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J. W. MARDEN ET AL
 PRODUCTION OF ALKALI METAL TUBES
 Filed Oct. 27, 1927

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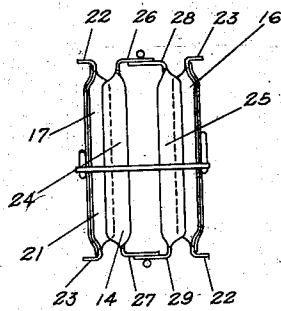


FIG. 2.

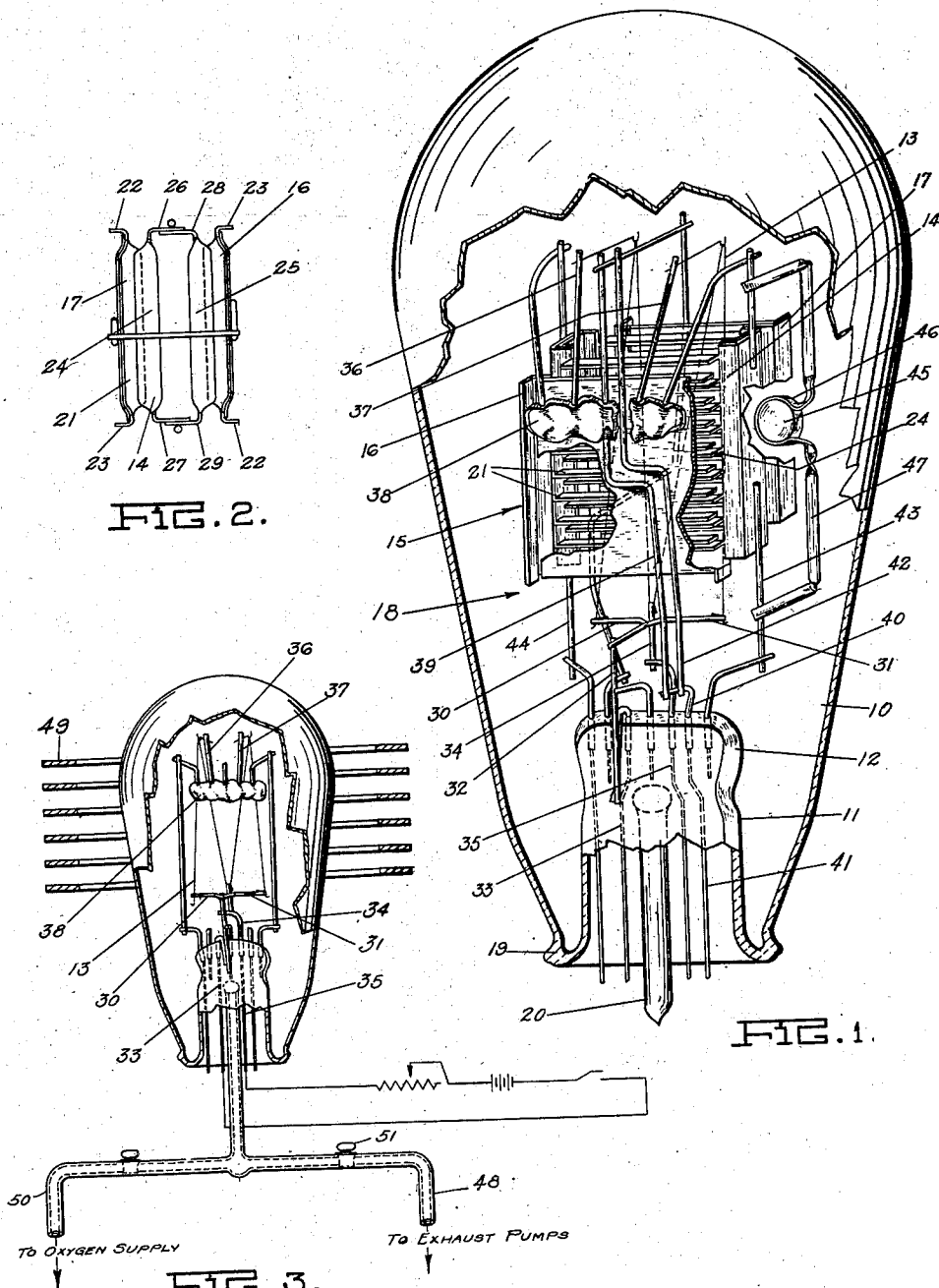


FIG. 1.

