Nov. 8, 1927. 1,648,312

K. H. KINGDON ET AL.

ELECTRON DISCHARGE DEVICE

Filed Nov. 6, 1923

Fig. 1.

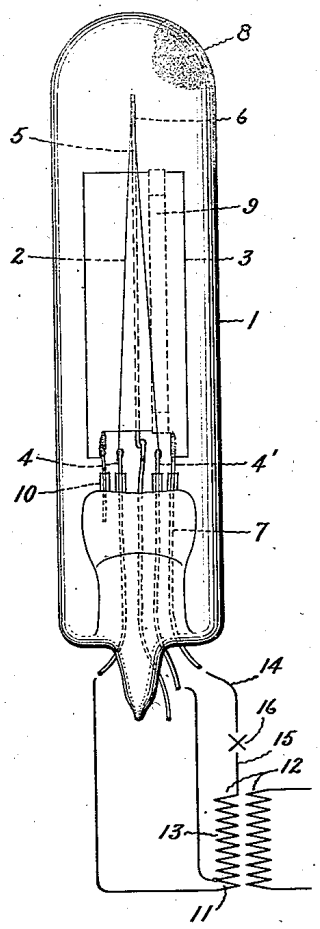


Fig. 2.

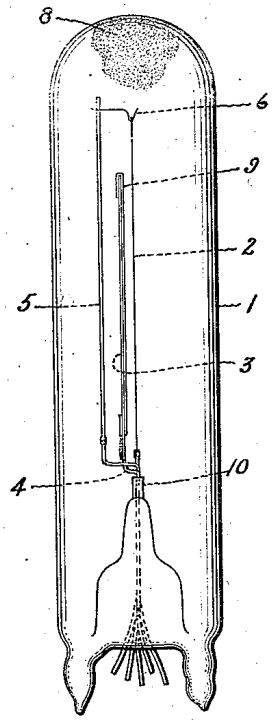


Fig. 3

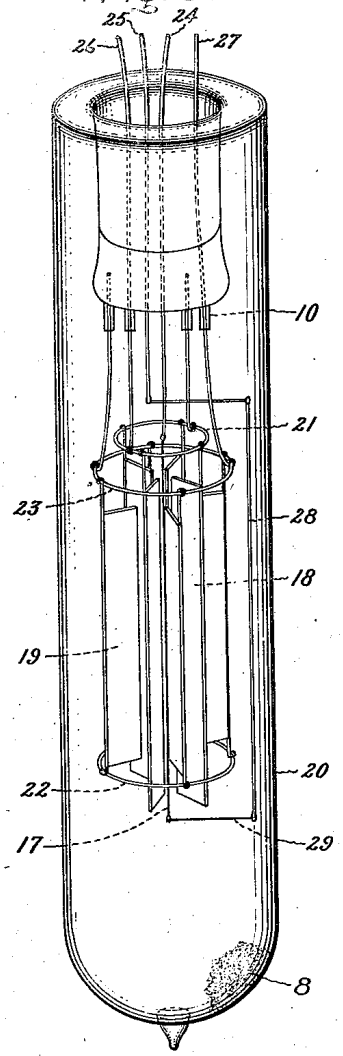
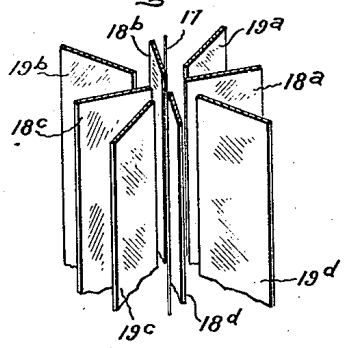


Fig. 4.



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UNITED STATES PATENT OFFICE.

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ELECTRON-DISCHARGE DEVICE.

Application filed November 6, 1923. Serial No. 673,165.

Our present invention relates to electron discharge devices, and especially to devices in which the discharge is carried principally by negative electrons in the absence of substantial ionization by collision.

When the vapor of an alkali metal, such as cæsium or rubidium, for example, is supplied to the space surrounding a hot cathode in a discharge device, an electron emission can be produced from the cathode under certain conditions which is much greater than that which would be produced in the absence of the alkali vapor. In a device containing a tungsten electrode and cæsium vapor at a pressure below that at which substantial ionization by collision will occur, it has been found that the temperature of the cathode at which the emission is at a maximum is in the neighborhood of 700° K. At higher vapor pressures, the permissible maximum cathode temperature progressively increases with a corresponding increase of electron emission.

