I. LANGMUIR.

ELECTRON DISCHARGE APPARATUS AND METHOD OF PREPARATION.

APPLICATION FILED JULY 15, 1914. RENEWED JUNE 25, 1917.

1,244,216. Patented Oct. 23, 1917.

Fig. 2.

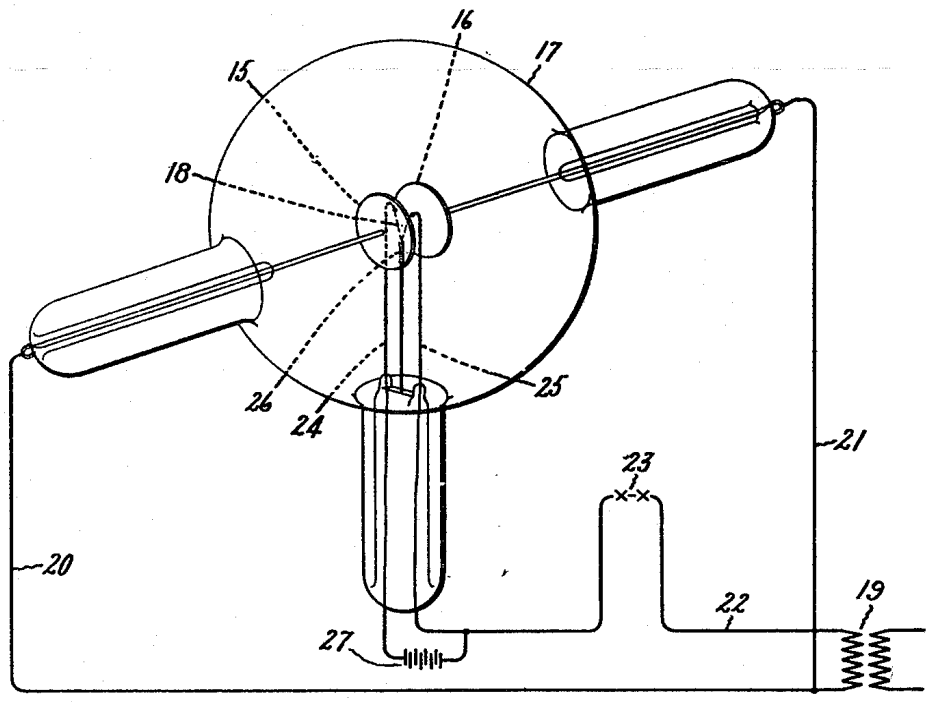

Fig. 3.

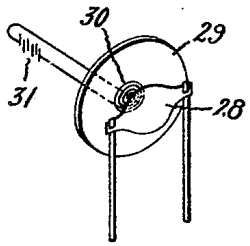

Fig. 1.

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UNITED STATES PATENT OFFICE.

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ELECTRON-DISCHARGE APPARATUS AND METHOD OF PREPARATION.

1,244,216. Specification of Letters Patent. Patented Oct. 23, 1917.

Application filed July 15, 1914, Serial No. 851,095. Renewed June 25, 1917. Serial No. 176,926.

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-Discharge Apparatus and Methods of Preparation, of which the following is a specification.

The present invention relates to electrical devices operating with a pure electron discharge and comprises a novel cathode material and the method of its preparation.

In a previous application, Serial No. 795,610, filed October 16, 1913, I have described and claimed a new type of electrical discharge apparatus comprising an envelop containing electrodes one of which emits electrons and being so highly evacuated that positive ionization is negligible. Some of the characteristics of this "pure electron discharge" are absence of conductivity in the space between independent unheated electrodes, a variation of the current over a certain range with the 3/2 power of the voltage, the absence of blue glow in the space, the absence of gas fluorescence and the lack of cathodic disintegration.

Various refractory materials, platinum, carbon, tungsten and molybdenum, have been used as cathode materials and it has been found that the emissivity of electrons of these various materials while differing to some degree is of the same order of magnitude.

I have discovered that the electron emissivity of pure thorium is of an entirely different order of magnitude than the emissivity of refractory materials heretofore used in electron discharge devices. It is not necessary that the electrode should consist entirely of thorium. When, for example, a thorium compound, such as the oxid, has been added during the process of production to one of the highly refractory metals, for example, tungsten, and the metal subjected to a preliminary heat treatment in a high vacuum, the electron emission in a high vacuum is enormously increased. This increased emissivity is not due to the presence of thorium oxid in the manner of the Wehnelt cathode for various reasons hereinafter explained, but according to all indications is a property of metallic thorium on the surface of the cathode.