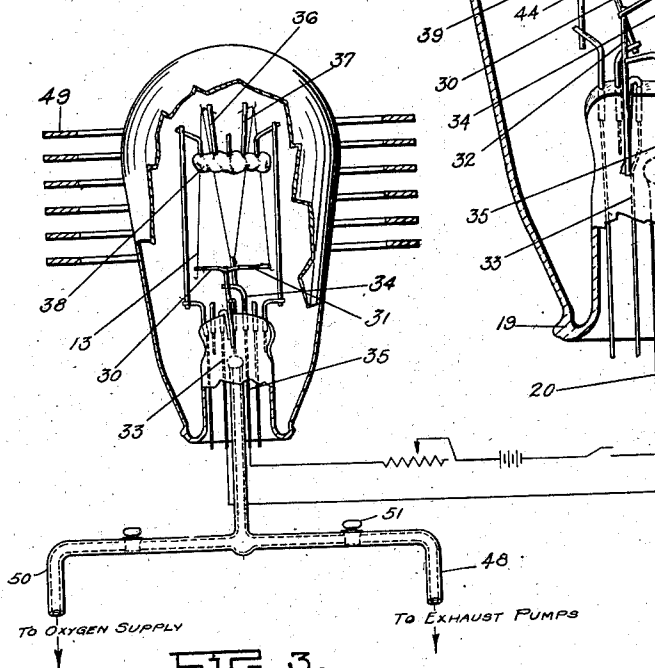


FIG. 3.

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PRODUCTION OF ALKALI METAL TUBES

Application filed October 27, 1927. Serial No. 228,994.

This invention relates to a vacuum electric device employing a thermionically active cathode and more particularly to such a device in which thermal emission is imparted to the cathode by the presence of an alkali metal vapor such as caesium, rubidium or the like.

It has been found that the alkali metals under proper conditions greatly increase the electron emission of a refractory metal cathode such as a tungsten cathode in a thermionic device so that high electron emissivity is imparted thereto at a temperature so low that in the absence of such alkali metal vapor no substantial emission would occur. This phenomenon is explained on the theory that a film of the alkali metal forms continuously on the refractory metal body, as for instance a filament, which film resists evaporation at temperatures much in excess of the vaporization temperature of the alkali metal when the refractory cathode consists of a suitable metal such as tungsten or molybdenum.

The formation of the alkali metal film, preferably caesium, is greatly facilitated by the presence of an electro-negative gas on the surface of the refractory body. Oxygen has been most successfully used in this connection and when an oxide or an oxygen film is produced on the surface of the tungsten or molybdenum body it renders this body capable of holding on to or causing the alkali metal atoms to adhere thereto, more strongly than does the plain surface of the tungsten or molybdenum electrode.

In the construction of devices of this nature, difficulty has been encountered due to the sensitivity of this active film of alkali metal which serves as the electron-emitting material and to the ease with which the oxide or oxygen layer produced on the tungsten or molybdenum is destroyed, as by the presence of hydrocarbon or other reducing materials in the device. The alkali metals are extremely active and if the proper precautions and methods of construction are not carefully followed, the alkali metal will completely combine with impurities, etc., and will not be effective for accomplishing the desired results.

One of the objects of the present invention is to provide a method of producing electron discharge devices employing alkali metal cathodes which will have a high emission at a relatively low cathode temperature, a long life and uniform operating characteristics.

A further object is to provide a mode of manufacturing tubes employing alkali metal cathodes in which the alkali metal will be maintained in a highly active state.

A still further object is to provide a method of producing an electron discharge device employing a thermionically active cathode and of producing and maintaining on said cathode an active film of an alkali metal.

A further object is to provide a method of rendering a refractory metal body thermionically active by the formation thereon of an active deposit of an alkali metal such as caesium.

