

March 18, 1947.

G. A. BECKER

2,417,461

ELECTRON TUBE AND METHOD OF MAKING SAME

Filed Aug. 31, 1945

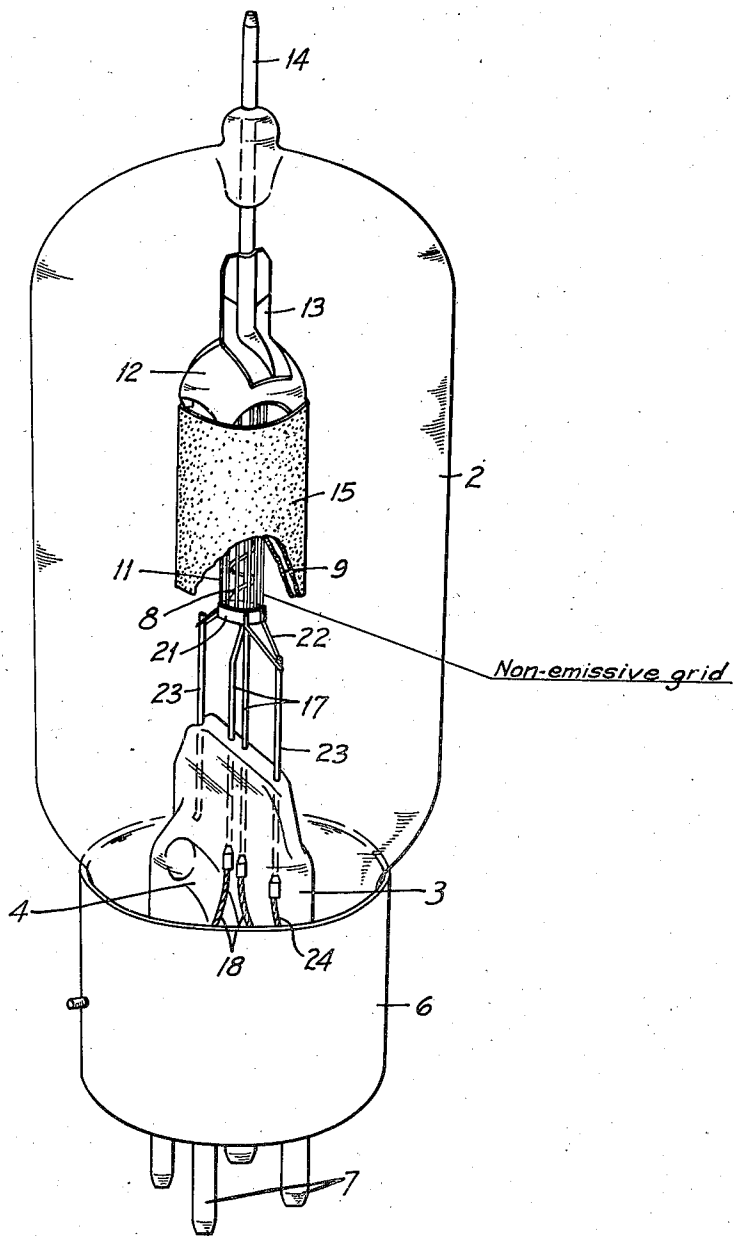


Fig. 2

Fig. 1

INVENTOR.
George A. Becker
BY *Harold Eng*
ATTORNEY

UNITED STATES PATENT OFFICE

2,417,461

ELECTRON TUBE AND METHOD OF
MAKING SAME

George A. Becker, San Bruno, Calif., assignor to
Eitel-McCullough, Inc., San Bruno, Calif., a
corporation of California

Application August 31, 1945, Serial No. 613,894

7 Claims. (Cl. 250-177)

1

This is a continuation-in-part of my copending applications, Serial Nos. 467,455, filed November 30, 1942; 501,721; 501,722; 501,723; and 501,724, filed September 3, 1943.

My invention relates to electron tubes and more particularly to improvements in non-emissive electrodes having a surface layer including a refractory metal oxide of the type disclosed in the application of William W. Eitel and Jack A. McCullough, Serial No. 527,294.

It is among the objects of my invention to provide an improved method of forming a non-emissive coating on an electrode.

Another object is to provide an electrode of the character described having a coating comprising particles sintered together to form a continuous sheath about a core.

A further object is to provide a method of making a coated electrode, which method simplifies the subsequent processing and evacuation of a tube incorporating the electrode.

The invention possesses other objects and features of advantage, some of which, with the foregoing, will be set forth in the following description of my invention. It is to be understood that I do not limit myself to this disclosure of my invention as I may adopt variant embodiments thereof within the scope of the claims.

Referring to the drawing:

Figure 1 is a perspective view of a tube having a grid electrode embodying the improvements of my invention; and

Figure 2 is an enlarged cross-sectional view of one of the coated grid wires.