Apparatus suitable for preparing and utilizing a thoriated cathode in an electron discharge apparatus is somewhat diagrammatically shown in the accompanying drawings, in which Figure 1 shows a simple type of apparatus in which the anode consists of a film of refractory metal on the inside wall of the envelop produced by vaporizing a refractory metal at high temperature; Fig. 2 is a device operable as a rectifier having a thoriated cathode and plate-shaped anodes; and Fig. 3 illustrates a modification in which active thorium material may be transferred to the cathode from an independent thoriated conductor.

The device shown in Fig. 1 comprising an envelop 1 consisting of glass, quartz or the like provided with two filamentary conductors 2, 3, of highly refractory metal, such for example as tungsten, at least one of which, say filament 2, is thoriated. They are connected to leading-in wires 4, 5, sealed into a stem 6 in the well-known manner. The envelop is connected to a vacuum system by a tube 7, containing a trap 8 which may be surrounded by a freezing bath, such as liquid air, contained in a Dewar flask 9 or even an ice and salt mixture. It is the function of the freezing bath to prevent mercury, or other vapors, from the vacuum pumps from reaching the envelop 1.

The preliminary evacuation of the envelop is carried out by the usual methods of producing high vacuum, which includes baking out the envelop to remove water vapor. The final stage of the evacuation is preferably but not necessarily carried out by a Gaede molecular pump to the highest possible vacuum obtainable by this means,—that is, to about .001 micron. While the apparatus is still on the pump the filaments 2, 3, are heated to a temperature of about 2900° K. (absolute) for a short time and the envelop 1 is baked out in an oven at a temperature of about 360 to 450° K. The apparatus may then be sealed from the vacuum system at the contraction 10. It is then preferably immersed in liquid air and both filaments 2, 3 aged by heating for about ½ hour to a temperature of 2400 to 2500° K. One of the filaments, for example, filament

3, is then incandesced by a passage of current to a temperature of about 3000° K. which causes rapid vaporization of the metal, thereby producing a gas-free conducting deposit or coating 11 which has been shown on the inner surface of the envelop. Conductors 12, 13 sealed into the envelop make contact with this coating and enable it to be used as an anode for an electrical discharge. A device having a gas-free film anode and the method of its preparation has been described and claimed by me in a co-pending application, Serial No. 843,569, filed June 6, 1914. The method of producing high vacua by vaporizing tungsten is claimed by me in a co-pending application, Serial No. 838,768, filed May 15, 1914. Pressures much below .001 micron of mercury may be attained thereby. The cathode conductor 2 is prepared by introducing a thorium compound, such as the nitrate of thorium to the oxid of the refractory metal before reduction, or by adding either thorium nitrate or thoria to the metal powder after reduction but before consolidation of the metal by sintering and mechanical working to the solid metal state has taken place as described, for example, with reference to thoriated tungsten in U. S. Patent No. 1,082,933. The proportion of thoria in the unsintered metal usually varies from about $\frac{1}{2}$ to 10% but in some cases may be even greater. The proportion of thorium compound in the cathode within the above limits makes little difference in the maximum electron emission that may be obtained under the best conditions but with a greater proportion of thorium compound the desired active condition of the filament may be reached and maintained with greater ease than with a lesser amount.

The thoriated cathode 2 is now heated to about 2900° K. for about one minute. The treatment of the filament at a temperature of 2900° has no marked effect on the subsequent electron emission of the cathode when at lower temperature but appears to be desirable for purifying the surface of the cathode. The cathode is then incandesced within the range of about 2000° to 2400° K. and by this temperature treatment some change is produced in the cathode which enormously increases its electron-emitting property under the condition described. The greatest activity is obtained between about 2200° to 2300° K. and the treatment at this temperature is usually continued for about one minute, but even outside of this range a marked change is produced. Apparently a concentration of metallic thorium or of some other oxidizable thorium material takes place on the surface of the filament. The filament 2 may now be used as a cathode at a temperature below this forming temperature.

With a filament thus prepared I have obtained at a temperature of about 1300° to 1380° K. substantially the same electron emission per sq. cm. as with a pure tungsten filament at about 2000° K., that is, about three milliamperes per sq. cm. Preferably a thoriated cathode is operated around 1700° to 1800° K., at which temperatures its life is indefinitely long.

Subsequently heating the filament to a higher temperature, for example, to 2800° K., causes some change, apparently a distillation of the film of thorium from the surface, as the electron emitting power of the cathode falls to the same order of magnitude as pure metal. When the cathode after being thus heated is re-subjected to a temperature of 2200° to 2300° K., the active condition is restored.