This emissivity effect is apparently due to the continuous formation on the hot electrode of an adsorbed film of the alkali metal, the rate of evaporation of which is very much less than that of the pure alkali metal in bulk. The adsorbed film forms a surface which is capable of emitting electrons much more freely than a surface made up entirely of the foundation material, constituting the heated electrode or cathode. While there is a continuous evaporation of this adsorbed film there is also a continuous reformation of the film by atoms of the alkali metal striking the heated surface. When the temperature is increased above the critical temperature for any particular vapor pressure, the cæsium film evaporates off to such an extent that the electron emission decreases.

In a prior patent specification Serial No. 132,012 filed August 27, 1926, by Ernest E. Charlton and George M. J. Mackay, as a continuation of an earlier application, Serial No. 604,077, filed November 29, 1922, generic claims are made on an electron discharge device wherein a high electron emission is secured from an adsorbed film of alkali metal.

The prior application of which the present application is in part a continuation describes the effect of certain electronegative gases in forming a binder layer upon a thermionic cathode and thereby increasing the stability of the adsorbed film of alkali metal. In the presence of these binder materials advantage may be taken of operating temperatures higher than 700° K. to secure a correspondingly higher electron emission from the cathode without reducing or destroying the effectiveness of the adsorbed film. For example, at vapor pressures cæsium corresponding to temperatures approximately room temperature the maximum electron emission obtainable from a tungsten cathode embodying our invention is 5,000 fold greater than the maximum emission obtainable from an ordinary tungsten cathode. This feature which constitutes the invention of ourselves is broadly described and claimed in the present application.

In the present application claims are made upon the method of forming a binder or foundation layer upon a cathode, which layer has the property of increasing the affinity of the heated foundation for alkali metal at higher temperatures, and for an apparatus embodying such a cathode. We also have described and claimed further improvements herein whereby an adsorbed film of alkali metal upon a heated cathode is rendered more stable, particularly with respect to the effect of high temperatures.

In accordance with one feature of our invention, we have provided chemical agents in our improved devices for combining with gases deleterious to a high electron emissivity which are given off in minute amounts during operation. The foregoing and other novel features of our invention will be set forth and explained with greater particularity in the following specification and appended claims.

The accompanying drawing illustrates in Figs. 1 and 2 a two-electrode device embodying our invention. These figures are side views taken at an angle of about 90° to each other. Figs. 3 and 4 illustrate a three electrode device.

As explained by Langmuir in the Transactions of the American Electrochemical Society, Vol. XXIX, 1916, page 125, there

is an absorption of energy when electrons are emitted from heated metals which is measurable as heat absorbed and which may be calculated in terms of a potential difference in volts, which is a quantitative measure of work done in separating an electron from an emitting surface. This value has been called the "electron affinity" of the emitting material. This electron affinity has been determined in volts for a number of materials. The value for tungsten is 4.52 volts while the value for a tungsten cathode coated with cæsium is about 1.4 volts.

The ionizing potential of cæsium is 3.88 volts. If a cæsium atom comes near a tungsten surface the tungsten having a higher electron affinity that the cæsium atom robs the cæsium atom of an electron and leaves it in the form of a positive ion. These cæsium ions when close to the tungsten surface induce a negative charge on the tungsten surface and are therefore held to the tungsten surface by electrostatic force. It is this force which causes the formation of the adsorbed film of cæsium. As the work function of this cæsium film is but 1.4 volts a cathode on which such a film is formed is operable at high efficiencies at relatively low temperatures. If the temperature is too high the adsorbed film will be driven off in spite of this force. When there is an electronegative film on the surface of the cathode, the cæsium is apparently held more tenaciously to the cathode because of the fact that the surface has a still higher electron affinity than tungsten.

The device shown in Fig. 1 represents an embodiment of our invention in a device of simple structure. It comprises an exhausted receptacle 1 containing a thermionic cathode 2, and an anode 3. The cathode 2, which is a V-shaped filament, consists of a refractory metal, as for example, tungsten or molybdenum. It is connected at its terminals to the usual leading-in conductors 4, 4′ and is supported at the bent or looped end by a support 5 carrying an anchor wire 6. The anode 3 may consist of tungsten, nickel, copper, or other suitable conductive material, electrical connection being made by a sealed in conductor 7. An external base has been omitted for the sake of simplicity.

