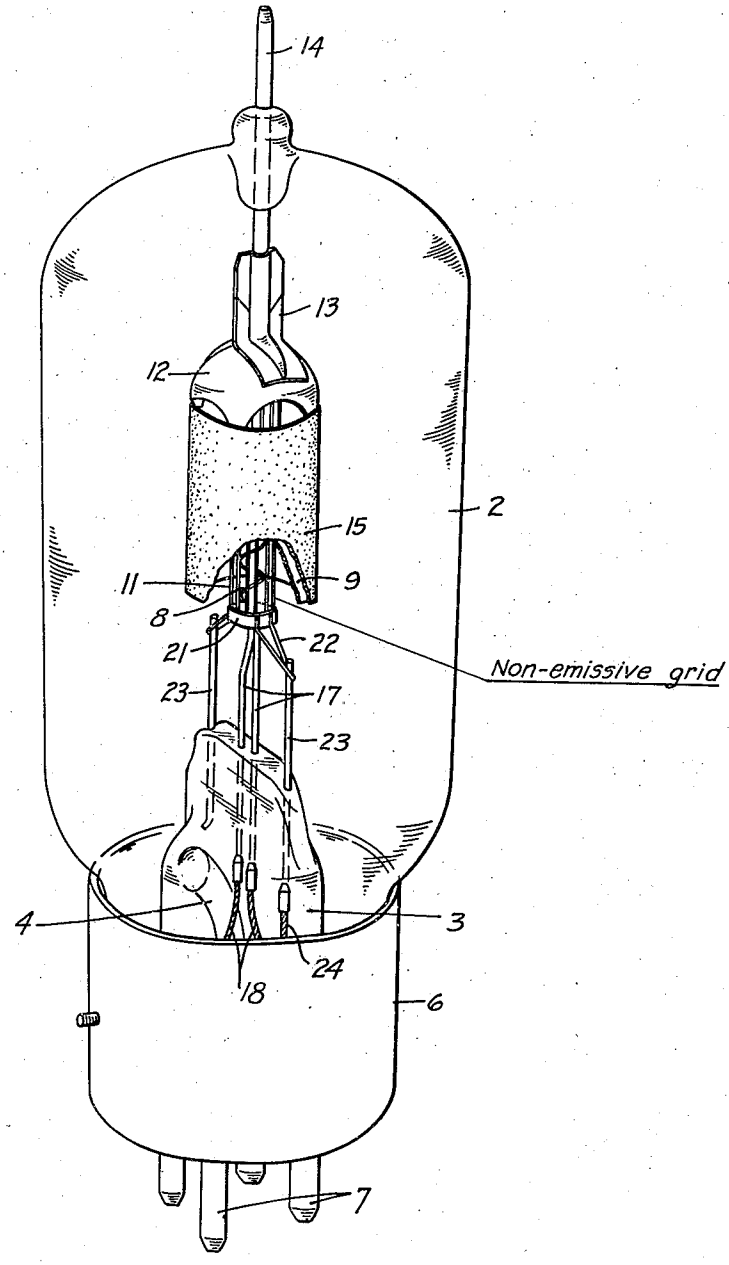
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NON-EMISSIVE ELECTRODE FOR ELECTRON TUBE AND METHOD OF MAKING SAME

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NONEMISSIVE ELECTRODE FOR ELECTRON TUBE AND METHOD OF MAKING THE SAME

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This is a continuation-in-part of our copending application Serial No, 496,686, filed July 28, 1943, in turn a continuation-in-part of application Serial No. 430,390, filed February 11, 1942.

Our invention relates to electron tubes, and more particularly to a non-emissive electrode for such tubes.

The broad object of our invention is to provide an electrode, such as a grid, from which primary emission is substantially wholly and permanently eliminated.

Another object is to provide an electrode of the character described which retains its non-emissive properties at high temperatures.

Still another object is to provide a tube embodying an electrode which will not become emissive by contamination with thorium from a thoriated filament.

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

Referring to the drawing:

The figure is a perspective view of a tube embodying the improvements of our invention.

One of the most serious problems in vacuum tubes for transmission purposes is grid emission. Primary emission from the grid results in a reverse grid current which not only makes the tube unstable and erratic in its operation, but limits the output and prevents use of the tube in certain types of service. The problem is particularly aggravated in tubes where the grid normally runs at a relatively high temperature. Under these conditions usable grid materials are limited to refractory metals having high melting points, such as tungsten, tantalum, molybdenum and the like. These metals unfortunately are subject to contamination and exhibit undesirable amounts of primary emission.

There are two factors mainly responsible for primary grid emission, One is thermionic emission from the grid material per se, which depends upon the work function of the material used in making up the grid in the first instance. The other and most troublesome factor is lowering of the initial work function by contamination of the grid with material of higher emissivity such as thorium from a thoriated filament. Thus, even if a grid starts out as a non-emitter it ends up with a high primary emission due to activation by thorium sputtered or otherwise deposited on it.

