

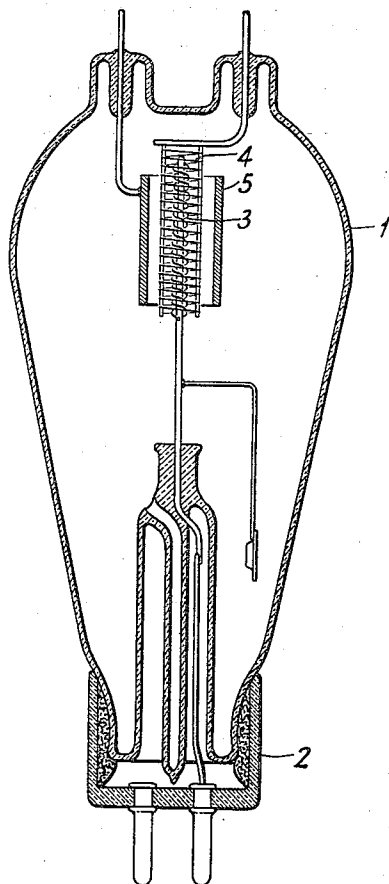
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REDUCTION OF UNDESIRE EMISSIONS OF ELECTRONIC DISCHARGE DEVICES

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REDUCTION OF UNDESIRE EMISSIONS OF  
ELECTRONIC DISCHARGE DEVICESClarence W. Hansell, Port Jefferson, N. Y., assign-  
or to Radio Corporation of America, a corpora-  
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6 Claims. (Cl. 250-177)

This invention relates to an improved method of reducing all undesired electron emissions of electronic discharge devices and is particularly adapted to the reduction of primary and secondary emissions from the anode and grid electrodes of short wave transmitting tubes.

An object of this invention is to improve the operating characteristics and to increase the output of electronic discharge devices by reducing undesired primary and secondary emissions from the grid and anode elements of vacuum tubes. In some instances, where undesired emission makes vacuum devices inherently unstable and incapable of operating, my invention may save the devices from failure of operation.

A feature of this invention resides in the partial plating or coating of one or more electrodes of an electron discharge device with a metal which differs in electron affinity from a base material or metal of the electrode.

Briefly, this invention improves an electron discharge device by substantially reducing both primary and secondary emission from the grid and plate electrodes of an electron discharge device. This invention is not to be confused with that of the prior art which consists of coating the cathode of a vacuum tube to increase the electron emission from the cathode electrode. In fact, in this invention, I desire an absolutely opposite result insofar as treated surfaces are concerned. Vacuum tubes as known in the prior art occasionally gave trouble known as "blocking" of the tube, which was found to be due to excessive reverse grid current, due to both primary and secondary grid emission when the tubes were operated at a point near their maximum output. By this invention, the objectionable features of blocking of the tubes is substantially reduced by plating certain of the electrodes with platinum or other suitable materials.

This invention will best be understood by referring to the accompanying drawing.

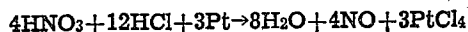
Referring now to the drawing, 1 is the glass envelope of a simple vacuum tube or electron discharge device, 2 is the base, 3 is the cathode, 4 the grid and 5 the plate element. The grid and plate elements according to one example of this invention are of tantalum, molybdenum or tungsten metal and are partially coated with platinum, by dipping the metal in a solution of platonic chloride, alcohol, and a small percentage of oil of lavender and Burgundy or Wisconsin pitch. A resultant layer of platonic chloride solution is obtained which adheres well to the metal surfaces. The metal is then heated, preferably in

an oven, or by any other suitable method which will keep the surfaces clean, to vaporize the solvents and to reduce the platonic chloride to a metallic platinum which completely covers the active portion of the electrode. A temperature somewhat higher than two hundred and fifty degrees centigrade is required to decompose the chloride and reduce it to metallic platinum. The coated metal can be brought up to a bright red heat without destroying the coating or causing excessive oxidation. A resultant layer of platinum is then obtained which adheres well to the metal. The heating of the metal to a bright red and the subsequent cooling causes the platinum coating to change its physical structure, for if the coating is observed under a microscope before heating to a high temperature, the platinum coating looks blotched and has frequent holes and cracks like a thin layer of dried clay mud. After heating to a high temperature, it looks wrinkled up, like a dried-up apple, with fewer gaps and holes, probably because the platinum is made to flow over the surface of the metal while heated to a high temperature.