Other objects and advantages will hereinafter appear.

In order that this invention may be more fully understood, reference will be had to the accompanying drawing in which:

Fig. 1 illustrates, partly in section, an electron discharge device of the hot cathode type employing an alkali metal for imparting electron emission to the cathode thereof;

Fig. 2 is an end view of the plate and control electrode structure shown in Fig. 1; and,

Fig. 3 is a diagrammatic illustration of the tube shown in Fig. 1 in connection with the gas supply and exhaust connections employed in the manufacture thereof.

The discharge device shown in the figures includes a bulb 10 having a flare tube 11 provided with the usual press 12. Extending from the press are a plurality of support-members for securing the several electrodes in position as will be more clearly hereinafter described.

The electrode assembly includes a filament 13, a control electrode or grid 14 and a plate electrode or anode which is designated as a whole by the numeral 15 and which is composed of two plate-members 16 and 17 disposed on opposite sides of the control electrode 14. The electrodes are secured to the support wires extending from the press and

constitute the mount 18. The flare tube 11 having the mount 18 thereon is sealed to the bulb 10 at the juncture 19 and the bulb may be exhausted through an appropriate exhaust tube 20 which extends from the interior of the flare tube.

Each of the plate members 16 and 17 of the plate electrode or anode 15 is composed of a ladder-like structure having a plurality of horizontal rungs or vanes 21 in the form of flat metallic strips struck out from a plain sheet of metal and connected at their ends to support-members 22 and 23 (see Figure 2) integral therewith. The vanes 21 are arranged in parallel spaced relation and in planes substantially transverse to the support-members 22 and 23 so that when the plate-members are in position the edges of the vanes will be positioned toward the filament.

The grid-member 14 includes a set of vanes 24 and 25 connected to support-members 26, 27 and 28, 29 respectively, arranged so as to hold the vanes in spaced relation to form a lattice-like enclosure.

The vanes 21 of the plate and the vanes 24 and 25 of the control electrode or grid are disposed in spaced overlapping relation. By reason of this construction, the filament or cathode is protected from positive ion bombardment due to the electric field produced between the vanes of the respective electrodes.

The filament 13 is of M-shape and is connected at its ends to arms 30 and 31 secured to a common support-member 32, sealed in the press 12 and connected to current conductor 33. The central loop of the filament is connected to a support-member 34 also sealed in the press and terminating in a conductor 35. The upper loops of the filament are engaged by resilient supports secured to arms 36 and 37 extending from a glass bead 38. This bead is secured to an upright member 39 attached to a support 40 sealed in the press. The support 40 is connected to a conductor 41 for supplying current to the plate electrode 15 through the rod 42.

The grid 14 is secured to supports 43 and 44 which extend upwardly through the press 12 and are welded to the side members 26 and 29.

In order to provide a supply of alkali metal in the device, a pellet 45 which may be composed of a compound of the alkali metal and a reducing agent is supported by a loop 46 in the metallic strip 47 secured to a suitable support as, for instance, the grid support 43. The pellet is supported in a loop in such manner that it may be readily heated by high frequency induction current to decompose the alkali metal compound and liberate the alkali metal as will be more fully brought out hereinafter.

The mechanical construction of this device forms the subject matter of a co-pending ap-

plication of the present inventors, Serial No. 228,995, filed October 26, 1927, and entitled Electron emission device.

The present invention is concerned more particularly with the procedure involved in the manufacture of the apparatus described and in accordance therewith, we prefer to thoroughly clean the anode and control electrode plates after they are formed and before mounting to remove as far as possible the oxygen, oxides, grease, impurities, etc., thereon by baking these parts in hydrogen gas for a sufficient period, usually 5 to 10 minutes, at a relatively high temperature, that is, around 1000° C. The cleaned and deoxidized plates and grid parts are then mounted together with the tungsten or molybdenum filament 13 upon a previously formed press. After mounting, if the filament has not been previously cleaned, it should be cleaned and straightened by flashing the same in an inert gas, such as forming gas, (composed of hydrogen and nitrogen, the latter being in the proportion of about 80%) for a short time, that is, from four to five seconds, at a temperature of about 1400° C. This step has been conveniently carried out in a bell jar with a slow stream of forming gas flowing there-through. This procedure cleans the filament so that the oxygen or oxide film may be more readily produced thereon in a subsequent operation.

