

Oct. 24, 1944.

V. L. HOLDAWAY ET AL

2,361,203

ELECTRON DISCHARGE DEVICE AND METHOD OF MANUFACTURE

Filed Jan. 1, 1942

FIG. 1

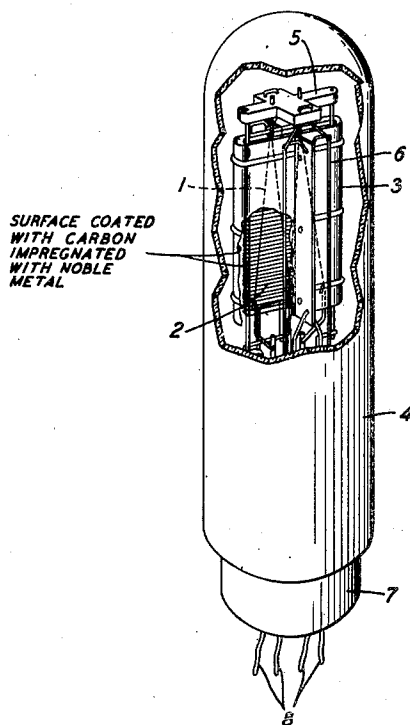


FIG. 2

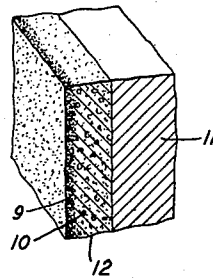
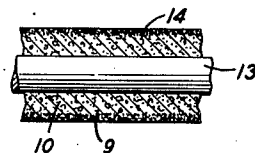


FIG. 3



INVENTORS: V. L. HOLDAWAY
E. A. THURBER
L. A. WOOTEN

BY
T. B. Jackson
ATTORNEY

Patented Oct. 24, 1944

2,361,203

UNITED STATES PATENT OFFICE

2,361,203

ELECTRON DISCHARGE DEVICE AND METHOD OF MANUFACTURE

Vivian L. Holdaway, Midland Park, N. J., Elmer
A. Thurber, Brooklyn, N. Y., and Leland A.
Wooten, Maplewood, N. J., assignors to Bell
Telephone Laboratories, Incorporated, New
York, N. Y., a corporation of New York

Application January 1, 1942, Serial No. 425,272

10 Claims. (Cl. 250-177)

This invention relates to bodies having at least a surface layer thereof formed of a composite mass of carbon and finely divided particles of a noble metal, and to methods of preparing such bodies. The invention is particularly advantageously employed in connection with electron discharge devices comprising one or more electrodes having at least the surface layer of such nature and possessing exceptional advantages, and for this reason will be discussed hereinafter in detail in connection with electron discharge devices.

Electron discharge devices, of which amplifying and rectifying tubes are examples, contain in an evacuated or gas-filled envelope, electron emissive means and an anode to which the electrons migrate. The electron emissive means usually comprises a cathode which is adapted to be heated and which is formed of or coated with a thermionically active material capable of emitting electrons when heated. Usually one or more grids or control electrodes are also disposed in the envelope of the device.

The anode, and the grid, if any is employed, tend to become heated from the heat generated by the cathode and from bombardment by electrons emitted by the cathode, or by ions in a gas-filled tube activated by the cathode. This is particularly true in high power tubes where high voltages are employed. It is desirable that such heating of the anode or grid be inhibited to as great an extent as possible, since otherwise the temperature of these elements may become high enough to damage them and cause undesired electronic emission from one or both of them.

In most electron discharge devices electron emission from the anode or grid is undesired and should be avoided to as great an extent as is possible. When an electrode from which electronic emission is undesired emits electrons in sufficient quantities the operation of the electron discharge device is deleteriously affected. Thus, loss of grid control, arc-back, blocking effect, or detrimental changes in input and output impedance may result.

Noble metals such as gold, platinum, iridium, palladium, osmium, ruthenium and rhodium, and particularly gold, platinum and iridium, tend to provide advantages when employed on the surfaces of grids or anodes, particularly the former, since they tend greatly to inhibit if not entirely prevent electronic emission for reasons which are not entirely clear. It appears that such a noble metal inhibits primary electronic emission by neutralizing electron emissive material which may be deposited on a surface of such metal from the cathode and inhibits secondary electronic emission because of its high work function. Because of the high cost of noble metals it is commercially impractical to employ anodes or

5 grids which are formed entirely of such metals, and it is necessary to employ only surface coatings of such metals. Moreover, when such metals have comparatively low melting points, as has gold, it is desirable to form a surface coating of such a metal on a material of higher melting point and good heat conductivity, such as molybdenum or tungsten, in order that the heat conductivity of such a base material will keep the operating temperature of the electrode employing the noble metal surface below the melting point of such noble metal.

10 However, when anodes or grids of the usual metals employed for such electrodes, such as molybdenum, nickel, tungsten, iron, stainless steel, etc., are provided with surface coatings of noble metals which are directly applied to the base metal of the electrodes, as by plating, the electron emission inhibition properties of such noble metals are considerably reduced as compared with those which would be present if the anodes or grids were formed entirely of such noble metals. It appears that such reduction of the electronic emission inhibition properties of the noble metal in such circumstances is largely caused by alloying of the noble metal with the supporting base metal of the anode or grid, such alloying taking place either during the application of the noble metal to the base metal or during the high temperature outgassing and operating conditions of the electron discharge device.

