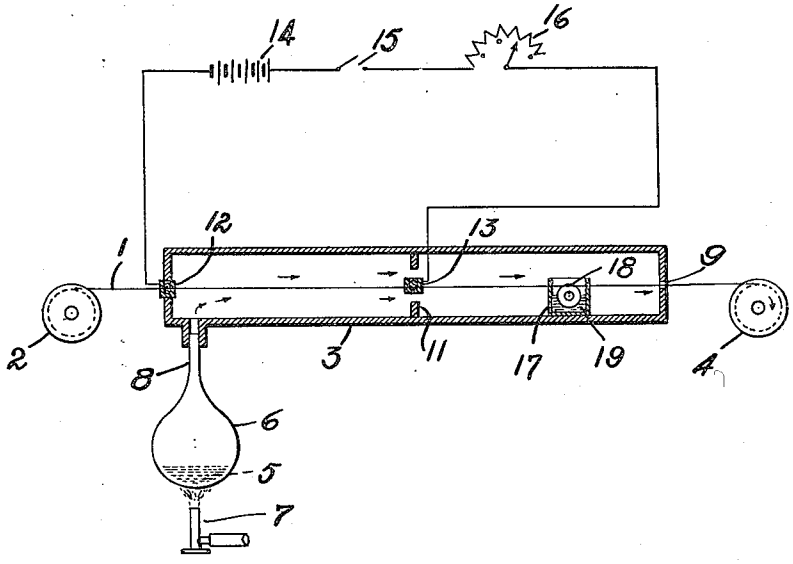
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DEPOSITION OF THORIUM FROM ITS VAPORIZABLE COMPOUNDS

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DEPOSITION OF THORIUM FROM ITS VAPORIZABLE COMPOUNDS.

Application filed December 9, 1922. Serial No. 605,772.

This invention relates to the deposition of thorium from compounds thereof in vaporous or gaseous form and more particularly to the coating of wire, electrodes or the like with metallic thorium, by heating the same in an atmosphere of the vapor of a compound of thorium.

An object of our invention is the formation of a coating of thorium from the vapor of a volatile compound thereof.

Another object of our invention is the production of thorium metal plated upon filamentary material by a convenient and continuous process, whereby the material is rendered more suitable for electron-emission or other purposes.

A further object of our invention is the activation or coating with metallic thorium, of comparatively great lengths of wire, consisting of tungsten or the like, by drawing the same, while heated, through an atmosphere comprising the vapor of a thorium compound.

A still further object of our invention is the coating of filamentary material with thorium, either before or after introduction into an evacuated envelope for an electron device, by heating the filamentary material in an atmosphere comprising the vapor of a thorium compound.

Other objects and advantages of the invention will be apparent from the following detailed description.

Because of the fact that metallic thorium is such a good electron-emission material, various methods have been devised for developing the same on, or applying it to, wire or filamentary material for use as hot cathodes in electron devices. For example, in the copending application of Ralph E. Myers, Serial No. 578,470, filed July 29, 1922, Activation of thoriated filaments and assigned to the Westinghouse Lamp Company, is disclosed a method whereby a coating of thorium is developed on the surface of thoriated wire, composed of tungsten or the like, by heating the same in a hydrocarbon atmosphere. This result is accomplished by the reducing action of carbon on the thoria in the filament or wire.

In the copending application of Marden, Conley and Thomas, Serial No. 578,813, filed July 31, 1922, now Patent No. 1,487,174, of March 18, 1924, Electrolytic deposition of thorium and assigned to the Westinghouse Lamp Company, is disclosed a method of electroplating filamentary material with metallic thorium, simultaneously with another metal, such as lead or iron. It should be noted that, in the former application, it is necessary to use a filament containing thorium oxide, whereas, in the latter application, the coating of thorium is not pure but is mixed or alloyed with another metal.

According to our present invention, we have devised a means for applying a pure coating of thorium to tungsten, molybdenum or other similar material, by deposition from the vapor of a thorium compound. An attempt has been made to deposit thorium on a tungsten filament heated to a high degree in the vapor of thorium chloride. This experiment was not successful possibly because of the fact that the chloride was heated in glass and only a relatively low vapor pressure of the compound obtained. We have found that filamentary material may be successfully coated with thorium by heating to a high degree in the vapor of certain organic thorium compounds, that is, compounds of thorium, carbon and hydrogen. This method has been used successfully for "activating", that is, causing an increase of electron emissivity in, tungsten wire.

Thorium forms certain organic compounds which are volatile or easily vaporized and may be distilled without decomposition. One of these compounds is thorium acetyl acetonate, $Th(C_5H_7O_2)4$. This compound can be made very simply by adding acetyl acetone to a solution of thorium nitrate and after collecting and drying the precipitate crystallizing it from alcohol. In conducting our experiments, a little of this compound was placed in a radio tube with a non-thoriated tungsten filament and while the filament was heated to about 1600° C. the tube was also heated to about 350° C. to volatilize the compound, the excess of which was distilled out of the tube and the portion which came in contact with the filament caused a deposition of thorium thereon. This result was determined by measuring the electron-emission of the filament so activated, as com-

pared with a similar filament which had not been activated. There are, undoubtedly, many other organic thorium compounds which may be used for the same purpose, for example, thorium methyl, $Th(CH_3)4$ and thorium ethyl, $Th(C_2H_5)4$.

