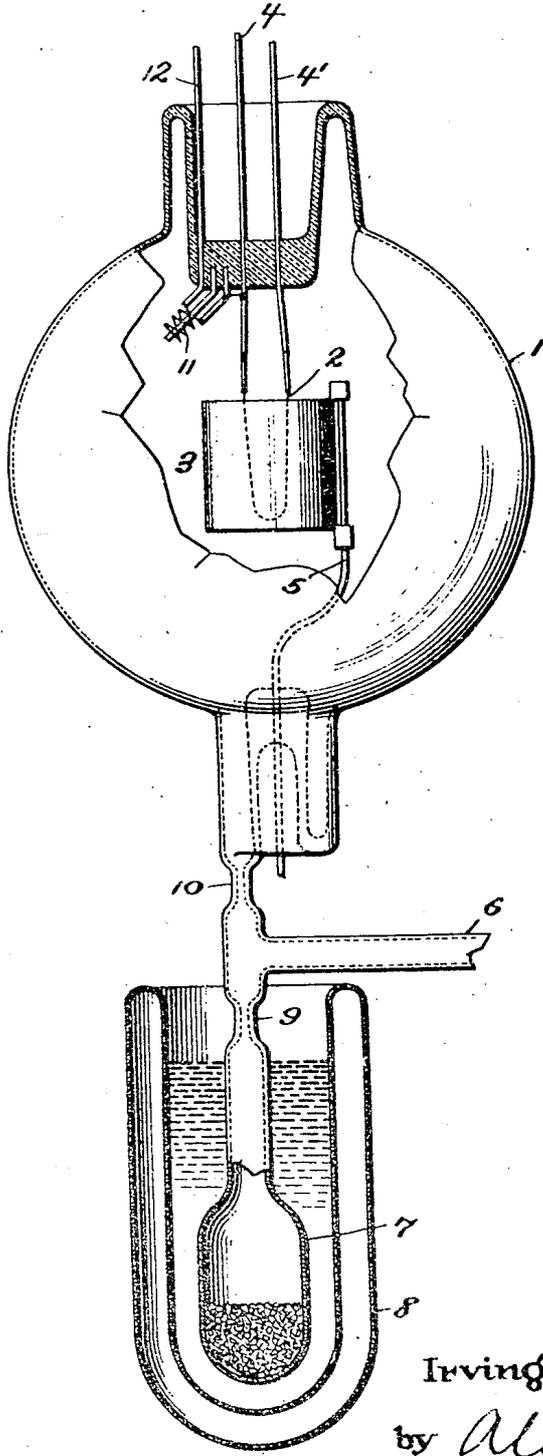


March 10, 1925

EBW
1,529,597

ELECTRON EMITTING DEVICE AND METHOD OF PREPARATION

Filed Aug. 11, 1921



Inventor:
 Irving Langmuir
 by *Albush, Davis*
 His Attorney

UNITED STATES PATENT OFFICE.

IRVING LANGMUIR, OF SCHENECTADY, NEW YORK, ASSIGNOR TO GENERAL ELECTRIC COMPANY, A CORPORATION OF NEW YORK.

ELECTRON-EMITTING DEVICE AND METHOD OF PREPARATION.

Application filed August 11, 1921. Serial No. 491,634.

To all whom it may concern:

Be it known that I, IRVING LANGMUIR, a citizen of the United States, residing at Schenectady, in the county of Schenectady, State of New York, have invented certain new and useful Improvements in Electron-Emitting Devices and Methods of Preparation, of which the following is a specification.

10 This invention comprises an improvement in the electron emitting cathodes of the type described in my prior U. S. Patents Nos. 1,244,216 and 1,244,217.