In the above prior application certain methods of obtaining the beneficial results of electronegative gases have been set forth which first will be described, and then our improved method of forming a binder layer will be described.

After the envelope has been exhausted by the best approved methods for electron devices, and cæsium or rubidium has been introduced, a few microns of nitrogen or carbon monoxide may be admitted into the container. If the cathode then is heated to about 700° K. in the presence of the gas, the electron emission from it will be found to have increased about 50 fold. The excess gas then may be pumped out and the high emission will persist for a considerable time. The tube then is sealed off from the pump.

On the other hand, it may be preferred to leave an appreciable amount of gas in the bulb, pa ticularly if the device is to be operated at low voltage.

In some cases the gas for treating the cathode may be derived from the anode.

For example, a device having an anode made of ordinary commercially prepared nickel may be exhausted and heated during exhaust to remove water vapor from the container; then while a device, such as shown in Fig. 1, when provided with a nickel anode, is still connected to the pump, the anode may be heated, for example, by a high frequency field, to expel gas therefrom and cæsium may be introduced. In some cases the gas furnished in this way may deposit as a binder layer on the cathode and the cæsium adsorbed on this layer gives the desired maximum emission without further treatment. In other cases it may happen that deleterious gases are also evolved from the anode, which also deposit on the cathode and prevent the desired maximum emission from being at first apparent. Therefore, if the increased emission is not at once produced at a temperature of 900° K., the cathode may be heated to a temperature of from 1300° to 1500° K. for a few seconds to remove the deleterious gases from the adsorbed layer. The beneficial adsorbed layer is not removed by this treatment. If the temperature of the cathode is then reduced to the desired operating temperature the improved results will be obtained.

When the cathode is found to operate in a satisfactory manner the device is sealed off from the pumping system. Care should be exercised during the sealing off operation to avoid the introduction of gas.

Although nitrogen and carbon monoxide may be used to sensitize the cathode and to increase the electron emission in the presence of cæsium about 50 to 100 fold, the beneficial effect produced tends to decrease with the lapse of time.

We have discovered that a more stable and lasting effect will result when using oxygen to form the binder layer. In fact, the behavior of the gas derived from nickel renders it probable that the beneficial action of this gas is due to oxygen contained therein.

A device such as shown in Fig. 1 is thoroughly evacuated and the filament heated to a high temperature, in the case of tunsten at least 2000° K. to free its surface of impurities, and to remove occluded gas. Then oxygen is admitted to the container to a pressure of about 20 to 30 microns (0.02–

0.030 mm.), the filament preferably being heated to a temperature of about 1400 to 1500° K. for a few seconds, which causes the formation of a thin layer of adsorbed oxygen upon the cathode. The remaining oxygen then is pumped out and a quantity of cæsium or rubidium is distilled into the container, which may form a condensate on the wall, as shown at 8, as preferably enough of the metal is introduced to provide a surplus of unevaporated cæsium at any desired operating temperature.

Preferably the alkali metal, such as cæsium, for example, is introduced after evacuation from a side tube (not shown) which contains a mixture of a reducing agent, such as calcium or magnesium and a suitable compound of the metal to be introduced, for example, cæsium chloride. This method is described and claimed in an application filed on March 26, 1926, by Ernest E. Charlton, Serial No. 97,717.

When the anode consists entirely of unoxidized material, enough oxygen is admitted after the introduction of cæsium to oxidize part of the cæsium. The resulting mixture of cæsium and cæsium oxide will eliminate deleterious gases, especially hydrogen. In addition about half as much hydrogen (by volume) as the amount of oxygen previously introduced, may be admitted and allowed to "clean-up," the tube finally being sealed off with the exhaust pump operating. The introduction of hydrogen, in addition to the oxygen, produces both cæsium hydride (CsH) and cæsium hydroxide (CsOH). The mixture of cæsium and cæsium compounds has the property of removing carbon monoxide by chemical combination.

In some cases the anode may be constituted wholly or in part of a suitable oxidized metal. As shown at 9 in Fig. 1, a strip of oxidized metal has been affixed to the anode. This strip may consist of oxidized copper. When such a strip is provided no oxygen need be admitted after the introduction of the alkali metal as the cæsium reacts with the copper oxide to form cæsium oxide. Hydrogen may be admitted as before if desired.