Instead of activating the filament in an electron tube after the same is in place therein as the cathode thereof, this activation may be accomplished by continuous processes by means of which long pieces of wire or filamentary material may be activated and afterwards introduced into electron devices.

The invention will better be understood by referring to the accompanying drawing which illustrates, partly in longitudinal section and partly diagrammatically, apparatus for practicing our invention.

In the drawing, a wire or filament 1 of tungsten, molybdenum or other similar refractory material, which it is desired to activate, may be unwound from a spool 2, through a treating chamber 3, upon a spool 4, driven from any suitable source of power (not shown). The treating chamber 3 is provided with an atmosphere of a vaporizable or volatile thorium compound, adapted to be decomposed by heat. This may be accomplished by heating an organic compound of thorium 5 in a retort or flask 6, as by means of a Bunsen burner or the like 7, to vaporize or distill the thorium compound, which may be thorium acetyl acetonate, or other suitable thorium compound and cause it to pass through the tube or neck 8 of the retort into the treating chamber 3.

The vapor will then flow to the other end of the treating chamber 3 and emerge therefrom at aperture 9. As shown, chamber 3 is preferably formed with a partition 11 and has two mercury contact cups 12 and 13, connected to a battery 14 or other suitable source of electricity through a switch 15 and rheostat 16, for the purpose of suitably heating the filament 1, preferably to a temperature of about 1600° C., while passing between said mercury contact cups.

As the filament emerges from the treating chamber 3, it may be wound up on the spool 4, or it may be coated with a protective varnish-like material prior to emerging from the treating chamber. Such coating may be accomplished by providing a getter cup or other coating device 17, as indicated, with a pivoted pulley or wheel 18 partly submerged in a solution 19 of nitro-cellulose in amyl-acetate or other suitable varnish-like material, whereby the filament, by passing over or around said pulley, 18, becomes coated with said material and is protected from oxidation before coming in contact with the atmosphere.

The coating of the filament as above described is desirable in some instances, as where the filament is to be kept a considerable length of time before it is used in an electron-emitting device, but is not essential to the practice of our invention. After passing from the coating device 17, the filament emerges from the treating chamber 3 through the aperture 9 and may be wound upon the spool 4.

The reaction which takes place when the filament is heated to a high degree in an atmosphere of the vapor of thorium acetyl acetonate is not definitely known, but it is believed that said thorium compound decomposes to deposit thorium on the filament, with the formation of carbon monoxide, one or more hydrocarbons and perhaps hydrogen.

However, a filament treated according to the afore described process is activated so that, when used in an electron device, it shows an emissivity characteristic of metallic thorium.

Instead of activating such a filament before introduction into an electron device, the same result may be accomplished by activating the same after it is in place in an electron tube or the like, that is, a quantity of thorium acetyl acetonate, or other suitable organic compound of thorium, may be introduced into an electron tube containing a filamentary cathode of tungsten or the like and said cathode heated to a suitable temperature to cause a decomposition of the thorium compound used. At the same time the tube, which may be evacuated if desired, should be heated in the vicinity of the enclosed thorium compound, to cause a vaporization thereof, so that the same may be distilled into contact with the glowing filament.

The amount of thorium deposited on the hot filament depends on the concentration of the vapor of the thorium compound while the filament is glowed and the length of time the process is continued, as well as other factors, such as the degree of vacuum.

Although thorium acetyl acetonate has been mentioned as the preferred material, it is obvious that various other compounds of thorium, carbon and hydrogen may be used in the practice of our invention without departing from the spirit and scope thereof.

According to our invention, we have devised a means whereby filamentary material or the like may be coated with pure thorium, unalloyed or mixed with other metal and in which it is not necessary to start with a material to be coated containing a thorium compound.

Although we have described what we now consider to be preferred embodiments of our invention, it is to be understood that the same are merely illustrative and that modifications will suggest themselves to those skilled in the art, within the spirit and scope of the appended claims.

What is claimed is:

1. Filamentary material for electron emis-

sion purposes comprising tungsten free from thorium compounds upon which has been thermally plated metallic thorium unmixed with other metallic material.

2. An electron device comprising an evacuated envelope containing a filamentary cathode and a quantity of a vaporizable thorium compound, decomposable by heat to deposit thorium on said cathode, whereby the electron-emissivity thereof may be increased.

In testimony whereof, we have hereunto subscribed our names this 8th day of December 1922.

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THOMAS PHILIP THOMAS.
JOHN EDWARD CONLEY.