During the handling and mounting of the plates and grids, these members become more or less contaminated with grease from the fingers, etc. It has been found desirable to bake the completed mount at this point of the procedure for 30 minutes to one hour at about 300° C. in the air. This may be omitted but it has been found that accumulated grease and dirt are very largely removed in this manner either by volatilization or oxidation.

We next prefer to coat the press 12 and the glass bead 38 in which conducting wires are sealed with a material which serves to prevent electrical conduction between the elements of the tube. This electrical conduction usually called "leakage" is due to a deposit of the alkali metal on the press and the bead. A material which we have found particularly effective for this purpose is petrolatum from which the volatile constituents have been removed as is more fully described in applicants' co-pending application Serial No. 218,138, filed September 8, 1927, and entitled Prevention of electrical leakage.

Briefly, this process consists in slowly heating commercial petrolatum up to about 380 to 400° C. for one-half hour while maintaining a pressure of one to two cm. which procedure removes the volatile gases and vaporizable impurities. A solution of 1 to 10% of this purified petrolatum residue in chloroform is made and is applied to the press and

bead in any convenient manner as by painting, spraying or the like.

In lieu of the petrolatum coating, we may use a coating of shellac or other resinous material as set forth in co-pending application of Emil G. Widell, Serial No. 30,662, filed May 16, 1925, and entitled Electron discharge device. However, in using shellac, greater precaution must be taken during the exhaust operation and we prefer to employ the petrolatum solution as the leakage preventor.

After the complete mount has been sealed into the bulb 10, the same may be exhausted through the exhaust connection 48 (see Fig. 3). The bulb in the meantime, being baked to a temperature of about 300° C. when employing petrolatum on the press and bead or to about 220 to 250° C. when employing shellac on these glass parts. The exhaust process is, of course, continued until no further gas comes from the envelope, but ordinarily should be completed in about ten minutes, depending upon the pumps employed.

It should be understood that the temperature and time of baking are inter-dependent. For example, baking for ten minutes at 300° C. gives about the same degree of exhaust as baking at 400° C. for three to four minutes provided that the vacuum pumps employed are rapid enough to remove the gases during a shorter higher temperature treatment. In actual factory practice the higher temperature more rapid exhaust is to be preferred.

Since oxidizing conditions should, as far as possible, always prevail during the exhaust of the bulb, it is essential to have the grease baked out of the bulb and driven far enough away from the place where the exhaust tube is sealed off so that this grease is not vaporized back into the bulb during the sealing off process. In order to accomplish this, we prefer rather long exhaust tubes on the bulbs and to place the bulbs so that they are well up in the exhaust oven.

After exhaustion, the plate and grid electrodes are heated to as high a temperature as they may stand by high frequency induction current to drive out any gas contained therein. In heating these elements, however, they must not be subjected to a sufficient temperature to cause the press or the bead to attain an excessive temperature. The high frequency induction coil employed for treating out these electrodes is indicated at 49 in the position in which it should be employed with the construction illustrated.

Referring, for instance, to Figure 2, it will be noted that the grid electrode forms in plan view a complete loop, the two opposed sides being joined throughout their length by the integral end portions 26, 27 and 28, 29, thus the grid becomes highly heated by the high frequency induction current directly by induction and the plate electrode which is arranged relatively close thereto becomes heat-

ed by radiation. The gases liberated by this high frequency treatment are removed by the pump in the usual manner.

The next step in the manufacture of the tube is that of forming the electro-negative gas layer on the surface of the filament and this step is of extreme importance, since the life and emission of the filament is largely dependent upon the proper formation of such layer of electro-negative gas.