In these tubes containing alkali metals, care should be taken to avoid condensation of metal on the stem as such condensation will cause electrical leakage between wires passing through the stem. Condensation of this kind is particularly apt to occur on those places where cæsium oxide is present. Therefore if oxygen is introduced into the tube, the stem should be freed from condensed cæsium by heating, and the parts where cæsium has deposited should be cooled sufficiently to avoid perceptible vapor pressure of cæsium when the oxygen is introduced. To reduce electrical leakage, it is advantageous to surround the electrode leads with short glass tubes spaced away from the leads as shown at 10, in Figs. 1 and 2 of the drawing.

After the tube is sealed off when prepared by either method, the cathode should be activated by heating for a few seconds to about 1300° to 1500° K. This treatment removes deleterious substances on the oxygen layer and puts the cathode into condition to give a high electron emission. Thereupon the device may be utilized, for example, for the rectification of alternating current, as illustrated diagrammatically in Fig. 1, as well as for other uses to which hot cathode tubes have been put. The cathode is heated by current derived from a section 11 of the secondary of the transformer 12, the cathode and anode being connected to the terminals of the main secondary section 13, by the conductors 14, 15 in series with the load 16.

When the device prepared as above described by the admission of gaseous oxygen is operated with the cathode at a temperature of about 900° K., the bulb as a whole being at a temperature of 30° C. (303° K.), an electron emission from the cathode of the order of about 200 to 300 milliamperes per sq. cm. of surface is obtained. This emission is of the same order of magnitude as the emission from a tungsten filament operating in a vacuum in the absence of cæsium or similar activating substances at a temperature of about 2500° K., but the energy required is much less.

The oxygen binder layer on the cathode does not evaporate rapidly until the temperature is raised above 1600° K. If the tube contains cæsium metal at about 30° C. the electron emission from the cæsium film adsorbed on the oxygen layer increases steadily with filament temperature up to about 900° K. A further increase in temperature reduces the electron emission as the filament surface becomes partly bared or devoid of cæsium. The optimum operating temperature is therefore about 900° K. and at this temperature there is no measurable evaporation of the oxygen layer. At higher bulb temperatures and hence correspondingly higher vapor pressures of cæsium, the cæsium film will be maintained intact at higher cathode temperatures, providing provision is made to prevent undue bombardment of the cathode by positive ions. The election emission at the optimum cathode temperature with the bulk at 43° C. is approximately double the maximum obtainable with the bulb at 20° C. The binder layer when comprising oxygen will be referred to herein as an "oxygenous layer" regardless of whether the oxygen is elemental or combined. In general, as stated in our prior application Serial No. 608,243, when the alkali vapor is maintained at a pressure be-

low the point at which ionization by collision becomes appreciable, the temperature of the cathode should not be increased much above 1000° K., as in such case the electron emission decreases and falls to negligible values at about 1200° K.

The oxygenous layer may however be removed by positive ion bombardment. For example, cæsium ions which have the energy due to an accelerating potential of 40 volts remove the layer at a measurable rate. Other ions, such as hydrogen ions, may react chemically with the oxygenous layer. Ions which do not have enough energy to remove the film may stick to the film and reduce its power of adsorbing cæsium. This is true of carbon monoxide ions of about 20 volts.

It is therefore desirable to avoid positive ion bombardment of the cathode, and the construction shown in Fig. 1 is favorable to the operation of the device at voltages high enough to produce considerable positive ionization of residual gas. In the absence of a large amount of positive ionization, the walls of a container in which electrons are present become negatively charged by the impingement of electrons on them. As these negatively charged walls are in unobstructed relation to the cathode in a device as shown in Fig. 1 such positive ions as may be generated are attracted by the charged walls and hence do not bombard the cathode.

Fig. 3 illustrates a three-electrode device embodying our invention, which may be used as a radio detector or relay. This device comprises a linear filamentary cathode 17, carried by a support 28, terminating in a spring 29, an input or a control electrode 18, and an anode or plate 19, all mounted within an extended bulb 20. Both the control electrode and the anode consist of flat plates which are radially positioned with respect to the cathode. The control electrode 18 consists of the longer of two sets of interleaved plates which are connected by wires to a ring 21. The spacial relation of the plates of the control electrode to the anode has been shown in Fig. 4, the control electrode plates being lettered 18^a, 18^b, 18^c and 18^d and the anode plates 19^a, 19^b, 19^c and 19^d. These plates are connected by the rings 21, 22 and 23 to prevent displacement.