15 In these patents I have described the preparation and advantages of a vacuum tube containing a cathode adapted to be operated at incandescence and containing distributed throughout its mass thorium (or a compound of thorium) as a constituent. This type of electrode consists of a refractory conducting material, such for example as tungsten, with an addition of a material capable of increasing the electron emissivity of the cathode, such for example as thoria, the latter being subjected to modifications during the preparation of the cathode in the electron discharge device so that the active material in a finished device according to all indications, consists of metallic thorium or at least of a lower oxide of thorium than thoria (ThO_2). The cathode prepared according to the methods set forth in my first Patent 1,244,216 which is commonly known as a "thoriated cathode", is very sensitive to traces of oxidizing gas in the bulb, as for example, small traces of water vapor which may be given off from the walls of the bulb during the normal operation of the device. In order to prevent loss of activity of the cathode, I have described in my second Patent No. 1,244,217, the beneficial results obtained by the admission to the bulb of a small amount of alkali metal, such as potassium or sodium, or of a hydrocarbon compound.

45 My present invention in one of its aspects is based on the discovery that carbon in a cathode of the thoriated type, when present in a definitely limited amount, will prevent not only reoxidation of active thorium material but what is more important, will act beneficially to reduce thoria to the active state. Although the thoriated cathodes described in my prior patents can be used

with satisfactory results, I have found that a further improvement in regularity and stability can be effected by using carbon as hereinafter described, not only as in accordance with my prior patent in restricted quantities, as an oxidation preventing agent, but, as hereinafter described, as an ingredient of a thoriated cathode.

An accordance with another feature of my invention my improved cathode is used in conjunction with a non-carbonaceous reducing agent which is provided in the bulb, as for example, a highly oxidizable metal.

A thoriated cathode may be deleteriously affected by positive ion bombardment, that is, when voltages materially higher than the ionization voltages are impressed between the thoriated cathode and a positive electrode in the presence of ionizable gas, then the beneficial effect of the thorium may be largely or entirely destroyed by positive ion bombardment. Although the alkali metals are entirely satisfactory as agents to remove deleterious gases when the operating temperature of the bulb is only moderately above room temperature, as in the case of radio receiving tubes, these alkali metals have a sufficiently high vapor pressure at the operating temperature of power devices in which cathodes of the thoriated type are used to become ionized at higher voltages and to cause removal of the active film of thorium from the cathode by bombardment. I have found that it is advantageous in many cases to provide a device containing a cathode of the thoriated type with a material having an affinity for gases, such as magnesium, for example, which at the operating temperature of the device has substantially no vapor pressure. My invention will be pointed out with greater particularity in the accompanying claims and described fully in conjunction with the accompanying drawing which shows somewhat diagrammatically. An apparatus used for carrying out the preparation of an incandescent cathode rectifier.

The rectifier shown in the figure is illustrative of one of the various forms of incandescent cathode devices. It consists of a bulb 1 containing a filamentary cathode 2 into which thoria has been introduced as described in my above mentioned prior patents, and an anode 3, consisting of tungsten,

2

1,529,597

molybdenum or other suitable material. These electrodes are respectively connected to lead wires 4, 4' and 5 sealed into the walls of the bulb. The bulb is connected to the usual pumping system by means of a tubulature 6. The bulb also communicates with an elongated tube 7 adapted to be surrounded by a freezing mixture contained within a double-walled receptacle 8.

10 In carrying out my invention, the bulb 1 is first baked out as usual to remove water vapor and is then exhausted. Within the tube 7 is placed a substance adapted to give a low pressure of carbonaceous vapor, as for example, anthracene ($C_{14}H_{10}$) or naphthalene ($C_{10}H_8$).

When the vapor pressure of the substance employed is relatively high, I prefer to reduce the pressure of the hydrocarbon vapor in the bulb 1 by surrounding the tube with a freezing agent contained in the receptacle 8. When employing naphthalene, which has a moderately high vapor pressure, I prefer to reduce the temperature of the containing tube 7 to about -20 to $-30^\circ C.$ to reduce the vapor pressure to about 0.1 to 0.01 microns. The bulb 1 which communicates with the side tube 7, therefore, is filled with hydrocarbon vapor at approximately this pressure. The quantity of hydrocarbon may be controlled by one or more constrictions, such as 9, 10 which may regulate the pressure with or without a freezing agent.

