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ELECTRON EMITTING ELEMENT

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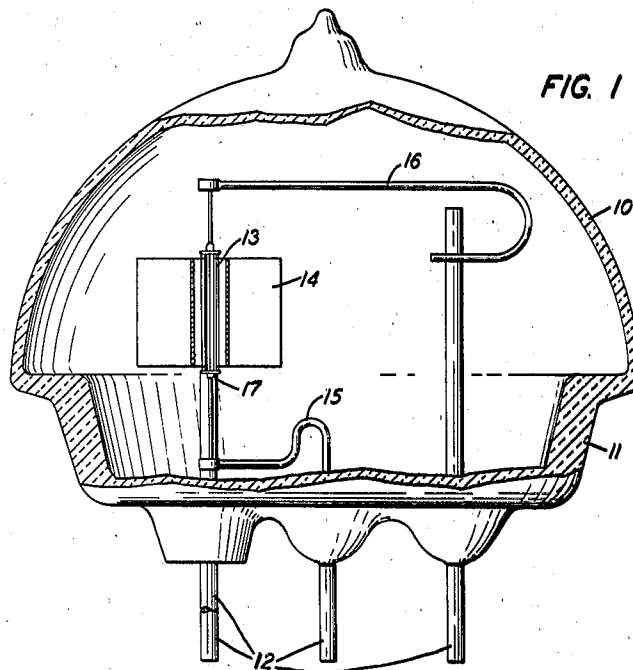


FIG. 2

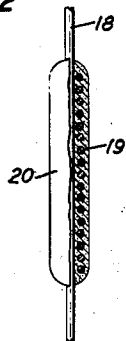
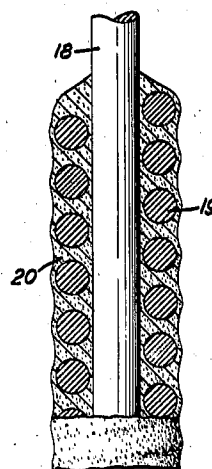


FIG. 3



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ELECTRON EMITTING ELEMENT

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9 Claims. (Cl. 250—27.5)

This invention relates to electron emitting elements for electron discharge devices and more particularly to methods of fabricating such elements.

For many years thoriated tungsten filaments have served their usefulness in the thermionic arts as a source of copious electron emission in amplifiers, oscillators and other types of devices, but their adaptability has been impaired by two inherent disadvantages, one being the costly activation process in hydrocarbon gas for carbiding the tungsten and initiating the conversion of the thorium compound to active metallic thorium and the other being the resulting embrittlement of the tungsten core by the carbide produced during this activation process. The latter fault predisposes the filament to frequent and unpredictable mechanical failures which in some cases, such as their use in airplane indicators where they are subjected to unavoidable shock and vibration, cause sudden and unexpected interruptions in service which might prove disastrous.

Since carbonization is indispensable to the maintenance of satisfactory emission by controlling production and distribution of metallic thorium in this type of emitter, the only alternative would be the production of an emitter of simulated characteristics without the decimating effect of the carbide.

An object of this invention is to overcome the difficulties usually attendant with thoriated tungsten emitter elements.

Another object of the invention is the production of a composite emitter having superior efficiency and rugged construction.

A further object is to facilitate the activation of the emitter without inherent brittleness and carbide formation in the core.

Still another object of the invention is to materially decrease the thermal emissivity of the improved emitter while maintaining the operating current uniform and controllable.

In accordance with this invention, a composite emitter is produced which resembles or exceeds a thoriated tungsten filament in electrical characteristics, emission and operating life, but which lacks the detrimental attributes of such a filament, by the application of a coating solution to a carrier core of tungsten wire or tubing having a wire or tubular helix of tungsten wound thereon to form a locking or retaining intermediate element between the core and the coating. The coating is sprayed or painted on the core and intermediate element and comprises a thorium compound mixed with a binder substance which

leaves no carbon residue upon heating the coating in vacuum, such as hexanitratated cellulose or gun-cotton dissolved in amyl acetate. The completely nitrated cellulose binder insures adequate adherence of the thoria coating to the core and when the coating is flashed to partially reduce the material to active metallic thorium, the binder is completely removed as gaseous products and no residual carbon remains in the coating or escapes into the core to cause embrittling action.

A feature of the invention relates to the preflashing of the powdered thorium compound to remove impurities, principally sulphur compounds, which are poisonous to thermionic activity and cause shrinkage and poor adherence of the coating on the core. This is accomplished by heating to approximately 1700° C. in a wet hydrogen atmosphere for a predetermined interval, to remove impurities and especially sulphurous contaminations so that a highly purified and sintered product is available for the coating mixture.

