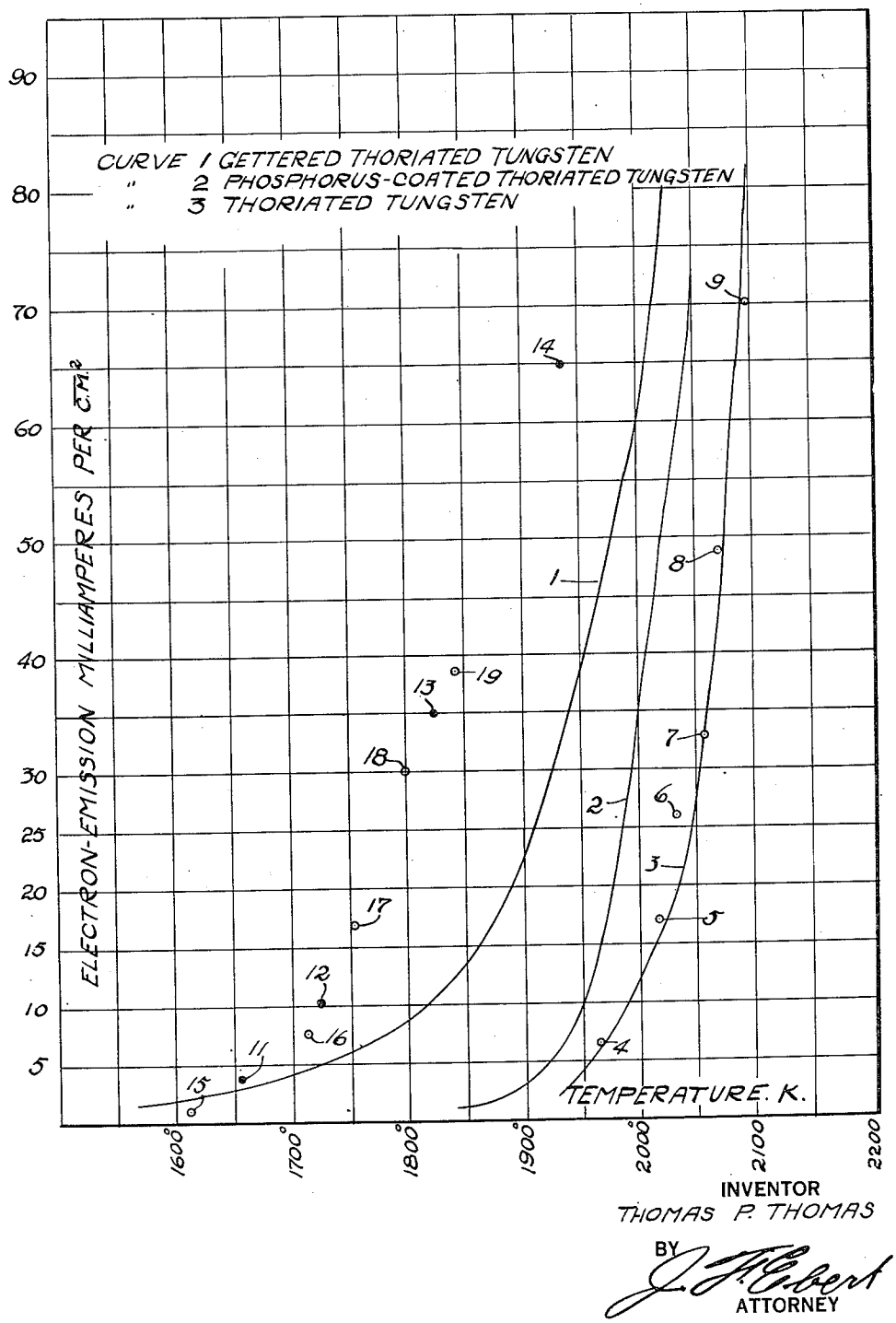
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ELECTRON EMITTING MATERIAL AND THE PREPARATION THEREOF

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## ELECTRON-EMITTING MATERIAL AND THE PREPARATION THEREOF.

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This invention relates to electron-emitting material and more especially to a substance for increasing the electron emissivity of such material.

An object of my invention is to produce an electron-emitting material for an electron discharge device, which material may constitutes a filamentary cathode in such a device, so treated that its electron emission is materially increased.

Another object of my invention is the treatment of a thoriated filament with a reducing agent, so that metallic thorium is produced on the surface of said filament.

A further object of my invention is the treatment of a thoriated tungsten filament by application of a phosphorous mixture thereto, whereby metallic thorium is liberated on the surface of said filament when the same is heated and the electron emissivity of the filament is increased.

A still further object of my invention is the maintenance of red phosphorus in intimate contact with a thoriated tungsten filament for an appreciable time during heat treatment thereof, thereby causing a reduction of thoria to thorium and an increase in the electron emissivity of the filament.

