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ELECTRON TUBE AND METHOD OF MAKING SAME

Original Filed Nov. 30, 1942 2 Sheets-Sheet 1

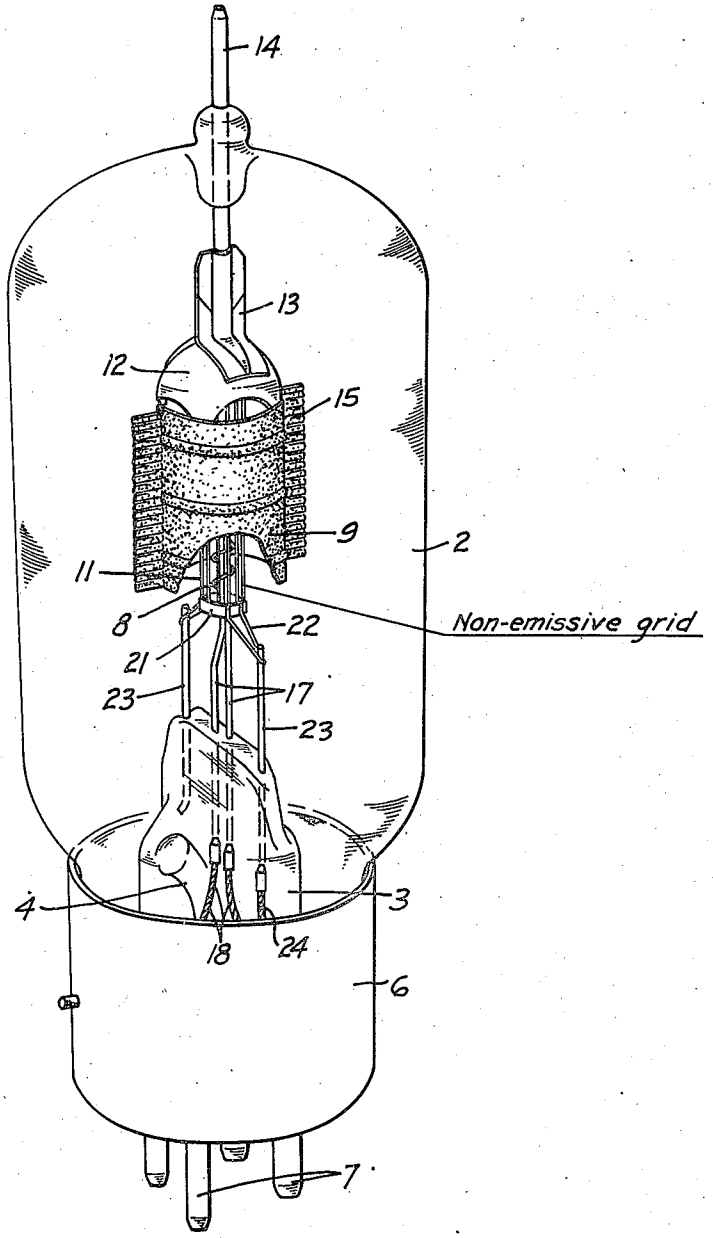



Fig. 1

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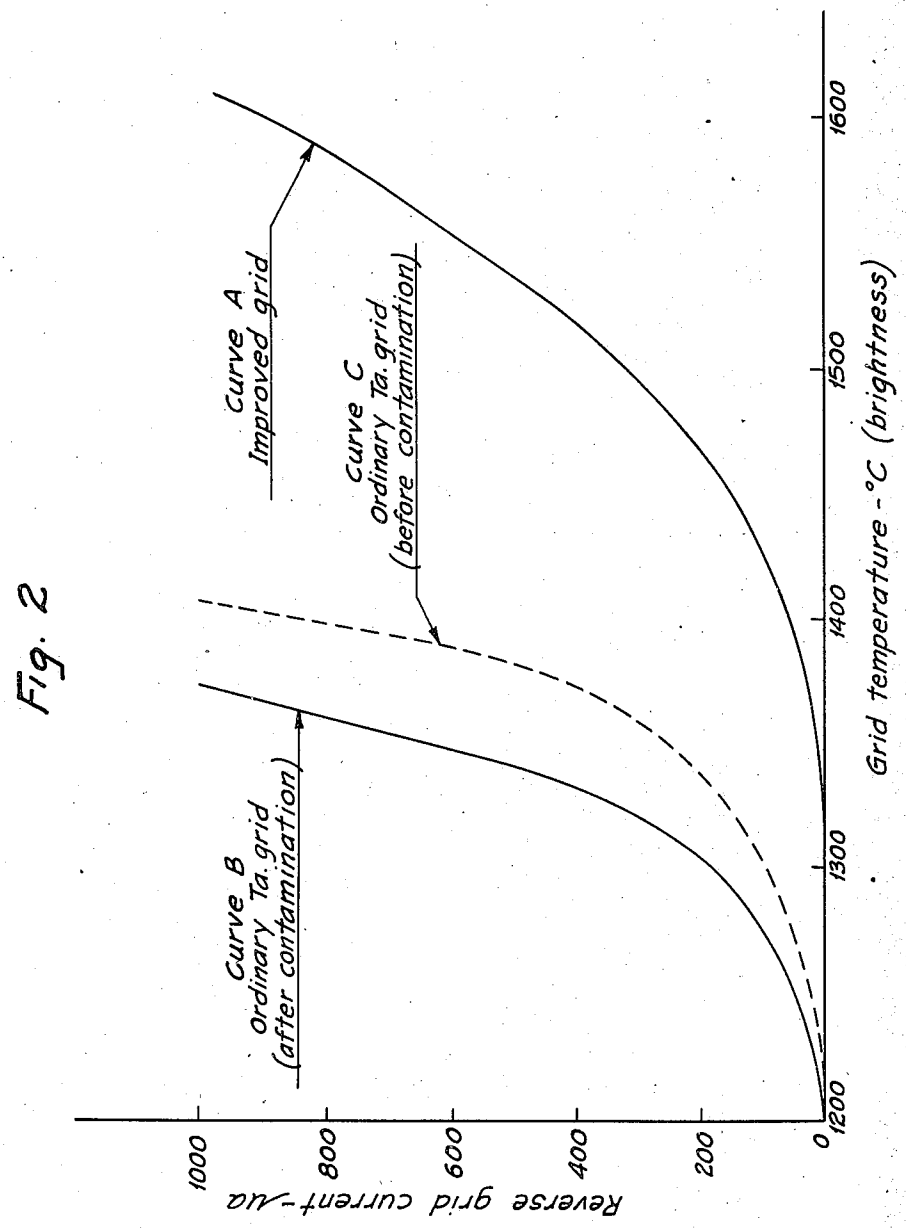



Fig. 2

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# UNITED STATES PATENT OFFICE

2,417,730

## ELECTRON TUBE AND METHOD OF MAKING SAME

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Original application November 30, 1942, Serial No. 467,455. Divided and this application September 6, 1944, Serial No. 553,133

1 Claim. (Cl. 250—177)

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This is a division of my copending application Serial No. 467,455, filed November 30, 1942.

My invention relates to electron tubes, and more particularly to improvements in electrodes for such tubes.

In an electron tube designed for transmission purposes it is highly desirable to eliminate primary emission from certain electrodes, particularly from the grid. Grid emission results in a reverse grid current which not only makes the tube unstable and erratic in its operation, but definitely limits the output and precludes use of the tube in certain kinds of service.

The broad object of my invention is to provide a non-emissive electrode from which primary emission is substantially wholly and permanently eliminated at the operating temperatures of the tube.

Another object is to provide an electrode of the character described which will not become emissive by contamination with foreign agents, such as thorium or the like from a thoriated tungsten filament.

Still another object is to utilize an initially ductile metal as the base material for the electrode, whereby the latter may be readily fabricated in its formative stages, and to provide a treatment for hardening the metal so that the electrode is capable of permanently maintaining its position of alignment in the tube.

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 species of my invention as I may adopt variant embodiments thereof within the scope of the claim.

Referring to the drawing:

Figure 1 is a perspective view of a tube embodying the improvements of my invention.

Figure 2 are the curves of reverse current plotted against temperature for both a treated tantalum grid and a grid of ordinary tantalum.

In terms of broad inclusion, my tube comprises an envelope enclosing an improved non-emissive electrode, such as a grid. The preferred method of making the electrode comprises forming it of a refractory metal, such as tantalum or molybdenum, coating it with a specially prepared composition, and then heating it in vacuum. The coating is composed of 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

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combined as an oxide of at least one of the refractory metals. This coating is applied in any suitable manner, as by spraying. Heating of the coated electrode in vacuum may be accomplished in the tube itself during exhaust, or the freshly coated electrode may be preheated in an evacuated furnace prior to mounting in the tube. The improved electrode has remarkable non-emissive properties and resists activation by contamination from a thoriated cathode.

In greater detail, Figure 1 of the drawing shows a triode type of tube having a grid embodying the improvements of my invention, it being understood that this is merely for purposes of illustration and that the improvements may be applied to other electrodes and in 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 evacuating 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 material such as tantalum, and is preferably provided with heat radiating fins 15.

