the double carbonate is to be preferred over the single and that little further advantage is gained by use of the triple carbonate. The double carbonate most commonly available for this purpose is a coprecipitant of equimolar portions of barium carbonate and strontium carbonate.

In addition to the carbonates listed above, there may be added to the emitting mixture a binder material. The binder is considered to function as an adherent and suit-

able materials for this purpose are well known to those skilled in the cathode art. Common binder materials which will operate satisfactorily include nitrocellulose or acetone solutions of stearic acid or isobutylmethacrylate. Binders are added to the mixture in minium quantities to assure maximum density and to avoid possible contamination due to impurities contained therein.

Referring again to the figures, FIG. 1 is a schematic front elevational view of a diode structure utilized in the processing herein described. Such structure includes outer envelope 1, containing cathode element 2 which is disk shaped of outside diameter of approximately 200 mils, having a thickness of approximately 50 mils and having an emissive surface 3 which is disk shaped, of a diameter of 100 mils and is 25 mils distant from anode element 4. The cathode is heated by a heater element 5, said heater element being enclosed within tube 6. Paired electrical leads make connection with heater 5, cathode 2 and anode 4, respectively, and pass through glass base 7 which is hermetically sealed with envelope 1. Reference is made to FIGS. 2A and 2B in the general description of the inventive process.

As shown in FIG. 2A tubes T_1 - T_3 - T_x are sealed to the station and forepump 11 is started, stopcocks G1 and G2 being closed and stopcock G3 being open. The tubes are then pumped to a pressure of the order of 10^{-3} millimeters of mercury within a time period ranging from 5-10 minutes after which liquid nitrogen trap 21 is filled in order to avoid back diffusion of mercury. Diffusion pump 31 is then started and the pressure in the system is reduced to a pressure of the order of 10^{-6} - 10^{-7} millimeters of mercury in about 30 minutes. Stopcock G3 is closed, isolating the tubes from the pumps. Stopcock G2 is opened admitting dry hydrogen to the system and stopcock G1 is opened permitting hydrogen to flow through the tubes. The hydrogen is flushed through the system for 5-10 minutes at a flow rate of from 100 cubic centimeters to one liter per minute. The cathodes are then heated with hydrogen flowing by means of internal heaters (not shown) so that in about 5-10 minutes the cathodes reach a temperature of 1000° C. The tubes may be heated individually or all may be heated simultaneously by connecting the heater in series. It is during this hydrogen treating step that the barium carbonate, barium-strontium carbonate or barium-strontium-calcium carbonate is reduced to the oxide form. The heating power is then turned off and the cathode allowed to cool to room temperature with hydrogen flowing for a period of 5 minutes. At this point the system may be flushed with dry nitrogen as a safety precaution so that the hydrogen will not be pulled through the mechanical pump. With nitrogen flowing, stopcock G1 is closed, stopcock G2 is closed and stopcock G3 is open so as to evacuate gas from the system. The tubes are then pumped until a pressure of the order of 10^{-6} - 10^{-7} millimeters is reached. The cathodes are reheated to a temperature of the order of 900 - 950° C. in about 5 minutes in order to eliminate occluded gases after which tubes are cooled to room temperature, the getter flashed and the tubes sealed.

An alternative method of processing and pumping the tubes is shown in FIG. 2B wherein tubes T_4 - T_6 - T_x are sealed to a station having an ion pump 41 and a cryogenic or titanium pump 51. In accordance with this method, the system is flushed with hydrogen for 5-15 minutes with stopcocks G4, G5 and G6 open at a flow rate of 100 cubic centimeters to one liter per minute. The cathodes are then heated with hydrogen flowing by means of internal heaters (not shown) so that in about 5-10 minutes the cathodes reach a temperature of 1000° C. The tubes may be heated individually or all may be heated simultaneously by connecting the heater in series. The heating power is then turned off and the cathode is allowed to cool to room temperature with hydrogen flowing for a period of 5 minutes. Stopcocks G4 and G6

are closed and cryogenic or titanium pump 5 is started thereby lowering the hydrogen pressure in the system to a pressure of the order of 10^{-2} - 10^{-3} millimeters of mercury. Stopcock G5 is then closed and ion pump G4 started after which the tubes are pumped until a pressure of the order of 10^{-6} - 10^{-7} millimeters of mercury is attained. The cathodes are then reheated to a temperature of the order of 900 - 950° C. in about 5 minutes in order to eliminate occluded gases. The tubes are then cooled to room temperature, the getter is flashed and the tubes are sealed.