In a tube of this construction the positive ions are almost entirely formed in the space between the anode and control plates and not between the filament and the plates. The ions are therefore produced at points where the electric field draws them to the grid, and they are thus prevented from striking the cathode. These respective electrodes are connected by the usual sealed-in conductors, the cathode conductors being lettered 24, 25, the input conductor 26 and the anode conductor 27. For the sake of simplicity no base is shown. This device may be used as a radio detector or as an amplifier, with the usual circuit connections for three electrode devices.

A quantity of cæsium is distilled into the bulb after the bulb is evacuated and the cathode has been sensitized as above described. When herein we have referred either in the specification or claims specifically to cæsium, we wish it to be understood that rubidium is regarded as an equivalent for cæsium and may be used in place of cæsium, although the electron emission obtained with rubidium is somewhat smaller.

With a device of this construction voltages materially above the ionizing voltages may be used. A commercially useful life has been obtained with voltages of about 45 volts. Other tubes of the type shown in Fig. 1 have given a commercially useful life at 80 volts.

Our improved device has the advantage of requiring very low filament wattage. By suitably proportioning the length and diameter of the filament, an electron emission of from 5 to 10 milliamperes may be obtained, using a filament heating current of about 40 milliamperes taken from a single dry cell.

What we claim as new and desire to secure by Letters Patent of the United States, is:—

1. An electron discharge device comprising electrodes the cathode consisting of tungsten, an enclosing evacuated envelope, and a quantity of cæsium therein, said cathode having formed thereon a layer of oxygenous material whereby cæsium is held during operation upon the cathode surface more tenaciously than by unoxidized tungsten.

2. An electron discharge device comprising electrodes, the cathode consisting of refractory material, an enclosing evacuated envelope, and a quantity of alkali metal therein, said cathode having formed thereon a coating of oxygenous material whereby said alkali metal is held during operation upon the cathode surface more tenaciously than by the material of which the cathode is composed, and which coating will remain on said cathode at temperatures as high as about 1500° K. for a short time.

3. An electron discharge device comprising an enclosing evacuated envelope, a quantity of cæsium and cooperating electrodes, one of which is adapted to operate at an elevated temperature, the latter electrode being provided with a coating of oxygenous material, and a quantity of cæsium oxide present in said envelope.

4. An electron discharge device comprising an evacuated envelope, containing a quantity of cæsium, an anode and a cathode of highly refractory metal provided with an oxygenous surface layer which acts as a binder to form an adsorbed layer of cæsium.

5. An electron discharge device contain-

ing cæsium and a cathode of refractory metal having a surface layer of material which is capable of causing said cathode in the presence of cæsium vapor to have at about 900° K. an electron emission of the order of about 200 milliamperes per square centimeter.

6. An electron discharge device comprising a cathode of material capable of operating intact at temperatures of 900° K., an anode, an enclosing evacuated envelope and a quantity of cæsium therein, said cathode having thereon a coating which is capable of causing said cathode to exhibit the high electron emissivity imparted by cæsium at a materially higher temperature than the cathode material in an uncoated state.

7. An electron discharge device comprising a cathode of tungsten, an anode, an enclosing evacuated envelope, and a quantity of cæsium therein, said cathode being combined with oxygenous material, which is capable of causing said cathode to retain a high electron emissivity in the presence of cæsium vapor at temperatures as high as about 900° K.

8. An electron discharge device comprising an evacuated envelope, electrodes including a cathode capable of being heated to at least about 900° K. and being capable of absorbing alkali metal, a quantity of alkali metal and a material capable of combining with carbon monoxide and hydrogen all contained in said envelope.

9. An electron discharge device comprising an evacuated envelope, electrodes including a cathode capable of being heated to at least about 900° K. and having formed on the surface thereof a layer of oxygenous material, a quantity of cæsium and a material capable of combining with carbon monoxide and hydrogen all contained in said envelope.

10. An electron discharge device comprising a cathode adapted to be heated and enclosed in an evacuated receptacle containing alkali metal, said cathode having formed thereon a layer of a material having the property of holding alkali metal atoms more tenaciously than does the material of which the cathode is composed.

11. The method of increasing the electron emission from a cathode adapted to be heated in an evacuated receptacle containing cæsium which consists in supplying to the space surrounding said cathode a gas capable of so modifying the surface of the cathode, as to materially increase the property of holding cæsium atoms thereon at temperature sufficiently high to actively vaporize cæsium from the unmodified cathode surface.