35 The filament 2, which preferably consists of metallic tungsten, containing about $\frac{3}{4}\%$ thoria, is heated to a temperature of about $2300^\circ K.$ ($2000^\circ C.$) for a few minutes, in contact with the hydrocarbon vapor. At this temperature the incandescent filament decomposes the hydrocarbon vapor which comes in contact with the incandescent surface of the tungsten and causes the chemical combination with the tungsten of the carbon set free from the naphthalene vapor, with the formation of tungsten carbide (W_2C). The heating is continued for a length of time sufficient to give an increase in resistance of about 15 to 25% of the tungsten filament when cold, or at room temperature. This change in resistance corresponds to the presence of about two-thirds per cent of carbon by weight in the filament.

50 The carbon content most beneficial will vary with the conditions. In the case of a thoriated tungsten cathode all of the metallic tungsten will be converted to brittle tungsten carbide (W_2C) with a carbon content as high as 3%. Ordinarily a carbon content as high as about 1% is as high as permissible without unduly weakening the cathode. Although the presence of even minute amounts of carbon is highly undesirable in an incandescent lamp, a commercially long life can be obtained in a thoriated cathode containing carbon, as the cathode

need be operated only at a relatively low temperature, say at about the operating temperature of an ordinary carbon lamp, the electron emissivity of a thoriated cathode being so much greater than that of an ordinary pure tungsten cathode. The hydrocarbon vapor is removed from contact with the filament either by sealing off the tube 7 at the contraction 9 or cooling the side tube 7 by means of liquid air in the receptacle 8 to a temperature so low that the vapor pressure of the naphthalene is negligible, thereby removing the naphthalene vapor from the bulb 1.

In some cases carbon to a desired proportion may be combined with the cathode prior to the introduction of the cathode into the bulb 1. For example, a thoriated filament may be prepared by squirting tungsten and thoria with a carbonaceous binder in amounts adapted to leave a suitable restricted proportion of carbon in the finished product.

As the next step in the preparation of the device, the anode 3 is deprived of gases by the usual method of electron bombardment; that is, by passing a discharge between the cathode at incandescence and the anode, the exhaust pump in the meantime being operated to remove the vapors and gases which are liberated. During this step some of the carbon is removed by oxidation and evaporation from the cathode but with an original carbon content of about $\frac{2}{3}$ of one per cent. enough carbon remains subsequently to furnish a supply of active thorium material by reduction of the thoria.

After the cathode has been provided with a content of reducing agent a non-carbonaceous material capable of combining with water vapor and other deleterious gases may be introduced into the bulb. In some cases this non-carbonaceous reducing agent may consist of alkali metal, such as sodium or potassium. Caesium may be used to advantage in some cases, especially when some positive ionization is desired in the electron discharge device. Caesium can be conveniently provided by adding a mixture of caesium halide and metallic calcium as a paste to some part of the bulb, this method of introducing an alkali metal being claimed in an application, Serial No. 608,311, December 21, 1922, by Ernest E. Charlton.

When not desiring ionization of residual gases or vapors, I prefer to introduce for the reasons given above a reagent having a lower vapor pressure than the alkali metals, as for example, an alkaline earth metal such as magnesium, calcium, strontium, or the like. Conveniently this is done by providing within the bulb a small heating coil 11, consisting of tungsten or other suitable refractory material, and containing a small quantity of the metal to be vaporized. Pref-

erably I employ metallic magnesium. By heating the tungsten filament 11 with current conducted thru the lead wires 4, 12, some of the magnesium is volatilized and deposited on the inner surface of the bulb which is then sealed off at the contraction 10. As during the sealing off process there is a tendency to drive out a small quantity of gas from the heated glass, I prefer to heat up the filament 11 the second time, to volatilize a small additional quantity of magnesium, or the like, in order to combine chemically with what little gas may have gotten into the bulb during the sealing off operation.