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We have discovered that a grid having a metallic oxide layer on the surface has improved non-emissive properties when employed in combination with a thoriated type of cathode. The effective work function is increased and the grid does not become emissive by contamination with thorium. In explaining the resistance to contamination, it is our theory that the oxygen made available by an oxide on the surface of the grid functions to oxidize the thorium to thoria, which latter oxide is substantially non-emissive. We have also discovered a special grid surfacing material having great stability. This is a very important practical consideration; stability being required to insure non-emission at high temperatures and to provide long life. Our improvements are not to be confused with tubes made with oxide cathodes. The problems present in a tube with a thoriated cathode are wholly different than in a tube having an oxide cathode.

In terms of broad inclusion, our electron tube contains an improved non-emissive electrode comprising a metallic core having a stable surface layer including a metallic oxide. A special alloy is preferably used for the core to facilitate formation of the desired surface composition. This electrode is enclosed in an evacuated envelope together with a thoriated cathode. While we have shown a tube embodying the improvements in the grid, it is understood that this is merely for purposes of illustration and that other electrodes may be rendered non-emissive in a like manner.

In greater detail, and referring to the drawing, the tube chosen to illustrate the invention comprises an envelope 2 of glass or the like having a reentrant stem 3 carrying an exhaust tubulation 4. A suitable base 6 having prongs 7 is cemented to the lower portions of the envelope. The triode illustrated contains a cathode 8, plate 9 and the improved grid 11, all coaxially disposed in the envelope. Plate 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 molybdenum or tantalum, and, if desired, may be provided with a coating 15 of zirconium or the like to improve the gettering and heat radiating properties.

Cathode 8 is of the thoriated type, 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 is preferred because our improved grid exhibits special non-emissive prop-

erties in such a combination. By the term thoriated cathode we mean a cathode containing thorium as the active emitter material, which thorium may be incorporated either as a pure metal or as a compound. It is understood that the filament may assume other shapes than the spiral type illustrated.

Structurally speaking, grid 11 is preferably of the cage type comprising vertical wire bars terminating at a base ring 21 supported by bracket 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 its mounting means may be varied within wide limits.

The core of the grid is preferably initially fabricated from a tantalum-tungsten alloy comprising a major proportion of tantalum and a minor proportion of tungsten. An alloy including about 93% tantalum and about 7% tungsten has given good results and is preferred. This alloy is a refractory metal having a high melting point and sufficient ductility to permit fabrication of the grid structure. The alloy also has sufficient stiffness to provide a rigid grid capable of resisting shock and maintaining its position of alignment in the tube.

In order to improve the non-emitting properties of the grid we give it a special treatment. The first step is to oxidize the surface. This may be done in any suitable manner, as by heating the grid in an oxidizing flame. Because the core includes tantalum and tungsten, oxides of both of these metals are formed on the surface. Furthermore, since the core is an alloy the oxides are thoroughly intermixed and exist in a finely divided state of subdivision. The degree and length of heating may be varied within wide limits, depending upon the depth of oxide layer desired.

The oxidized grid is preferably next heated in a reducing atmosphere of hydrogen. The time and temperature of firing may be varied, satisfactory results being obtained by heating to around 1000° C. for about 3 minutes in an excess of hydrogen. The loss of weight involved points to at least a partial reduction of the tungsten oxide, this oxide either going to metal or to a lower order of oxide. Less reduction of the tantalum oxide is apt to occur because of the greater affinity of tantalum for oxygen. From the loss in weight measurements it is apparent that considerable oxygen is retained, hence the final composition includes the three elements: tantalum and tungsten and oxygen; the latter being combined as an oxide of at least one of these metals. Because the oxides initially formed from the alloy are in a very finely divided and intimately commingled state the resulting composition forms a dense, closely knit layer.

It is also apparent that the combination of two refractory metals with oxygen forms a very stable composition. A stable layer is very important from the standpoint of tube life and where high temperature operation is involved. We have made a surfacing of tantalum oxide alone (formed by oxidizing a plain tantalum core) and found that our preferred surface layer of two refractory metals and combined oxygen exhibits non-emission properties for a materially longer time and under much higher temperatures.

After the grid has been treated it is sealed into the envelope along with the plate and cathode; the latter being carbonized in accordance with the usual practice of making thoriated tungsten filaments. The envelope is then exhausted by connecting to a suitable vacuum pump through tubulation 4. During exhaust the electrodes are heated by suitable means, preferably by electron bombardment from the filament. This exhaust procedure is well understood by those skilled in the art. After exhaust the envelope is sealed off the pump and base 6 is applied.