These and other features of the invention will be more clearly understood from the following detailed description taken in connection with the accompanying drawing:

Fig. 1 represents an electron discharge device with the vessel broken away to show the internal electrode assembly embodying a composite electron emitter made in accordance with this invention.

Fig. 2 is an enlarged view in elevation, partly in cross section, of the composite emitter employed in Fig. 1; and

Fig. 3 is a fragmentary view, partly in cross section on an exaggerated scale, of the composite emitter constituting the subject of this invention.

Referring to Fig. 1, an ultra-high frequency triode device is disclosed having an evacuated enclosing vessel formed of a dome-shaped shell 10 and a dish stem 11 provided with conductors 12 sealed therein and projecting into the vessel. Two of the conductors support a grid or control electrode 13 and a flanged anode 14, respectively, in coaxial relation in an offset position with respect to the axis of the vessel. The anode is formed of molybdenum having a blasted surface produced by sand, silicon carbide or other abrasive. The other two conductors are provided with crook springs 15 and 16 having their free ends in aligned relation along the axis of the grid and anode and supporting therebetween a composite filamentary emitter 17 which represents the subject-matter of this invention.

The composite emitter comprises a highly refractory conducting core 18 of tungsten, tantalum, molybdenum or similar metallic material, provided with a helical intermediate element 19 applied to the entire core or any portion thereof located along the length of the grid and anode. The helix 19 has the turns in uniformly spaced relation on the core and is formed of a material similar to the core metal. Either the core or helix or both may take the form of a solid wire or a hollow tube, the latter structure being economically advantageous in that the higher electrical resistance materially reduces power consumption of such emitters when directly heated by an electric current.

The core and helix are coated with an electron emitting substance 20, for example, a thorium compound, such as presintered and prepurified thorium dioxide, mixed with a binder material of hexanitrate cellulose or gun-cotton having the formula of $C_{12}H_{14}(ONO_2)_6O_4$ dissolved in amyl acetate as a solvent. Other suitable solvents may be employed with the completely nitrated cellulose. The coating is applied preferably by spraying a mixture of thoria and binder over the helical covered portion of the core within the extremities of the grid to a thickness to completely embed the helix 19. Since the turns of the helix are spaced on the core, the coating is securely affixed to the core and helix so that when the completed coating is fired, it is intimately locked between the turns and adheres to the core 18.

The commercial or chemically pure thoria has been found to produce poor adherence since it is quite light and fluffy and causes considerable shrinkage when a coating is heated on a filament, core. It has also been found on chemical analysis that a typical sample of commercial thoria contains the following impurities.

	Per cent
Thorium sulphate	7.52
Thorium nitrate	0.06
Thorium chloride	<0.05
Magnesium oxide	<0.003
Silicon dioxide	<0.003
Iron	0.006

and traces of titanium, aluminum and tungsten.

The high sulphur impurities probably contribute to poor adherence due to the evolution of sulphurous gases during the operation of the emitter and the sulphur emanation also causes poisoning of the active emitting metal in the coating.

In accordance with this invention, the thoria is presintered and purified by a thorough firing at 1700° C. in a wet hydrogen atmosphere or hydrogen containing water vapor for a period from 15 minutes to one hour. In this treatment, the thoria powder is placed in a thoria boat or an aluminum oxide boat provided with a thoria coating and inserted in a heating furnace provided with a facilities for injecting the hydrogen flow during the sintering process. The sulphurous impurities, along with other impurities, are removed and the thoria is sintered to a compact mass which is later pulverized to such a degree that the particles will readily be suspended in the binder carrier or fluid. This treatment materially reduces the impurities and especially the sulphur content from a high value of 7.52 to as low as .007. This represents a reduction to $\frac{1}{1000}$ of original value and the purified thoria insures higher emission values in the cathode.

The binder is usually added as a 12.5 per cent solution by weight, of the completely nitrated cellulose or gun-cotton (nitrogen content 13.4 per cent) in amyl acetate. The constituent proportions of a typical spraying mixture are

Prepurified thorium oxide	grams	500
Gun-cotton solution	do	75
Amyl acetate	cubic centimeters	575

This mixture is placed in a ball-mill jar containing 500 grams of pebbles and run in a roller continuously for 48 hours after which the mixture is ready for use. This procedure produces a homogeneous mixture with the solid particles finely divided and well dispersed in the suspending medium.