Other metals than tantalum, molybdenum and tungsten can be platinized without much difficulty. For example, it is possible to coat iron wire with platinum. However, I have found that it will not stand heating to as high a temperature in air because of oxidation of the base metal, which destroys the platinum coating. If easily oxidizable metals are to be coated with platinum in accordance with this invention, they should be heated to reduce the chloride to platinum metal within vacuum chambers to reduce the amount of oxygen present or by carrying out the process in a hydrogen atmosphere. In fact, if facilities are available, heating in vacuum or in reducing atmospheres, such as hydrogen, is preferable for all metals. Almost any metal or ceramic material can be coated with platinum in a suitable atmosphere. This arrangement might be of considerable value for certain applications.

In order that others may be assisted in practicing my invention, I will give in greater detail one method for preparing the platinizing solution.

1. Mix nitric and hydrochloric acids to form aqua regia and dissolve in it a maximum quantity of metallic platinum.



2. Evaporate to dryness by slow heating, being careful not to overheat, to obtain dry platonic chloride  $\text{PtCl}_4$ .

3. Dissolve the platonic chloride in a minimum of commercially pure alcohol  $C_2H_5OH$ .

4. For each one hundred grams of soluble platonic chloride, in addition to the alcohol, add twenty-five cubic centimeters of natural oil of lavender (do not use the artificial product). Keep this solution available for further dilution as desired.

5. Dilute the solution with additional alcohol according to strength of solution desired. Various dilutions up to perhaps one hundred to one may be employed according to thickness of platinum coating desired. A small percentage of Burgundy or Wisconsin pitch may be added to solutions to give extra stickiness or adhesive properties.

6. Dip, spray or brush the solution onto the article to be platinized and then heat as previously directed.

7. Extra thickness of platinum can be added by dipping and heating several times but better results have been obtained by using a single application of solution of great enough strength to give the desired thickness of platinum coating.

For reference as to the electron affinities of certain elements, the following table, which was obtained from the Smithsonian Physical Tables, 8th revised edition, 1934, page 549, is given.

|            |        |
|------------|--------|
| Tungsten   | 4.52   |
| Platinum   | 4.4(?) |
| Tantalum   | 4.3    |
| Molybdenum | 4.3    |
| Carbon     | 4.1    |
| Silver     | 4.1    |
| Copper     | 4.0    |
| Bismuth    | 3.7    |
| Tin        | 3.8    |
| Iron       | 3.7    |
| Zinc       | 3.4    |
| Thorium    | 3.4    |
| Aluminum   | 3.0    |
| Magnesium  | 2.7    |
| Titanium   | 2.4    |
| Lithium    | 2.35   |
| Sodium     | 1.82   |

The ease with which secondary emission can be produced from pure metal surfaces is least for those elements having highest electron affinities. Therefore, clean platinum would be the most satisfactory surface material for grids and anodes of ordinary three and four element tubes where secondary emission should be held to a minimum.