The film of magnesium, or other equivalent metal, on the walls of the bulb will combine with any water vapor or oxygen which may be given off by the bulb, or any other parts of the device during its operation, and thereby prevent an oxidization of the active thorium material upon the surface of the cathode.

The tungsten cathode 2 is preferably heated for a very short time to about 2700° K. to volatilize any thorium oxide on its surface.

As a final step, the cathode is "activated", that is, brought into its highly active state by heating to a temperature of about 2200° K. for a few minutes. This results in the reduction of thoria by the carbon and causes the active thorium product to come to the surface of the cathode where it will be effective in increasing the electron emission during the operation of the device. The tube is then ready for operation.

As explained in my prior patents, a temperature materially higher than the activating temperature will result in the thorium being volatilized from the surface of the cathode. A fresh supply can be produced and caused to accumulate upon the surface by again activating or "forming" an electrode at about 2200° K. During normal operation, the cathode is heated to a temperature below about 2200° K. and as high as 2100° K. Under these conditions, the electron emission stays constant.

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

1. In an electron discharge device, a cathode body of the thoriated type containing carbon in an amount insufficient to convert all of the metallic constituents of said cathode to a carbide but sufficient to render said cathode less sensitive to the deleterious effect of gases than a cathode body unprovided with carbon.

2. In an electron discharge device, a tungsten cathode of the thoriated type adapted to emit electrons when heated, containing carbon in an appreciable amount but less than three per cent by weight.

3. A cathode adapted to emit electrons at

incandescence comprising tungsten, about three-quarters per cent thoria and about two-thirds per cent by weight of carbon.

4. The method of increasing the electron emissivity of an electrode of the thoriated type which consists in introducing carbon into said electrode in amounts insufficient to convert said metal to a carbide, sealing said electrode into a space substantially free from carbonaceous vapors and thereupon activating said electrode.

5. An electric discharge device comprising an evacuated envelope, electrodes therein one of which comprises a refractory metal, thorium oxide and carbon in an amount insufficient to convert said metal to a carbide, and a non-carbonaceous reagent capable of combining with deleterious gases in said envelope.

6. An electric discharge device comprising an envelope, an anode and a cathode of the thoriated type and a non-volatile material, which is capable of reducing thorium oxide, contained in said cathode in such small amounts that the durability of said cathode is not appreciably decreased.

7. An electric discharge device having a cathode comprising metallic tungsten, thorium oxide and carbon combined with said tungsten in an amount materially less than required to convert all the tungsten to a carbide.

8. The method of increasing the electron emissivity of a cathode of the thoriated type which consists in introducing carbon into said cathode in an amount less than about one per cent by weight, heating said cathode in a non-carbonizing and non-oxidizing environment to a temperature at which a carbide of said metal is formed, activating said electrode by heating to about 2200° K. and operating the same under such conditions that bombardment of the electrode by positive ions is inappreciable.

9. The method of increasing the electron emissivity of a cathode of the thoriated type which consists in introducing carbon into said electrode in an amount less than one per cent by weight, mounting said electrode in a bulb, evacuating the same, volatilizing magnesium in said bulb after evacuation, and activating said cathode by heating to an elevated temperature.

10. The method of preparing an electrode adapted to emit electrons at incandescence which consists in heating a conductor comprising refractory metal and thoria in a carbonaceous vapor to a temperature adapted to cause combination of carbon with said conductor, removing said vapor before the amount of carbon introduced into the filament exceeds one per cent, and heating said conductor in a non-oxidizing environment to a temperature at which electron emissivity is markedly increased.

11. The method of preparing an electrode adapted to emit electrons at incandescence which consists in heating to incandescence a conductor comprising tungsten and thoria in a carbonaceous vapor until a marked increase in cold resistance occurs by the introduction of carbon, discontinuing the heating before the tungsten has been largely converted to a carbide, and heating said conductor in the absence of said vapor in a reducing environment to produce a surface layer of thorium material having a markedly higher electron emissivity than the original conductor.