In terms of broad inclusion, my tube comprises an envelope enclosing a thoriated cathode and an improved non-emissive electrode. The latter electrode comprises a core of suitable metal coated with finely divided particles including a refractory metal oxide sintered together to form a continuous sheath about the core; the particles preferably comprising at least two different refractory metals and oxygen combined as an oxide of at least one of the refractory metals. This coating is initially applied in any suitable manner as by spraying. Sintering of the coating is accomplished by heating the electrode in an oxygen free atmosphere, preferably by heating in vacuum, prior to mounting the electrode in the tube.

In greater detail, Figure 1 of the drawing shows a triode type of tube having a non-emissive grid embodying the improvements of my invention, it being understood that this is merely for purposes of illustration and that the improvements

2

may be applied to other types of tubes. The tube illustrated comprises an envelope 2 of glass or the like having a re-entrant stem 3 carrying an exhaust tubulation 4. After evacuation of the tube and sealing off the tubulation a suitable base 6 having prongs 7 is cemented to the lower portions of the envelope.

A plurality of electrodes including cathode 8, plate 9 and the improved grid 11 are coaxially disposed within the envelope. Plate or anode 9 has a cap 12 connected by bracket 13 to a lead 14 sealed to the top of the envelope. The plate may be of any suitable metal such as tantalum, and is preferably provided with a dark coating 15 to improve heat radiation.

Cathode 8 is of the thoriated type, preferably a thoriated tungsten filament welded top and bottom to a pair of leads 17 sealed to stem 3. Flexible conductors 18 connect the cathode leads to a pair of base prongs. The thoriated cathode or filament is preferred because my improved grid exhibits special non-emissive properties in such a combination. By the term thoriated cathode I mean a cathode containing thorium as the active emitter material, which thorium may be incorporated either as a pure metal or as a compound.

From the structural standpoint, grid 11 preferably comprises vertical wire bars terminating at a base ring 21 supported by brackets 22 on a pair of rods 23 sealed to stem 3. One of these rods functions as a lead and is connected to a base prong by conductor 24. The shape of the grid and the character of its mounting means may be varied within wide limits.

My improved grid is initially fabricated by making the grid bars of suitable metal, which metal forms the core 25 (Figure 2) upon which my non-emissive coating is applied. The core metal is preferably a refractory metal such as tantalum or molybdenum. An ordinary commercial grade of tantalum or molybdenum wire may be used. Tantalum is preferred because its ductility lends itself to ready fabrication into a grid structure. After being formed on a suitable mandrel the grid bars are welded to base ring 21. The fabricated grid is then cleaned, after which coating 26 is applied.

Both tantalum and molybdenum have been used in the past for making grids. As is well known, such grids are subject to considerable thermionic emission, even at relatively low temperatures, and are receptive to contamination from a thoriated cathode. My improved coating 26, hereinafter described, overcomes this diffi-

culty and renders the grid permanently non-emissive from the standpoint of primary emission at operating temperatures normally contended with. Not only is primary (thermionic) emission largely eliminated, but also secondary emission is brought under control.

The final coating 26 comprises finely divided particles including a refractory metal oxide sintered together to form a continuous sheath about core 25. By the term refractory metal I mean a metal in the class having a relatively high melting point and low vapor pressure, the preferred metals in this class being tantalum, tungsten, molybdenum, columbium, titanium, chromium, zirconium, vanadium, and beryllium.

The preferred final coating comprises at least two refractory metals and oxygen combined as an oxide of at least one of the metals. I have had good results from a coating prepared from a base mixture of tantalum pentoxide and tungsten trioxide. The tantalum pentoxide (Ta_2O_5) used is preferably formed by burning 50 to 500 mesh tantalum powder in air until the whitish color characteristic of the pentoxide is produced. The tungsten trioxide (WO_3) employed is formed by burning in air tungsten powder, of a fineness similar to that of the tantalum powder, until the yellowish color characteristic of this oxide is produced. These finely divided oxide powders are then thoroughly mixed in the dry state. The preferred mixture comprises about 90% by weight of tantalum pentoxide and 10% by weight of tungsten trioxide. These proportions may be varied within wide limits, depending upon the characteristics desired in the final grid.

In my preferred process the base mixture is next fired in a reducing atmosphere, preferably hydrogen. Reduction may be accomplished by other means, as by heating in an atmosphere of carbon monoxide, or by firing in vacuum. The time and temperature of firing may be varied, good results having been obtained by heating to around 1000° C. for about 3 minutes in an excess of hydrogen. During this heating treatment the mixture loses some weight and darkens materially in color, ranging from grey to black depending on the temperature and time of firing. From the practical standpoint it is immaterial if treatment is stopped after the powder has turned grey or whether it is allowed to darken further. This fired mixture is still a powder, the particles retaining their finely divided granular form.