Another reference which further illustrates the advantage of a platinized coating is to be found in chapter I of the book "The Physics of Electron Tubes" by L. R. Koller. On page 17, the values of the work function  $\phi$  and the values of  $b_0$  are given which may be used in the calculation of the thermionic emission for metals at different temperatures. Lowest emission at a given temperature is obtained from those metals having the highest value of work function  $\phi$  and  $b_0$ . The values given by this reference are as follows:

|            | $b_0$  | $\phi$ |
|------------|--------|--------|
| Platinum   | 72,500 | 6.27   |
| Tungsten   | 52,400 | 4.52   |
| Molybdenum | 51,500 | 4.44   |
| Zirconium  | 47,900 | 4.13   |
| Tantalum   | 47,200 | 4.07   |
| Thorium    | 38,900 | 3.35   |
| Calcium    | 35,000 | 2.24   |
| Cesium     | 21,000 | 1.81   |

The thermionic emission from cathodes of these metals may be calculated from Koller's Equations 12 and 13 which are from Richardson and Dushman and are as follows:

$$(12) \quad I = AT^2 e^{\frac{-b_0}{T}}$$

$$(13) \quad \log \frac{I}{T^2} = \log A - \frac{b_0}{2.303T}$$

Where I is the current per unit area, T is the absolute temperature, e is base of Napierian logarithms (see example of calculation at bottom of pg. 9 of Koller's book).

This data indicates that, of all the metals available platinum would be least subject to primary emission due to heating, when used in constructing the grids of vacuum tubes. The use of one hundred percent platinum would be too expensive but the use of a layer of platinum on other metals, tungsten, molybdenum, tantalum, nickel, iron, copper etc., is relatively cheap and probably almost as effective as pure one hundred percent platinum construction.

Other features of importance in the construction of tubes are the melting and boiling points of the metals. These are given in the table below.

|            | Melting point | Boiling point |
|------------|---------------|---------------|
|            | Degrees C.    | Degrees C.    |
| Platinum   | 1,755         | 3,910         |
| Tungsten   | 3,400         | 5,830         |
| Molybdenum | 2,535         | 3,620         |
| Zirconium  | 1,700         |               |
| Tantalum   | 2,900         |               |
| Thorium    | 1,842         |               |
| Calcium    | 810           |               |
| Cesium     | 26            | 670           |
| Gold       | 1,063         |               |

From this table, it will be seen that platinum has a lower melting point than tungsten, tantalum and molybdenum which would make it more subject to destruction from internal arc-over in tubes and therefore less desirable structurally. However, when used only as a coating according to this invention, the boiling point is most important. The stability of platinum as a coating at least exceeds molybdenum.

Platinum has a further advantage in that it is not oxidized or readily combined chemically with gases or vapors present in minute quantities in a vacuum tube. This also probably tends to reduce electron emission since it is well known that complex surface conditions often increase electron emission.

What is claimed is:

1. The method of coating electrodes of an electron discharge device including the steps of coating said electrodes with a solution of platinum chloride, alcohol and a small percentage of oil of lavender and pitch, heating said electrodes to vaporize the solvents and reduce the platinum chloride to a metallic platinum.

2. The method of coating electrodes of an electron discharge device including the steps of coating said electrodes with a solution of platinum chloride, alcohol and a small percentage of oil of lavender and pitch, heating said electrodes to a temperature somewhat higher than two hundred and fifty degrees centigrade to vaporize the solvents and reduce the platinum chloride to a metallic platinum.

3. The method of coating easily oxidizable metallic electrodes of an electron discharge device including the steps of coating said electrodes with

a solution of platinum chloride, alcohol and a small percentage of oil of lavender and pitch, heating said electrodes in a reduced atmosphere to vaporize the solvents and reduce the platinum chloride to a metallic platinum.

4. A non-emitting electrode to provide small electron emission in an electron discharge device, said electrode having a base of metal and a coating of platinum mounted in the path of an electron stream.

5. A non-emitting electrode to provide small electron emission in an electron discharge device,

said electrode having a tungsten base and a coating of platinum mounted in the path of an electron stream.

6. An electron discharge device having at least an anode, grid and cathode, said anode and grid having a tungsten base and their surfaces which are directly exposed to the path of electron bombardment in the normal operation thereof coated with a thin layer of platinum to reduce undesired electron emissions therefrom.

10

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