12. An electrical discharge device comprising a sealed envelope, electrodes therein which include a cathode of the thoriated type and a substance, having a marked chemical affinity for water vapor, deposited as a film of extensive surface upon the inside of said envelope, said substance having a materially lower vapor pressure than the alkali metals.

13. An electrical discharge device comprising a sealed envelope, electrodes therein one of which is of the thoriated type and a film of magnesium deposited on the inner surface of said envelope.

14. An electron discharge device containing a cathode of the thoriated type, said cathode being provided with a reducing agent sufficient in quantity to promote activation of said cathode, but restricted to an amount which will permit operation of said cathode at a temperature of effective electron emission with a commercially long life.

15. A cathode of the thoriated type for electric discharge devices containing less than about three per cent by weight of carbon.

16. An electric discharge device comprising an envelope, electrodes therein one of which comprises a refractory metal, a material reducible by carbon to a state of higher electron emissivity than said refractory metal at a given temperature, and a quantity of carbon in an amount insufficient to convert said metal completely to a carbide.

17. An electrical discharge device comprising a container, electrodes therein one of which contains less than three per cent of carbon combined therewith and a material capable of materially higher electron emissivity at a given temperature than the main constituent of said electrode, but being sensitive to positive ion bombardment, and a quantity of alkaline earth metal deposited in said container out of immediate contact with said electrodes.

18. An electrical discharge device comprising a container, electrodes therein one of which contains a material capable of materially higher electron emissivity at a given temperature than the main constituent of said electrode, but being sensitive to positive

ion bombardment, and a quantity of alkaline earth metal deposited as a film on the inner surface of said container.

19. An electrical discharge device comprising a container, electrodes therein one of which contains a material capable of materially higher electron emissivity at a given temperature than the main constituent of said electrode, but being sensitive to positive ion bombardment, and a quantity of magnesium deposited as a film on the inner surface of said container out of immediate contact with said electrodes.

20. An electrical discharge device comprising a container, electrodes therein one of which consists largely of refractory metal and contains an oxide of a metal of high electron emissivity which when rendered active is sensitive to ion bombardment together with a reducing agent, and a quantity of alkaline earth metal, the latter being deposited as a film on the inner wall of said container.

21. An electrical discharge device comprising a glass bulb, electrodes therein one of which consists largely of refractory metal and contains a material capable when activated of substantially increasing the electron emission of the electrode with which it is associated but which is deteriorated by oxidation and positive bombardment, and a film of magnesium coating the inner surface of said bulb.

22. An electrical discharge device comprising a container, electrodes therein, one of which contains as a constituent a material capable of higher electron emission than the main constituent of said electrode but which is sensitive to positive ion bombardment, and to the chemical effect of water vapor under operating conditions, and a film of metal deposited from the vapor state in a vacuum on the wall of said container which metal has a high chemical affinity for water vapor and has a materially lower vapor pressure at the operating temperature of said device than the alkali metals.

23. The method of increasing the electron emissivity of a metallic electrode containing a compound capable upon reduction of materially increasing the electron emissivity of said electrode which consists in introducing carbon into said electrode in an amount insufficient to convert the metal constituting said electrode completely to a carbide and heating said electrode in a non-oxidizing and non-carbonizing environment to a temperature sufficiently high to activate said electrode, and thereupon operating said electrode under conditions which render the effect of positive ion bombardment of said electrode inappreciable.

24. An electrode material for an electrical discharge device consisting of a metal capable of stable operation at an elevated tem-

perature, a compound of a material capable
in a reduced state of higher electron emis-
sion than said metal, and carbon in a quan-
tity insufficient to deleteriously affect the
5 strength of said material, but being capable
of reducing a sufficient amount of said com-
pound to enable said electrode to be more
readily activated during use than would be
the case in the absence of said carbon.

25. A cathode material for electrical dis- 10
charge devices consisting largely of a metal
capable of operation at an elevated tempera-
ture, a reducible compound of a material of
high electron emissivity and less than about
one per cent of carbon. 15

In witness whereof, I have hereunto set
my hand this 8th day of August, 1921.

IRVING LANGMUIR.