The hydrogen breakdown treating is generally carried out at a temperature in the range of 750 - 1000° C. although temperatures below 750° C. may be employed. However, when the temperature is maintained below 750° C., 100 percent decomposition of the carbonate to the oxide form does not occur within practical time limits. When operating over the preferred range of 750 - 1000° C., 100 percent decomposition of the carbonate to the oxide occurs within a time period of the order of 5-75 minutes, the shorter times corresponding to the higher temperatures.

It is essential that the gas employed during the conversion be dry since the presence of moisture converts the thin oxide film into the corresponding hydroxide. It is therefore preferable to employ dry hydrogen containing less than one part per million of water.

The use of hydrogen itself is a hazard, however, this hazard can be minimized by using a mixture of hydrogen and an inert material such as argon, helium or nitrogen. It has been found that as little as 15 percent hydrogen may effectively be employed when using such mixtures.

The emission data presented in FIGS. 3, 4 and 5 is for cathodes having an emitting area of 0.050 inch which permits the drawing of high currents without overheating either the anode or the cathode.

FIG. 3, on two-thirds power paper, on coordinates of total emission in amperes per square centimeter against plate voltage in volts, shows the emission level obtained from both a vacuum and hydrogen converted barium-strontium-calcium oxide cathode on 220 grade nickel at 750° C. It is seen that the hydrogen converted cathode is able to sustain a maximum emission level of at least one ampere per square centimeter (corresponding with a plate potential of 87 volts) whereas the vacuum treated cathode is limited to about 700 milliamperes per square centimeter (corresponding with a plate potential of about 80 volts). The hydrogen converted cathode gave a continuing current increase as the plate potential increased so that within one hour it was completely active and able to furnish one ampere per square centimeter.

FIG. 4, on two-thirds power paper, on coordinates of total emission in amperes per square centimeter against plate voltage in volts, shows the emission levels obtained from both a vacuum and hydrogen converted barium oxide sprayed cathode on 220 grade nickel at 750° C. It can be seen that the hydrogen converted cathode proved far superior to the vacuum cathode. At a temperature of 750° C. the emission level of the former is of the order of 800 milliamperes per square centimeter compared to about 300 milliamperes per square centimeter for the latter.

FIG. 5, on two-thirds power paper, on coordinates of total emission in amperes per square centimeter against plate voltage in volts, shows emission levels obtained from both a vacuum and hydrogen converted barium-strontium oxide molded cathode at 850° C. It can be seen that hydrogen treatment enhances the workable emission level by at least a factor of two. At a temperature of 850° C. the emission level of the hydrogen treated cathode is of the order of two amperes per square centimeter whereas a similar treatment by vacuum yields an emission level of the order of one ampere per square centimeter.

FIG. 6, on two-thirds power paper, is a graphical rep-

resentation of total emission in amperes per square centimeter against time in hours and shows the life data for the .100 inch diameter cathode coating on pure nickel prepared in accordance with the procedure shown in FIG. 2A. This data was compared with that obtained by processing a diode identically to the manner shown in FIG. 2A with the exception that a vacuum breakdown was employed. Total emission is plotted against time and is measured by applying a 400 volt, 6μ second square wave with a repetition rate of one pulse per second. The pulse is superimposed directly over the steady state direct current operating conditions. The hydrogen treated tubes activated to 5-6 amperes per square centimeter in about 200 hours and continued at high levels of total emission for over 1500 hours whereas the vacuum control tubes reached a peak emission of 1-2 amperes per square centimeter at about 175 hours and dropped off rapidly to terminate life at about 300 hours. The results obtained clearly demonstrate that the oxide coatings converted in an atmosphere of flowing hydrogen show significantly better total emission characteristics than coatings converted in vacuum. It is seen also that a given emission level is more rapidly attained with hydrogen treatment.

In order that those skilled in the art may more fully understand the inventive concept herein presented, the following examples are given by way of illustration and not limitation.