A similar heat treatment of pure tungsten has no effect on its electron emissivity at incandescence. The active thorium material may be transferred by distillation to an adjacent surface. For example, if the filament 3 consisting of pure tungsten has not been completely destroyed during the preparation of the apparatus, the heating of the cathode to a temperature above 2300° after the preparation of the surface film results in the distillation of some of the thorium material to conductor 3 so that when the conductor 3 is used as a cathode with respect to the anode 11, it is found that its electron emission has been greatly increased.

One of the most striking proofs that the active surface film is not due to the effect of the thoria as in the Wehnelt cathode is furnished by the effect of a minute trace of oxygen on the behavior of the cathode. If in some manner a trace of oxygen is admitted, the electron emission immediately falls as low or even lower than the low value observed when a cathode of pure tungsten is slightly oxidized. In other words, the electron emission becomes very much lower than that of the unoxidized metal. When subsequent to oxidation a trace of hydrocarbon vapor is admitted, the electron emission suddenly rises as though reduction were taking place. If the carbon is in excess, the electron emissivity immediately drops to a low value as though a carbid were formed with the excess of carbon. In an application Serial No. 58,377 filed by me on October 28, 1915, I have more fully described and also claimed a thoriated cathode device containing reducing material.

Cathodes containing only a small amount of thorium compound are deleteriously affected by disintegration of the surface produced by positive ion bombardment and in this respect may be extremely sensitive. In this case, it is necessary when using voltages high enough to cause ionization of residual gases to carry the vacuum far beyond the

point at which a disruptive discharge no longer takes place, which ordinarily is about $\frac{1}{10}$ of a micron of mercury pressure. The Wehnelt or oxid cathode apparently depends on positive ionization for its activity. At any rate its emissivity is increased by an increase in positive ionization. When large amounts of thorium are present in my improved cathode, it is not so sensitive to positive ion bombardment and it is possible to obtain to a large extent the advantages of a thoriated cathode even in the presence of pressures of gas up to atmospheric pressure.

Another proof that the high electron emission is due to a skin of thorium is the fact that metallic thorium itself, particularly when free from surface oxidation, exhibits a very high electron emissivity for a given temperature as compared with tungsten. Difficulties are encountered with the use of metallic thorium as cathode material due to its relatively low melting point and its susceptibility to oxidation.

At 2000° to 2300° K., the active thorium is slowly diffusing to the surface from the interior of the metal. As the temperature is raised a point is reached where the distillation of thorium from the surface exceeds the rate at which the metal diffuses to the surfaces. It is possible, however, to operate a refractory thoriated cathode at a temperature between 2000° and 2200° K. for a long time without destroying its high electron emission, but operation at a higher temperature is not advisable. A sufficiently great electron emission can be secured through the indicated temperature range with an accompanying saving of energy necessary for heating the cathode.

The apparatus shown in Fig. 2 does not differ essentially from the apparatus shown in Fig. 1, plate-shaped anodes 15, 16 consisting of a highly refractory metal such as tungsten being used instead of the film anode of vaporized metal used in the apparatus shown in Fig. 1. The envelop 17 is baked out and evacuated as already described in connection with Fig. 1. The ionizable gas should be removed from the anodes during the final stages of the exhaust after the pressure has been reduced below about $\frac{1}{10}$ of a micron of mercury by subjecting the anodes to an electron discharge from the cathode 18 whereby ionizable gas is evolved, as disclosed in my co-pending application, Serial No. 795,610 of October 16, 1913. This gas should be removed as fast as liberated and the discharge voltage progressively increased, care being taken not to materially exceed the voltage at which blue glow takes place so as to avoid injury to the cathode. The final stage of the evacuation is produced by vaporizing a tungsten conductor in a side chamber (not shown in the drawing), thereby producing the very high vacuum necessary for the operation of the thoriated cathode. The anodes 15, 16 may be both connected to one terminal of a secondary of the transformer 19, by conductors 20, 21, the cathode being connected to the other terminal by conductor 22, including a load circuit 23. The cathode 18 has been merely indicated by dotted lines as being a V-shaped filament supported by terminal wires 24, 25, and maintained taut at its bight by a spring 26, but it is to be understood that it may have any convenient form. Thorium compound, for example, the oxid, is introduced during the process of manufacture as already described. The apparatus here shown is suitable for the rectification of alternating current when the cathode is maintained at incandescence by a battery 27, preferably at a temperature of 1700 to 1800° K.