Cathode 8 is preferably a thoriated tungsten filament, comprising a coil welded at top and bottom to a pair of leads 17 sealed to stem 3. Flexible conductors 18 connect the cathode leads with 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. It is understood that the filament may assume other shapes than the spiral type illustrated.

From the structural standpoint, grid 11 is preferably of the cage type comprising 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 of course be varied within wide limits.

My improved grid is initially fabricated from a refractory metal having a high melting point and low vapor pressure, such as tantalum or molybdenum. An ordinary commercial grade of tantalum or molybdenum wire may be used. Tantalum is preferred because it is initially very

ductile and because my process also functions to harden the tantalum, imparting desirable rigidity to the final electrode. After being formed on a suitable mandrel the grid is welded together and to base ring 21.

Both tantalum and molybdenum have been used in the past for making grids. As is well known however, such grids are subject to considerable thermionic emission, even at relatively low temperatures, and are receptive to contamination from a thoriated filament. My improved treatment, hereinafter described, overcomes this difficulty and renders the grid permanently non-emissive at operating temperatures normally contended with. Not only is primary (thermionic) emission largely eliminated, but also secondary emission is materially reduced.

After being formed and cleaned the grid is coated with a specially prepared composition. The base mixture for the coating preferably comprises 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, but at a sacrifice of optimum results 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 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 heat treatment the mixture loses some weight and darkens materially in color, ranging from gray to black depending upon the temperature and time of heating. From the practical standpoint it is immaterial whether the treatment is stopped after the powder has turned gray, or whether it is allowed to darken further. This fired mixture is still a powder, the particles retaining their finely divided granular form.

Just what happens during the firing step is not fully understood. The change in color and loss of weight involved, points to at least a partial reduction of the tungsten trioxide and also possibly the tantalum pentoxide to the lower order of oxides of these metals; the tungsten oxide possibly reducing, vaporizing and depositing on the tantalum oxide particles. 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. Whatever the precise nature of the composition may be, I have found that it produces the desired results in the final grid.

Oxides of other refractory metals may be used in the base mixture for the coating material. By the term "refractory metal" I mean metals in the class having a high melting point and relatively low vapor pressure, such as tungsten, tantalum and molybdenum.



The fired powder is then mixed with a suitable binder to cause adherence of the coating on the grid. A nitrocellulose binder is 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. With a larger diameter wire this coating would be proportionally heavier. The binder functions to temporarily hold the particles on the grid prior to further treatment, and the grid at this stage may be safely handled without disturbing the coating if reasonable care is taken.

The coated grid is then heat treated in vacuum. This may be accomplished wholly in the tube itself during exhaust, or the grid may be preheated in an evacuated furnace prior to final heating in the tube. Considering first the simpler although not necessarily the preferred procedure, the freshly coated grid is sealed directly into the envelope along with the plate and cathode; the latter being 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 vacuum 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 practice, for purposes of outgassing tube parts, is well known; comprising connecting the electrodes in a suitable circuit, energizing the filament, and applying positive potentials to the other electrodes. 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, such as the high frequency induction method, may be employed, but electron bombardment is preferred.

In a normal pumping schedule the grid is preferably heated up gradually until visible gassing ceases, and then held at say about 1550° to 1600° C. for about 15 minutes (these being "brightness" temperatures as indicated by an optical pyrometer). During the subsequent period of say about 1½ hours while the plate is outgassed by heating, the grid is preferably held at about 1450° to 1500° C. The times and temperatures will vary, depending upon the size of the tube and character of plate material; the total exhaust time being largely dictated by that required to outgas the plate, as will be understood by those skilled in the art. The actual grid temperature is somewhat higher than above indicated. This is because the outer viewed surface of the grid is cooler than the inner surface being bombarded, and also because the observed values are "brightness" temperatures as read directly by the optical pyrometer. After exhaust the envelope is sealed off the pump and base 6 is applied.

Instead of relying wholly upon heating the grid in situ during exhaust of the tube to accomplish the final processing step, the coated grid can be preheated in vacuum prior to mounting it in the envelope, and in many cases this is preferred. 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. Since the grid is subsequently exposed to the atmosphere prior to final mounting in the envelope, the grid should of course again be heated in the tube during exhaust. Preheating is desirable in most instances and especially in tubes having large grids, because it eliminates most of the occluded gas; thereby saving time in the final exhaust, keeping the envelope clean, and preventing poisoning of the filament. Preheating also has the advantage of baking the coating to a point where the grids may be readily handled without danger of scraping off the surface material, particularly if the core is of tantalum.