Other object and advantages will be apparent upon reading the following description.

In certain electrical discharge tubes, where a hot cathode is the sourse of electron current, such as radio bulbs, X-ray tubes, rectifiers and the like, it is desirable to have such cathode with a high thermo-electronic emissivity. It is also desirable that such cathode may be operated at temperatures so low that there will be no appreciable evaporation of the cathode material, since such evaporation shortens the life of the cathode and causes blackening of the bulb.

Hot cathodes in general use are either tungsten filaments or refractory metal filaments coated with oxides of such metals as calcium, strontium or barium. In order to get a large electron emission from tungsten, it is necessary to operate a tungsten cathode at a temperature so high that blackening of the bulb soon occurs and the life is shortened. The Wehnelt or oxide coated cathodes disintegrate and develop hot spots, finally burning out at these spots. Experimenters have investigated the electron emission from a number of refractory metals with the hope of discovering a metal which would prove more suitable for hot cathodes than those now in use.

It is known that, for any given temperature, the electron emissivity for thorium, titanium, uranium, zirconium, molybdenum and tungsten is in the order named. That is, of the above enumerated rare metals, thorium shows the highest electron emissivity and it would therefore be preferable to form a cathode of thorium were it not for the fact that this element has a relatively low melting point, compared with that of tungsten. The experiments with thorium show that it emits the same number of electrons per square centimeter or surface at 1720° K, as tungsten at 2180° K.

Thorium is not only objectionable as a hot-cathode material because of its low melting point but it is very difficult and expensive to prepare and is more readily oxidized than tungsten.

My invention obviates the difficulties attending the use of thorium as a hot cathode by using instead, one composed principally of tungsten with a small mixture of thoria or other compound of thorium. In order to approximate the electron emissivity of thorium, a reducing mixture is applied to the surface of a thoriated tungsten filament. This mixture or getter, when activated by the filament heated in a high vacuum, will partially reduce the thoria in the filament, leaving a minute coating of thorium on the surface thereof which greatly increases the electron emissivity of said filament.

My invention will be better understood by referring to the accompanying drawing which illustrates electron emissivity curves for various thoriated tungsten filaments obtained by plotting the milliamperes of current produced per square centimeter of said filaments as ordinates, against filament temperatures as abscissæ, compared with the electron emissivity of pure thorium and an alloy of thorium and tungsten.

In establishing the theory involved in this invention, a thoriated tungsten filament, that is, a filament comprising tungsten with about 2% of thoria mixed therein and treated by applying a getter thereto in which the ingredients are red phosphorus, cryolite and amyl-acetate-cellulose binder, was experimented with. The proportions of the con-

stitutents comprising the particular getter used are 13 grams of red phosphorus and 100 grams of cryolite mixed with 85 c. c. of amyl-acetate-cellulose binder liquid, but it is obvious that the exact proportions are not essential. The binder liquid is preferably of about the consistency of water and may be about a 2% solution of nitro-cellulose in a mixture of two parts by volume of amyl-acetate, four parts of alcohol and one part of ether. The electron emissivity of such a filament was determined by testing it in a highly evacuated tube surrounded by a cylindrical anode with an aperture therein through which the temperature of the filament was determined by means of an optical pyrometer.

An electro-motive force was applied between the cylindrical anode and the filament, kept at incandescence by a suitable source of electricity, and the electro-motive force gradually increased until a saturation electron current occurred between the incandescent filament and the cylindrical anode. In this way, a number of points were determined for the curve 1 in the drawing.

The curves 2 and 3 were similarly plotted, curve 2 being that for a red-phosphorus-coated thoriated tungsten filament and curve 3 being for an untreated thoriated tungsten filament. The points marked 4, 5, 6, 7, 8 and 9 adjacent to curve 3 are points for a curve for pure tungsten filament coated with the same form of getter as that used on the filament from which data for curve 1 was obtained. From these curves, it should be apparent that the electron emissivity for gettered thoriated tungsten is much higher than either phosphorus-coated thoriated tungsten, untreated thoriated tungsten or gettered pure tungsten.

Although I discovered that the red phosphorus is the active ingredient in the getter, a greater effect is produced by the getter than by the red phosphorus alone because of the impossibility of keeping the red phosphorus alone in intimate contact with the surface of the filament. The method for determining what the active ingredient of the getter was for increasing the electron emissivity of the filament is as follows.

Knowing the getter to consist of red phosphorus, cryolite and the amyl-acetate-cellulose binder, each of the constituents was placed on an individual thoriated tungsten wire and the emission from each of the three wires was tested in a manner similar to that previously described. The increased emissivity, represented by the difference between curves 2 and 3, was obtained only from the wire coated with the red phosphorus.