If desired the step of firing the grid in hydrogen may be eliminated, and the heating of the grid in vacuum during exhaust of the tube relied upon to effect reduction. Heating the grid above about 1000° C. during evacuation accomplishes the desired purpose. Prefiring in a reducing atmosphere is preferred however as there is less chance of contaminating other electrodes in the tube.

Other combinations of refractory metals besides tantalum and tungsten may be used to form the surface layer. The preferred refractory metals, any two or more of which may be used, include tantalum, tungsten, molybdenum, columbium, vanadium, chromium, titanium, zirconium, and beryllium. The first six of the above metals are cubic body centered crystal elements in groups 5 and 6 of the periodic table; the next two are hexagonal crystal elements in group 4; and the last is a hexagonal crystal element in group 2. In any event, the desired result is achieved by producing on the surface of the electrode a composition comprising two refractory metals and oxygen combined as an oxide of at least one of the metals.

The principle of operation underlying the improved grid is not fully understood. It is apparent however that the work function of the treated grid is increased so that the electrode material itself exhibits less primary emission at a given temperature. Its resistance to activation by thorium is less easily explained. As hereinbefore mentioned, the best theory seems to be that the surface layer maintains a reserve supply of oxygen for oxidizing thorium to a non-emissive oxide.

Another advantage of our electrode surfacing composition is that the oxygen is held in a layer that has electrical conducting properties due to the presence of more than one refractory metal in combination with the oxygen in the composition. If the layer had a high electrical resistance it would not be satisfactory as a surface layer on a grid, as will be readily understood.

Whatever the correct explanation may be, we have conclusively demonstrated that the improved grid has remarkably low primary emission and that the grid retains its non-emissive properties indefinitely under high temperatures.

It will be appreciated from the foregoing that in the practice of the invention, the operating characteristics of the electrode are determined by the nature of the surface layer, and that the oxidation and reduction of an alloy core, as described hereinbefore, merely constitutes a convenient method of forming the desired surface; the material of which the core is formed is not significant. Consequently, a composition consisting essentially of refractory metals and combined oxygen may be formed separately and applied to an electrode core as a coating in any conventional manner.

We claim:

1. An electron tube having a thoriated cathode and a non-emissive electrode, said electrode having a surface layer 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, for inhibiting primary emission on contamination of the electrode with thorium, said metals being selected from the group consisting of tantalum, tungsten, molybdenum, columbium, vanadium, chromium, titanium, zirconium, and beryllium.

2. The method of making an electron tube having a thoriated cathode and a non-emissive electrode, which comprises surfacing the electrode with a composition for inhibiting primary emission on contamination with thorium; said composition being prepared by forming a mixture of oxides of two different refractory metals, and then heating the mixed oxides in a reducing atmosphere 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; mounting the surfaced electrode and said thoriated cathode in an envelope; and evacuating the envelope.

3. The method of making an electron tube having a thoriated cathode and a non-emissive electrode, which comprises surfacing the electrode with a composition for inhibiting primary emission on contamination with thorium; said composition being prepared by forming a mixture of oxides of two different refractory metals selected from the group consisting of tantalum, tungsten, molybdenum, columbium, vanadium, chromium, titanium, zirconium and beryllium, and then heating the mixed oxides in a reducing atmosphere; mounting the surfaced electrode and said thoriated cathode in an envelope; and evacuating the envelope.

4. The method of making an electrode resistant to primary emission for electron tubes which includes the steps of forming the electrode of an alloy consisting essentially of a major proportion of tantalum and a minor proportion of tungsten, heating the electrode under oxidizing conditions and forming oxides of both metals of the alloy at the surface, and heating the electrode under reducing conditions to reduce the tungsten oxide at least in part to the metal and to leave the tantalum in the form of the oxide.

5. The method of making an electrode resistant to primary emission for electron tubes which includes the steps of forming the electrode of a composition consisting essentially of a tantalum-tungsten alloy, in which the proportion of tantalum in the alloy is about 93%, heating the electrode under oxidizing conditions and forming oxides of both metals of the alloy at the surface, and heating the electrode under reducing conditions to reduce the tungsten oxide at least in part to the metal and to leave the tantalum in the form of the oxide.

6. The method of making an electrode resistant to primary emission for electron tubes, which includes the steps of forming the electrode surface of a composition consisting essentially of a major proportion of tantalum and a minor proportion of tungsten, and combined oxygen, said composition being prepared by heating said metals under oxidizing conditions and forming oxides of both metals, and then heating the oxides thus formed under reducing conditions to reduce the tungsten at least in part to the metal and to leave the tantalum in the form of the oxide.

7. An electron tube having a thoriated cathode and a non-emissive electrode, said electrode having a surface layer including in intimate admixture two refractory metals and oxygen combined as an oxide of at least one of said metals, for inhibiting primary emission on contamination of the electrode with thorium, said metals being selected from the group consisting of tantalum, tungsten, molybdenum, columbium, vanadium, chromium, titanium, zirconium, and beryllium.

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