The mixture is sprayed onto the composite core as indicated above and after preliminary drying in air the composite coated emitter is mounted in the device as shown in Fig. 1. The completed device is then baked on the pump station at 400° C. and the anode is outgassed at 1000 to 1050° C. by high-frequency current for two minutes with the filament incandesced at 1.3 ampere currents. After the removal of the gases by the pumps and a high vacuum is attained, the filament is flashed at 2.0 amperes for one half minute with the high-frequency reduced to give about 900° C. anode temperature. The filament current is reduced to the operating point of 1.3 amperes and when the pressure attains the value of 1×10^{-5} millimeters of mercury, the device is sealed off the station.

During the flashing treatment of the thoria coating, the high temperatures cause the evolution of water vapor and carbonaceous gases spontaneously due to the reaction between the nitrogen, carbon, hydrogen and oxygen so that the binder material is completely removed as 100 per cent gaseous products and the thoria is partially reduced to active metallic thorium. The resultant coating is carbon-free since there is more than sufficient oxygen in the hexanitrate cellulose to completely burn out all the carbon so that no carbon is diffused into the core or intermediate helix and the coating matrix to depreciate the emissive properties of the coating or cause embrittling of the core material. The thermal emissivity of the coating matrix is substantially constant over a long period of operating life and the total emission values are exceedingly high, being of the order of 100 mills per watt or 3 amperes per square centimeter.

The filament processed in accordance with this invention has a low constant thermal emissivity, and therefore a low operating current, thus materially enhancing efficiency. An operating life of well over 20,000 hours may now be secured with the improved emitter of this invention since the operating temperature of such carbon-free coatings is easily controllable around 1700° K. Heretofore it has been found that the gradual loss of only a few micrograms of residual carbon will increase the temperature of a filament to well over 100° above the optimum operating point thereby greatly accelerating vaporization of the thoria and reducing the operating life of the emitter to a considerable extent. In tubes where abnormally high activity is paramount the higher thermal operating point may be employed with somewhat shorter but satisfactory life due to reduced evaporation and improved adherence of the matrix coating of thoria, presintered according to this invention.

It is, of course, understood that the invention is

not restricted to the specific construction set forth except in certain aspects with respect to the prefired emitting material and the completely nitrated cellulose binder ingredients. Therefore, the invention is to be construed by the scope of the appended claims.

What is claimed is:

1. An electron emitter comprising a metallic core, and a coating matrix thereon consisting of purified electron emitting material and a binder including completely nitrated cellulose.

2. An electron emitter comprising a metallic core, and a coating matrix thereon consisting of purified and sintered thoria suspended in a binder fluid including completely nitrated cellulose.

3. An electron emitter comprising a metallic core, and a coating matrix uniformly deposited thereon consisting of purified and prefired thoria, free from carbon residue.

4. An electron emitter comprising a metallic core, a helical winding thereon having spaced turns in contact with said core, a carbon-free thoria matrix uniformly applied on said core, and said helical winding embedded therein, said thoria being partially reduced on the surface to serve as a source of electron emission.

5. An electron emitter comprising a tungsten core, and a prefired matrix coating thereon of thorium oxide applied with a binder of cellulose having a formula of $C_{12}H_{14}(ONO_2)_6O_4$.

6. A coating suspension for electron emitters, comprising a highly refractory prefired emitting

substance, completely nitrated cellulose, and a solvent therefor.

7. A coating suspension for electron emitters, comprising prefired and presintered thorium oxide, hexanitrated cellulose solution, and amyl acetate solvent in the proportions of 500 grams of the oxide to 75 grams of solution in 575 cubic centimeters of solvent.

8. The method of activating a composite emitter having a highly refractory material coated on a conducting core which comprises, applying said material suspended in a binder solution of hexanitrated cellulose dissolved in a solvent to a core to form a matrix, heating said matrix to a reaction temperature to spontaneously combine the excess nitrate content with the carbon of said cellulose, removing the resultant gaseous products, and reducing some of the refractory material to form emissive metal.

9. The method of activating a composite emitter having thorium oxide coated on a tungsten core which comprises, applying said thorium oxide suspended in a binder containing a cellulose material having the formula of $C_{12}H_{14}(ONO_2)_6O_4$ dissolved in amyl acetate to said core to form a matrix coating, heating said matrix to a reaction temperature to spontaneously combine the nitrate content with the carbon of said cellulose, removing the resultant gaseous products, and reducing some of the thorium oxide to metallic thorium.

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