The fired powder is then mixed with a suitable binder to cause adherence of the coating on the grid, a nitrocellulose binder being preferred, using amyl acetate as a thinner. Sufficient amount of the liquid binder or vehicle is mixed with the powder to produce a fluid mixture having the proper consistency for spraying. An ordinary spray gun is preferably employed for applying the coating. On a grid made of .012" wire the coating applied is preferably about .002" thick. The binder functions to temporarily hold the particles on the grid prior to further treatment.

The coated grid is then prefired by heating in an oxygen-free atmosphere, preferably in vacuum, prior to mounting it in the envelope. I have preheated coated grids in an evacuated furnace to about 1700° C. (brightness temperature) for about 15 minutes with good results, utilizing heat radiated from an adjacent heating element. This preheating is important for sintering of the coating particles together and to the core, it being understood that up to this point the particles are merely held by the temporary binder. The

sintering operation also knits the particles sufficiently to insure formation of a continuous sheath about the core, and provides a hard surface layer so that the grid may be safely handled during assembly into the tube without danger of dislodging the coating. Sintering the particles to effect bonding has the further advantage of making it unnecessary to have any foreign binder material in the final coating. In my process the temporary binder is volatilized during the firing operation.

The sintered grid is next sealed into the envelope along with the plate and cathode; the latter being preferably carbonized in accordance with the usual practice of making thoriated tungsten filaments. This carbonizing may be done either before or after the cathode is mounted in the envelope. The tube to be exhausted is connected with a suitable pump through tubulation 4. An oil diffusion pump is preferred, capable of reducing the pressure to a low value.

During exhaust the electrodes are heated in situ by suitable means preferably by electron bombardment from the filament. This method of exhausting tubes is well known; comprising connecting the electrodes in a suitable circuit, energizing the filament and applying positive potentials to the plate and grid. Heating of the plate and grid is caused by the kinetic energy dissipated when the fast moving electrons are suddenly stopped, the temperature depending upon the potentials applied. Other systems of heating the electrodes in the tube, such as the high frequency induction method, may be employed. After exhaust, the envelope is sealed off the pump and base 6 is applied.

The step of preheating the grid in vacuum prior to mounting it in the envelope has several advantages. It not only accomplishes the desired sintering of the particles, but it also functions to outgas the coating. Considerable gas is trapped between the particles when the coating is applied, and some gas is occluded in the solid particles. Unless this gas is removed from the coat prior to evacuating the tube it can cause much damage. For one thing, gas liberated during the exhaust of the tube can poison the filament. Also, excessive gassing of the coated electrode produces undesirable ionization in the envelope, and prolongs the time required to exhaust the tube. In my process of firing the electrode in vacuum the coating is thoroughly outgassed prior to evacuating the tube.

In a modified procedure I have omitted the step of firing the oxide powder prior to coating the electrode. This condensed method merely involves mixing the metallic oxide or oxides with a binder, coating the electrode therewith, and then firing the coated electrode (preferably in vacuum) prior to mounting it in the tube; the basic mixture of tantalum pentoxide and tungsten trioxide, hereinbefore specified, being preferred. In this modified procedure, firing of the oxide mixture to effect reduction takes place as an integral part of the sintering step. The process first described is preferred however, because the results are better and more consistent.

Just what happens to the mixture of oxides during the firing step is not fully understood. The change in color and loss of weight points to at least a partial reduction of at least one of the oxides. The fact that the oxides are in intimate admixture during reduction appears to be important. In the case of the preferred mixture of tantalum and tungsten oxides there is probably at least a partial reduction of the tungsten tri-

oxide and also possibly of the tantalum pentoxide to the lower order of oxides of these metals. From the loss of weight however, it is evident that considerable oxygen is retained so that the final mixture includes the three elements: tantalum and tungsten and oxygen, the oxygen being combined as an oxide of at least one of these metals.

Combination of two or more refractory metal oxides other than those of tantalum and tungsten may be used in the basic mixture for the coating. For example, some of the combinations I have used with especially good results include: molybdenum and columbium oxides; tungsten and columbium oxides; molybdenum and tungsten oxides; molybdenum and tantalum oxides; tantalum and columbium oxides; tungsten and chromium oxides; tantalum and titanium oxides; titanium and zirconium oxides; tantalum and zirconium oxides; and zirconium and beryllium oxides.