The theory underlying the operation of the improved grid is not fully understood. When applied over a core of certain metals, such as molybdenum for example, the composition retains its identity as a well defined coating on the core. In the case of a tantalum core the coating material is more or less integrally united with the core, the surface layer having a sintered or clinker-like appearance and adhering so tightly that it is very difficult to remove. Furthermore a hardening agent is introduced into the tantalum core, converting the ductile tantalum into a hard, brittle-like material characterized by small cubic or pyramidal crystals. This could be explained by migration of oxygen and/or metallic oxides from the coating into the lattice work of the tantalum core. However this may be, hardening of the tantalum core is a desirable result because the stiffness and rigidity of the final electrode enables it to maintain its position of alignment in the tube under mechanical shock and in the presence of large electrostatic and magnetic forces.

In any case, whatever the character of core metal employed, the composite electrode exhibits remarkable non-emissive properties. There are several contributing factors. Firstly, the surface of the electrode is dark and rough, and thermally speaking approaches a black body. Its good heat emissivity enables it to operate at lower temperatures per watt input, which is favorable for the depression of thermionic emission. Secondly, the work function is increased so that the electrode exhibits less primary emission at a given temperature; the work function for the processed tantalum for example being around 7 compared to about 4.3 for ordinary tantalum.

Thirdly, the improved electrode or grid does not become electronically emissive by contamination with foreign agents, such as thorium or the like from a thoriated cathode. Most grid materials, including ordinary tantalum and molybdenum, are subject to contamination and become increasingly emissive with prolonged operation. This activation by contamination does not occur with my grid, the improved electrode retaining its non-emissive properties as a permanent attribute. Even when the grid is heated excessively and some primary emission develops because of the very high temperatures involved, there is no evidence of contamination. Upon lowering the temperature again the grid returns to its non-emissive state. On the theory that oxygen plays an important role in this action, it is possible that a reserve supply of the oxygen is so held at or near the surface of the electrode as to be available for converting thorium to the non-emissive oxide state. In this connection the tungsten may act as a catalytic agent for releasing oxygen



at the surface. On the other hand, the materials applied to the core may merely form a protective barrier layer or sheath about the core, imparting to the electrode the necessary surface and/or other characteristics to account for phenomena involved.

Figure 2 shows the emission characteristics of a processed tantalum grid compared to one of ordinary tantalum. The curves in each instance were produced by plotting the reverse grid current in microamperes against grid temperature in degrees centigrade; these and other electrode temperatures specified herein being "brightness" temperatures. Curve C was plotted before the ordinary tantalum grid had become activated by material from the thoriated cathode, and is included for comparison with curve B to show the detrimental influences of contamination. The improved grid permanently resists contamination, the reverse current always following curve A. Referring to curves A and B it will be noted that at 1350° C. the reverse current with my grid is substantially zero compared to over 600 microamperes for ordinary tantalum. Also, the emission from the ordinary tantalum grid reaches a milliampere at about 1375° C., whereas the reverse current with the improved grid at that temperature is only about 20 microamperes. Furthermore, the new grid may be operated at a temperature well above 1500° C. before a reverse current of even 500 microamperes develops.

Whatever the explanation may be, it is clear that a composite electrode is provided, embodying (1) means enhancing its heat emissivity, (2) means increasing its work function, and (3) means rendering it resistant to activation by foreign agents such as thorium or the like. It is also clear that with a tantalum-cored electrode means is furthermore provided for hardening the core.

In a modified process I have used tungsten oxide alone in the coating instead of the mixed oxides. Grids made in this way however tend to contaminate more readily, and therefore the coating made of mixed oxides is preferred.

In another modified procedure I have omitted the step of firing the oxide powder prior to coating the grid. This condensed method merely involves mixing the metallic oxide or oxides with a binder, coating the grid therewith, and then heating the coated grid in vacuum; the basic mixture of tantalum pentoxide and tungsten trioxide, hereinbefore specified, being preferred. As before, heat treatment of the coated grid may be effected wholly in the envelope during exhaust, or preheated in a vacuum furnace prior to final heating in the tube. In this modified procedure, firing of the oxide mixture takes place as an integral part of the grid heating step. The process first described is preferred however, because the results are better and more consistent. Another variation of the preferred process is to coat the grid with the mixed oxides, fire the coated grid in a reducing atmosphere (preferably hydrogen) and then heat the grid in the evacuated envelope.

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 and treated in accordance with my invention makes an excellent anode for a rectifier tube where the elimination of reverse current is highly desirable.

I claim:

The method of making an electron tube hav-

ing a cathode and another electrode within an envelope, which comprises coating said other electrode with finely divided particles containing a mixture of refractory metal oxides, heating the coated electrode in vacuum to effect at least a partial reduction of the mixture, mounting the cathode and coated electrode in the envelope, evacuating the envelope, and heating the coated electrode while within the envelope by bombardment with electrons from the cathode.

GEORGE A. BECKER.

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