12. The method of increasing the electron emissivity of a cathode of refractory metal which consists in subjecting said cathode to attenuated oxygen in the substantial absence of other gases, heating said cathode to about 1300° to 1500° K., removing excess oxygen and introducing cæsium vapor into contact with said filament.

13. The method of increasing the electron emissivity of a cathode of refractory metal in the presence of cæsium, which consists in producing on the surface of said cathode an oxygenous coating, introducing cæsium vapor into contact with said filament, oxidizing said cæsium in part and adding hydrogen in an amount insufficient to reduce the oxidized cæsium.

14. The method of increasing the electron emission from a cathode adapted to be heated which consists in forming a layer upon said cathode, which is capable of enhancing the adsorptive property of said cathode, supplying an alkali vapor in contact with said cathode at a pressure so correlated with the operating temperature of the cathode that a materially higher electron emission is obtained at a given temperature than would be obtained from the cathode in the adsence of said layer and preventing substantial bombardment of said cathode by positive ions.

15. The method of increasing the electron emission from a tungsten cathode in a device in which said cathode is heated, which consists in forming an oxygenous layer upon said cathode, supplying cæsium vapor to said cathode at a vapor pressure corresponding to about 30° C., maintaining the cathode at a temperature of about 900° K. and preventing substantial bombardment of the cathode by positive ions.

16. The method of obtaining a high electron emission from a cathode in the presence of cæsium vapor at a pressure corresponding to a temperature of about 30° C. which consists in providing on said cathode an oxygenous layer in the absence of deleterious impurities, preliminary to bringing cæsium into contact therewith, activating said cathode by heating to a temperature at least as high as about 1300° K. in the presence of cæsium vapor and thereafter operating said cathode at a temperature of about 900° K.

17. An electron discharge device comprising an evacuated envelope, a charge of alkali metal therein, electrodes therein including a cathode constituted of a foundation material capable of stable operation at elevated temperatures and provided with an electronegative surface layer of material having the property in conjunction with the vapor of said alkali-metal of giving an electron emission at a given cathode temperature of a much higher order of magnitude than said foundation material would have in the presence of said alkali metal.

18. An electron discharge device comprising an evacuated envelope, a quantity of cæsium therein, an anode, and a thermionic

cathode having a higher electron affinity than the ionizing potential of cæsium, and having the property of giving an electron emission in the presence of cæsium vapor at a pressure corresponding to about 30° C. of the order of 100 milliamperes per square centimeter at a cathode temperature at which the electron emission of the material constituting said cathode is substantially zero.

19. An electrical discharge device comprising a closed container, electrodes therein, and a quantity of cæsium, one of said electrodes having provided thereon a binder whereby said electrode in the presence of cæsium vapor at a pressure too low to permit of substantial ionization by collision is rendered capable of coacting with cæsium when operated at temperatures about 900° K. so as to secure an electron emission of a higher order of magnitude than would be secured in the absence of said binder.

20. An electron discharge device comprising an evacuated bulb, a quantity of cæsium therein and electrodes including a thermionic tungsten cathode having an oxygenous surface layer which is removable by positive ion bombardment whereby the adsorption of said cathode for cæsium vapor is enhanced when operated at about 900° K. with the bulb at about 30° C., thereby rendering said cathode capable of electron emission of about 200 to 300 milliamperes per square centimeter under said conditions.

21. An electron discharge device comprising electrodes, including a thermionic electrode, and an enclosing evacuated envelope provided with a source of alkali metal vapor, means for increasing the adsorption or affinity of the thermionic electrode for said vapor thereby enabling said vapor to enhance the electrical emissivity of said thermionic electrode over a range of cathode temperatures at which said vapor otherwise would be substantially ineffective.

22. An electrical discharge device, comprising an evacuated container, electrodes therein including a thermionic cathode and a quantity of cæsium in said container, means whereby the affinity of said cathode for cæsium vapor at vapor pressures too low to permit of substantial ionization by collision is materially increased at cathode operating temperatures above about 700° K. and thereby is rendered capable of materially higher electron emission than would be obtainable in the absence of said means.

In witness whereof, we have hereunto set our hands this 5th day of November, 1923.

KENNETH H. KINGDON.
IRVING LANGMUIR.