It is not absolutely necessary that the thorium should be introduced into the body of the metal during the process of manufacture. As shown in Fig. 3 a cathode 28 located opposite an anode 29 is provided with a film of active thorium material vaporized from the coiled filamentary cathode 30 heated by a battery 31. The cathode 30 may consist either of a thoriated cathode prepared as already described, or of metallic thorium. The inclosing envelop has not been shown, but it is to be understood that these parts are to be operated in the high vacuum already indicated as being desirable. When the coil 30 consists of thoriated wire it is first rendered active by heat treatment at a temperature of 2200° to 2300° K., as already described, and is then heated to a temperature of about 2900° K. to distil off active material, some of which is condensed on the cathode 28. When the coil 30 consists of metallic thorium, it should be heated to a temperature near its melting point to distil some of the thorium over on to the surface of the cathode 28.

As positive ionization is very much decreased at low voltages, it is permissible to have present an inert gas at a pressure of say .01 micron when the voltage impressed between the cathode and anode does not arise above the ionizing potential of the gas. Advantage can be taken of this fact to use an electron discharge device containing a thoriated cathode as a voltage sensitive cut-out device. Below the voltage at which disintegration of the surface begins, a device such as shown in Fig. 1 may be used to pass a current of about $\frac{3}{10}$ of an ampere per sq. cm. when the cathode is at a temperature of about 1700° to 1800° K. When the voltage rises above the critical value, the current immediately drops to a very small value, thus practically interrupting the circuit. The cathode may be restored when the voltage

has fallen by again heating it to about 2200° to 2350° K.

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

1. In an electrical discharge device, an electrode comprising in part at least oxidizable thorium material, said electrode having at a temperature of about 1300 to 1380° absolute an electron emission substantially equal to that of tungsten at about 2000° absolute.

2. In an electrical discharge device, an electrode comprising in part at least oxidizable thorium and having when at incandescence in a vacuum so highly attenuated that positive ionization is substantially absent, an electron emission materially greater per unit of surface than tungsten at the same temperature.

3. A cathode for electron-discharge apparatus consisting largely of a highly refractory metal and a surface layer of material having an electron emissivity at a given temperature materially greater per unit surface than said refractory metal independently of and in the absence of positive ionization.

4. In a device operating by pure electron discharge independent of positive ionization, a conductor comprising a refractory metal and a surface film of thorium material vaporizable at a temperature above about 2300° K. and having a greater electron emission when at incandescence in a non-striking vacuum than said refractory metal.

5. In an electrical discharge device, an electrode comprising metallic tungsten and a surface film of thorium material vaporizable at a temperature above about 2300° K. removable from said surface by positive ionization and having an electron emission per unit surface many times greater than pure tungsten at the same temperature.

6. In an electrical discharge device, an electrode comprising metallic tungsten and thoria said electrode having been subjected to a temperature of about 2200 to 2350° K. and having an electron emission a thousand times as great per unit of surface as tungsten in a vacuum too high to permit of positive ionization.

7. In an electrical discharge device, a cathode comprising metallic tungsten and thoria, said electrode having received a heat treatment at about 2000 to 2350° K. and having an electron emission when at incandescence at a given temperature of a higher order of magnitude than pure tungsten at the same temperature.

8. The process of preparing an electrode comprising a refractory metal and thoria for use in a pure electron discharge apparatus which consists in heating said electrode to a temperature adjacent the melting point of said refractory metal and then heating to a temperature of about 2200 to 2300° absolute.

9. The process which consists in heating a conductor comprising tungsten and thoria to a temperature of about 2800 to 2900° absolute and then lowering the temperature to about 2200 to 2300° absolute holding said temperature for a short interval and finally operating said conductor as cathode in a non-striking vacuum at a temperature below 2000° absolute.

10. A cathode for electron discharge apparatus consisting largely of tungsten and containing thorium, said cathode having an electron emissivity, independently of and in the absence of positive ionization, at a given temperature materially greater per unit surface than tungsten at the same temperature.

11. In an incandescent cathode device, an electrode comprising a highly refractory metal and containing oxidizable thorium material, said electrode having an electron emissivity per unit surface many times greater than said refractory metal alone at the same temperature, the electron emissivity of said cathode being lowered by the presence of oxygen and by positive ionization.

In witness whereof, I have hereunto set my hand this 14th day of July, 1914.

IRVING LANGMUIR.

Witnesses:
WILLIAM C. WHITE,
HELEN ORFORD.