To show that an emissivity approaching that of pure thorium or tungsten-thorium alloy is obtained with such a getter applied to a thoriated tungsten filament, the copending application of Rentschler et al., Serial No. 480,301, filed June 25, 1921 and assigned to the Westinghouse Lamp Company, may be inspected. The points 11, 12, 13 and 14, determined by the applicants in said copending application, are plotted showing the electron emission from a thorium filament for various temperatures. The points 15, 16, 17, 18 and 19, determined by the same applicants, are plotted to show the emissivity of a tungsten-thorium alloy consisting of 75% tungsten and 25% thorium.

From a comparison of the curves shown and the points for the thorium emissivity curve and also for the thorium-alloy curve, it will be apparent that the red phosphorus-cryolite getter applied to a thoriated tungsten filament gives to such a filament, a characteristic electron emissivity, curve 1, approaching that of pure thorium or an alloy thereof. That is, the red phosphorus in the getter when activated in very close relation to the thoria in the doped filament appears to reduce some or all of said thoria on or near the surface of said filament leaving metallic thorium thereon, whereby, when such a filament is heated, an electron emission is obtained therefrom, vastly higher than that from a thoriated tungsten filament, curve 3, or a gettered pure tungsten filament, points 4, 5, 6, 7, 8 and 9, and approaching, to a large extent, the emissivity from a pure thorium or thorium alloy filament.

It will be seen that, although, for higher temperatures, there is quite a divergence between the curves for the thorium and thorium alloy and that for the gettered thoriated tungsten filament, yet between 1600° and 1700° K., these curves practically coincide. That is, at fairly low temperatures an electron emission obtained by the use of this red phosphoros-cryolite getter applied to a thoriated tungsten filament, is substantially the same as that obtained from a pure thorium filament.

It is obviously a great advantage to be able to run an electron-emitting device with the filament at a comparatively low temperature and retain a reasonable electron emission for, by so doing, the life of such a device is enormously increased and the blackening of the bulb may be thereby indefinitely postponed.

By comparing the curves 1 and 3, it will be seen that the same electron emission, for example, that of 5 milliamperes per square centimeter, may be obtained from gettered thoriated tungsten at 1735° K. as is obtained from either untreated thoriated tungsten or gettered pure tungsten at about 1958° K. Also 10 milli-amperes per square centimeter, may be obtained from gettered thoriated tungsten at 1820° K., which is equal to the

emissivity of either untreated thoriated tungsten or gettered pure tungsten at about 1990° K. These differences in temperature, amounting to 223° and 170°, respectively, are of very great importance and affect the burn-out life of a filament to a very great extent.

Although I have described a getter comprising red phosphorus, cryolite and amyl-acetate binder applied to thoriated tungsten, it is to be understood that, as the active ingredient is red phosphorus or other similar reducing agent, any substance or mixture of substances may be used with said red phosphorus or the like which will cause the same to intimately adhere to the surface of the filament, which may be tungsten or other thoriated refractory material, and my invention is not restricted to the use of the precise ingredients mentioned, but is only limited by the scope of the appended claims.

What is claimed is:

1. The method of increasing the electron emission of a thoriated filament comprising applying phosphorus thereto and heating said filament while maintaining the phosphorus in intimate contact therewith.

2. The method of increasing the electron emitting power of a thoriated filament comprising applying phosphorus thereto and heating said filament in a vacuum whereby thorium is produced in the filament by the reducing action of the phosphorus.

3. The method of increasing the electron emissivity of a thoriated metallic filament comprising applying mixture containing phosphorus and cryolite thereto and heating said filament to a high temperature for a sufficient period to reduce a quantity of the thoria in the filament to thorium.

4. The method of treating a thoriated filament whereby its capacity for emitting electrons is increased comprising applying a mixture of phosphorus and cryolite thereto and heating the same thereby causing a partial reduction of the thoria in the filament.

5. The method of treating a thoriated filament comprising applying thereto red phosphorus and cryolite in a suitable mixture of amyl-acetate and cellulose and heating said filament in a high vacuum whereby a partial reduction of the thoria in the filament occurs causing an increase in its capacity to emit electrons.

6. The method of treating a thoriated tungsten filament comprising preparing a liquid mixture of phosphorus, cryolite, amyl-acetate and cellulose, coating said filament with said mixture and heating the same in a high vacuum to cause a formation of thorium on the surface of said filament.

7. The method of treating a thoriated tungsten filament whereby its capacity for emitting electrons approaches that of thorium comprising applying a coating of red phosphorus with a binder to hold the same in intimate contact with said filament and heating the filament in a vacuum.

In testimony whereof, I have hereunto subscribed my name this 19th day of June, 1922.

THOMAS PHILIP THOMAS.