In any case, an electrode surfacing layer is produced which inhibits primary emission. The presence of two refractory metals with the combined oxygen gives the coating electrical conducting properties, which is desirable, particularly on grids, as will be readily understood. Another feature of an electrode coating formed by my process is that the step of prefring the coated grid to sinter the particles may be controlled to give either a rough or smooth surface, thereby controlling the secondary emitting properties of the grid. Thus, if more secondary electrons are desired from a particular grid, a smoother coating is produced. If little or no secondary emission is desired, a rough coating is provided. The smoothness of the surface depends upon the degree of sintering, which is determined by the temperature of firing. For a rough surface the sintering operation is carried only far enough to fuse adjacent surfaces of the particles, leaving the coating with a clinker-like appearance. For a smooth surface the sintering temperature is raised to a point where the particles of the coating more completely fuse or flow together. For example, an electrode coated with a mixture of 50% tantalum pentoxide and 50% titanium dioxide, and fired to 1850° C. in vacuum, produces a smooth enamel-like surface having fairly good secondary emitting properties. This sintering at higher temperatures to get a smooth surface does not adversely affect that property of the coating which inhibits primary emission.

I have also used coatings made from single oxides instead of using the mixed oxides. Grids made in this way tend to contaminate more readily, have a higher resistance surface, and therefore coatings made of mixed oxides are preferred.

My improved electrode exhibits remarkable non-emissive properties, particularly in combination with a thoriated cathode. Primary emission is of a low order and does not increase upon contamination of the electrode with thorium from the cathode.

While I have described my improvements in connection with a grid, it is understood that other electrodes may be so treated to suppress emission. For example, a plate coated in accordance with my invention makes an excellent anode for a rectifier tube where elimination of reverse current is highly desirable.

I claim:

1. A non-emissive electrode having a coating comprising finely divided particles sintered together, said particles including two refractory

metals and oxygen combined as an oxide of at least one of said metals, formed by reduction of a mixture of oxides of said metals said metals being selected from the group consisting of tantalum, tungsten, molybdenum, columbium, vanadium, chromium, titanium, zirconium and beryllium.

2. An electron tube comprising a thoriated cathode and a cooperating electrode having a coating comprising finely divided particles sintered together, said particles including two refractory metals and oxygen combined as an oxide of at least one of said metals, formed by reduction of a mixture of oxides of said metals said metals being selected from the group consisting of tantalum, tungsten, molybdenum, columbium, vanadium, chromium, titanium, zirconium and beryllium.

3. The method of making an electrode for an electron tube, which comprises coating the electrode with a mixture of finely divided oxides of two refractory metals selected from the group consisting of tantalum, tungsten, molybdenum, columbium, vanadium, chromium, titanium, zirconium and beryllium, and then heating the coated electrode in vacuum at a temperature sufficient to effect reduction of the mixture and to form particles comprising the metals and oxygen combined as an oxide of at least one of said metals, said reduction being effected prior to placing the electrode in the tube.

4. The method of making an electrode for an electron tube, which comprises coating the electrode with a mixture of finely divided oxides of two refractory metals selected from the group consisting of tantalum, tungsten, molybdenum, columbium, vanadium, chromium, titanium, zirconium and beryllium, and then heating the coated electrode in an atmosphere from which free oxygen is excluded at a temperature sufficient to effect reduction of the mixture and to form particles comprising the metals and oxygen combined as an oxide of at least one of said metals, said reduction being effected prior to placing the electrode in the tube.

5. The method of making an electrode for an electron tube, which comprises mixing together finely divided oxides of two refractory metals selected from the group consisting of tantalum, tungsten, molybdenum, columbium, vanadium, chromium, titanium, zirconium and beryllium, heating the mixed oxides in a reducing atmosphere at a temperature sufficient to effect reduction of said oxides and to form particles comprising the metals and oxygen combined as an oxide of at least one of said metals, and then coating the electrode with the mixture.

6. The method of making an electrode for an electron tube, which comprises mixing together finely divided oxides of two refractory metals selected from the group consisting of tantalum, tungsten, molybdenum, columbium, vanadium, chromium, titanium, zirconium and beryllium, heating the mixed oxides in a reducing atmosphere at a temperature sufficient to effect reduction of said oxides and to form particles comprising the metals and oxygen combined as an oxide of at least one of said metals, then coating the electrode with the mixture, and then heating the coated electrode in vacuum prior to mounting it in the tube.

7. In the manufacture of an electron tube wherein an electrode is coated with finely divided particles of primary emission inhibiting material comprising two refractory metals and oxy-

gen combined as an oxide of at least one of said metals, formed by reduction of a mixture of oxides of said metals, the step of heating the coated electrode to a temperature sufficient to completely fuse and sinter said particles together into a smooth-surface coating prior to mounting it in the tube, to enhance secondary emission from said electrode.

GEORGE A. BECKER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

	Number	Name	Date
	1,981,620	Giard	Nov. 20, 1934
5	2,213,558	Veenemons	Sept. 3, 1940
	2,348,045	Wooten	May 2, 1944

FOREIGN PATENTS

	Number	Country	Date
10	555,324	German	July 21, 1932