Example I

Two diodes were prepared using a 220 grade nickel base having thereon a machine sprayed triple carbonate (barium-strontium-calcium oxide) coating of a thickness of .001 inch and a coating density of 0.7 gram per cubic centimeter. The weight of the coating was 5 milligrams per square centimeter. One tube was processed in hydrogen on the apparatus shown diagrammatically in FIG. 2A. Although the temperature was raised to 1000° C., breakdown was initiated over a lower range as discussed. The other tube was processed according to conventional prior art vacuum techniques and the emission levels for both tubes were determined at an operating temperature of 750° C. The results of these tests showed that the emission level of the hydrogen converted diode was of the order of one ampere per square centimeter whereas the vacuum converted diode produced an emission level of 0.6 ampere per square centimeter for the same operating conditions.

Example II

The procedure of Example I was repeated with the substitution therein of a single carbonate (barium) coating on 220 grade nickel. The results of the emission tests showed that the hydrogen converted diode produced an emission level of 0.6 ampere per square centimeter whereas the vacuum converted diode produced an emission level of 0.25 ampere per square centimeter at 750° C.

Example III

The procedure of Example I was repeated with the substitution therein of a double carbonate (barium-strontium) coating on 220 grade nickel. The results of the emission tests showed that the hydrogen converted diode produced an emission level of one ampere per square centimeter whereas the vacuum converted diode produced an emission level of 0.6 ampere per square centimeter at 750° C.

Example IV

Two diodes were prepared using molded cathodes which had been prepared by adding 0.2 gram of zirconium hydride powder of an average particle size of 15 microns to 20 grams of carbonyl nickel powder of an average particle size of 150 microns and of a chemical purity of 99.9 percent by weight. The powders were mixed in a

mortar and pestle for 10 minutes. To this there was added 20 cubic centimeters of acetone in which was dissolved 0.4 gram of isobutyl methacrylate as mixing was continued. The powders were mixed for about 30 minutes after which time all of the acetone had evaporated. An emitting mixture was flowed by dry mixing 3 grams of alkaline earth double carbonate (coprecipitated barium-strontium carbonate) in a mortar and pestle with 7 grams of the nickel mix prepared as above. The molded cathodes were completed by firing and sintering. The emitting surface of the cathodes contained a mixture, in weight percent, of 30 percent double carbonate, 68 percent pure nickel and 2 percent zirconium hydride and had a pressed coating area 50 mils in diameter and a thickness of 5 mils. One tube was processed in hydrogen according to the method as shown diagrammatically in FIG. 2A, breakdown of the carbonate to the oxide occurring at a temperature of 1000° C. The other tube was processed according to conventional prior art vacuum techniques and the emission levels for both tubes were determined at an operating temperature of 850° C. The results of these tests showed that the emission level of the hydrogen converted diode was of the order of 1.50 amperes per square centimeter whereas the vacuum converted diode produced an emission level of 0.6 ampere per square centimeter.

It will be understood by those skilled in the art that the thickness of the cathode coating may vary from .0005 inch to .004 inch. The .0005 inch coating is generally a high density coating (1.5 grams per cubic centimeter), the actual weight of which is about 2.5 milligrams per square centimeter. The .001-.002 inch coatings are of low density (0.5-0.9 gram per cubic centimeter) and the actual weight is of the order of 5.0 milligrams per square centimeter.

The hydrogen treatment as set forth herein applies equally as well to sprayed oxide coated cathodes as to the molded cathodes. The molded cathode because of the large amount of carbonate present and its complex pore structure is more susceptible to the adverse oxidizing environment present during breakdown than is so with the sprayed oxide cathode. With hydrogen conversion this oxidation is largely eliminated and therefore the nickel particles which make up the cathode and which are in contact with the carbonates remain oxide free.

As will be evident to those skilled in the art, many variations and modifications can be practiced within the scope of the disclosure and claims to this invention. It is seen that the invention resides in a method whereby cathodes containing the alkaline earth carbonates are converted to their respective oxides in a hydrogen atmosphere rather than by the conventional vacuum method.

What is claimed is:

1. The method of processing an assembled thermionic tube containing a cathode, the latent emissive surface of which comprises at least one alkaline earth carbonate, which comprises the steps of flowing a gas consisting essentially of dry hydrogen through said tube at a temperature in the range of 750-1000° C. thereby reducing said carbonate to the oxide and evacuating said tube.

2. The method according to the procedure of claim 1 wherein said cathode is heated at a temperature from 750-1000° C. for a time period in the range of 5-75 minutes, the shorter times corresponding to the higher temperatures.

3. The method of claim 1 wherein said gas consists of a mixture of hydrogen and an inert gas.

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