In carrying out this step, we admit oxygen through the stop-cock in the connection 50 at such pressure as to make 5 to 50 cubic mm. at atmospheric pressure available for the oxidation of the filament. The exact pressure depends upon the volume of the exhaust manifold and upon the number of tubes on the manifold. In any case, although the exact pressure of oxygen required by a filament is not very critical, we have found that best activation is obtained when 5 to 50 cubic mm. are allowed for each filament. Higher pressures can be used but due to excessive oxidation of the tungsten filament it is difficult to get predetermined filament voltages and currents under these conditions.

These conditions are suitable for the production of a tube having filament characteristics on operation of 1 volt and 60 ma. The filament weight in this case is about 1.5 to 2.0 m. g. per 200 mm. length. In case very much larger tungsten filament is used, larger quantities of oxygen are required.

The filament is flashed in this oxygen atmosphere at a temperature of around 2000° C. for about one-half minute. The effect of this high temperature flashing is to clean the filament thoroughly of any grease or hydrocarbons or other impurities which might otherwise react with the oxygen or oxide layer formed thereon. The filament after this cleaning operation becomes oxidized to a sufficient extent to cause the alkali metal which is subsequently liberated to adhere thereto very much more tenaciously than it would to the unoxidized filament.

If desired, the filament may be heated in vacuum and the oxygen admitted after such heating, inasmuch as the high temperature is not required for oxidation but merely for cleaning. In place of pure oxygen, ordinary atmospheric air may be used, but in such case, it is necessary to employ a pressure of from three to four times that for oxygen. A still further means for providing an oxygen supply for the filament may be by means of an appropriate compound of the alkali metal, which upon being heated, will liberate oxygen, as will more fully appear in connection with the step of flashing the alkali metal pellet 45.

Where only a small amount of alkali metal is introduced, it is sometimes desirable to permit the metal parts to cool after the high frequency treatment thereof before the

oxygen is admitted, since as these parts are still at a high temperature they will readily oxidize and during the subsequent operation or during the life of the device this oxide on the grid and plate combines with the alkali metal and destroys its effectiveness for rendering the filament thermionically active. We have found, however, that one minute permits sufficient cooling to prevent such action.

After the oxidation of the filament, the oxygen or air is pumped from the device and if desired, in order to insure the removal of any hydrocarbons or other impurities which may have been liberated from the filament during the flashing, the bulb may be flushed again with oxygen at substantially the same pressure. It is very essential to remove all reducing material from the bulb in order to protect the oxide layer on the filament. The above flashing is merely a precautionary measure to insure the retention of the oxide layer on the cathode.

After the complete removal of the oxygen from the bulb, we proceed to introduce the desired alkali metal, preferably caesium by heating the pellet 45 as by high frequency induction to decompose the alkali metal compound in the envelope. In heating the pellet 45, it will be noted that it has been disposed in such manner that the closed loop of which the metal strip 47 forms a part is arranged at right angles to the loop formed by the grid electrode so that the high frequency induction coil should be arranged with its axis substantially normal to the side wall of the bulb for the heating of this getter material. This is desirable, since care must be taken not to reheat the metal parts during the flashing of the getter at a sufficiently high temperature to drive any additional gas therefrom which might attack the oxide or oxygen layer formed on the filament. The composition of the pellet 45 which we have found to produce the best results is a mixture of caesium permanganate and silicon as the reducing agent therefor.

The caesium permanganate and silicon mixture may be employed as a source of oxygen for oxidizing the filament and in such case, instead of admitting oxygen to the bulb from an external source, the pumps are sealed off as by the valve 51 and the pellet heated to a low temperature to evolve oxygen therefrom by the decomposition of the caesium permanganate. After the desired gas pressure has been developed by the evolution of oxygen in this manner, the heating may continue at a high temperature to cause the caesium compound to react with the silicon to liberate caesium metal. The temperature required for this decomposition is around 900° C. but may be lowered somewhat by the addition of aluminum or similar material to the mixture. The oxygen liberated by the getter is removed

by the pumps after which the tube is sealed off and based.

It is necessary to now activate the filament, to impart thereto the electron emitting properties of the alkali metal. This activation we prefer to conduct in two stages, a preliminary activation being first effected to render the filament sufficient thermionically active to permit seasoning of the tube to be accomplished to ionize and clean up residual gas. The final activation is then produced.

In order to produce the preliminary activation, we heat the filament with or without any potential on the grid electrode or on the anode and with an excess of filament current over that for which the filament is normally designed. For example, with a filament designed for a 50 ma. normal filament current we flash the filament for about 10 seconds with 140 ma. current. The filament current is then reduced to normal, that is to 50 ma. and with a plate voltage of about 200 volts and a negative grid bias of about minus 17 volts applied thereto, the tube is operated for about ten minutes. This treatment ionizes the residual gas and enables it to be cleaned up. Precaution must be taken during this seasoning to maintain a negative bias on the grid in order to prevent positive ion bombardment of the filament which might destroy the caesium layer formed on the cathode.

The final activation is then effected by flashing the filament for about 20 seconds at 170 to 200 ma. filament current, preferably with no voltage applied between the electrodes. This final activation completes the formation of the caesium film on the cathode and imparts thereto high electron emitting properties.

While we have outlined a specific order for carrying out the various steps, it is to be understood that many changes may be made therein and in the details of many of these steps without departing from the invention and we do not desire to be limited to the specific details described.

What is claimed is:

1. The method of producing a thermionic discharge device employing an alkali metal as the active electron-emitting material which comprises cleaning and degasifying the electrodes by heating in hydrogen, assembling the electrodes upon a mount, baking the assembled electrodes for a period of several minutes under oxidizing conditions, flashing the filament in an inert environment to degasify the same, sealing the mount into an envelope, heating the electrodes in vacuum to a high temperature to drive the gases therefrom, heating the filament in an atmosphere of oxygen introducing an alkali metal into the envelope and heating said filament in the presence of said alkali metal vapor to cause said alkali metal to adhere thereto.

2. The method of activating refractory metal filaments in a closed container which consists in heating said filament to a high temperature in oxygen at substantially atmospheric pressure, removing said oxygen atmosphere and creating an atmosphere of an alkali metal vapor, heating said filament to about the normal temperature thereof in said vapor to cause the alkali metal to effect a partial activation of said filament, ionizing the residual atmosphere in said container and cleaning up the same and subsequently heating said filament to above the normal operating temperature to complete the activation thereof.

3. The method of activating a refractory metal filament in an electron discharge device having a cooperating electrode which comprises oxidizing said filament, generating an alkali metal vapor in said envelope, heating said filament in said vapor to partially activate the same, creating a discharge between said filament and cooperating electrode to ionize the gas in the envelope to clean up the same and subsequently heating said filament to an abnormal temperature to complete the activation thereof.

4. The method of producing a thermionic discharge device employing an alkali metal as the active electron-emitting material comprising cleaning the electrodes under oxidizing conditions, sealing the same into an envelope, heating the filament to a high temperature in an atmosphere of oxygen, removing said oxygen, introducing an alkali metal into the envelope and heating said filament to a high temperature in said alkali metal vapor to impart thereto the electron emissivity of the alkali metal.

5. The method of activating a refractory metal filament having an oxidized surface in a closed container which consists in heating said filament to a high temperature in the presence of an alkali metal vapor to partially activate the same, ionizing the residual gaseous content of said container and cleaning up the same by said alkali metal and subsequently heating the filament to a high temperature to complete the activation thereof.

6. The method of producing a thermionic discharge device employing an alkali metal as the active electron-emitting material, comprising assembling the electrodes of the device upon a mount, heating the said mount under oxidizing conditions at a temperature of about 300° C. for from 30 to 60 minutes, sealing said mount into an envelope, introducing oxygen into said envelope, heating the filament to about 2000° C. in said oxygen, removing said oxygen, generating an alkali metal in the envelope, heating said filament to a temperature of around 1400° C. for a few seconds in an inert or reducing atmosphere, heating said electrodes therein to a

high temperature to degasify the same, and heating said filament to an abnormal temperature in said alkali metal.

In testimony whereof, we have hereunto subscribed our names this 26th day of October, 1927.

JOHN W. MARDEN.
ERNEST A. LEDERER.

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