15 These difficulties are overcome by the present invention, according to which an electron discharge device is provided with at least one non-emissive electrode, which may be an anode or grid, which comprises carbon and a noble metal.

20 Advantageously such an electrode comprises a base metal body having at least part of its surface which is subjected to the conditions which tend to cause undesired electronic emission coated with a layer of carbon having finely divided particles of a noble metal interspersed therein and, if desired, having a noble metal on the surface thereof. Since the noble metal is dispersed in the carbon in the form of finely divided particles or is dispersed on the surface of the carbon substantially all of the noble metal is separated by the carbon from the base metal of the electrode. Therefore the noble metal cannot alloy with the base metal of the electrode. Despite the fact that the noble metal is dispersed in the carbon, it retains substantially all of its electronic emission inhibition properties.

25 Particular advantages are provided when the noble metal particles are so interspersed in the carbon, and when the surface layer of noble metal, if any, on the carbon is so thin, that the surface of the composite material of the present invention is dark or black in color, in this case, the material has a high black body heat radia-

tion constant. An electrode having such a dark surface radiates heat readily, so that it is considerably cooler during operation of the electron discharge device than would otherwise be the case. Such lower operating temperature of the electrode also tends to reduce electronic emission. However, if desired, the surface of the carbon may be provided with a layer of metal of a thickness sufficient to impart a metallic appearance to the outer surface of the composite layer.

A composite coating on a metallic electrode according to the present invention may thus be superior to noble metal coatings applied directly to the surfaces of base metal electrodes, and to the pure carbon coatings heretofore employed on surfaces of electrodes. It is superior to such directly applied noble metal coatings in inhibiting undesired electronic emission because no detrimental alloying takes place between the noble metal and the base metal, and because the high black body constant which the coating may have keeps the noble metal at a lower temperature during operation of the electron discharge device and hence reduces the tendency to electronic emission; the composite coating is superior to a pure carbon coating in inhibiting electronic emission since it contains the finely divided particles of a noble metal which have electronic emission inhibition properties superior to those of pure carbon.

The features making possible these and other advantages of the invention which will be apparent to those skilled in the art will be explained in the following discussion of the invention in connection with the accompanying drawing. In the drawing:

Fig. 1 represents a perspective elevation of an electron discharge tube embodying the present invention, part of the envelope of the tube being broken away to show the interior elements thereof;

Fig. 2 represents to a greatly enlarged scale a perspective elevation of a portion of an anode for a tube of the type of Fig. 1 embodying the present invention, the base metal and coating thereon being shown in section;

Fig. 3 represents to a greatly enlarged scale an elevation of a portion of a grid wire for a tube of the type of Fig. 1 embodying the present invention, the composite coating material being shown in section.

The electron discharge device of the drawing is a three-electrode electron discharge tube comprising a cathode 1, control grid 2, and anode 3, which are contained in a sealed glass envelope 4 which is shown as broken away to reveal the electrodes in the tube. The electrodes are supported in said envelope by any suitable means, such as that shown comprising insulators 5, of which only the upper one is shown, and brackets 6 which are supported from the base 7. Leads 8 passing through said base 7 provide electrical connection to the electrode in the tube in the known manner.

In the illustrated embodiment the cathode is a directly heated filament formed of thermionic emitting material such as thoriated tungsten, or coated with thermionic emitting material, such as one or more alkaline earth metals or compounds such as the oxides thereof. Obviously, the cathode may be of the indirectly heated type.

In the illustrated embodiment of the invention, the anode and grid may be formed of any suitable metal, such as nickel, tungsten, molybdenum, iron or the like, and are preferably

formed of a refractory metal such as molybdenum or tungsten. In this embodiment, moreover, both the anode 3 and the grid 2 have a surface coating embodying the invention, although either one of said elements alone could be so coated. The anode 3 is advantageously coated at least on its interior surface, which is exposed to the cathode and hence particularly exposed to the conditions which cause undesired emission therefrom.

In the manufacture of an electron discharge device embodying the invention it is advantageous that the electrode to be provided with a coating be first coated with a firmly adherent carbon layer, after which the carbon layer, which is sufficiently porous, is impregnated with a solution of a decomposable compound of the desired noble metal in a suitable volatile liquid. A readily heat-decomposable compound of the metal, such as a halide of the desired noble metal in solution in a suitable liquid, in general is satisfactory. The impregnated carbon layer is then subjected to heat to decompose the compound to the noble metal and to drive off the solvent and undesired by-products of the decomposition.

As is shown in Figs. 2 and 3, the resulting coating comprises a layer of carbon 9 impregnated with finely divided particles 10 of a noble metal. Because the solution of the compound of the noble metal is applied from the exterior of the carbon layer, particles of the noble metal may also be disposed on the surface of the carbon layer and under suitable conditions may form a substantially homogeneous layer of noble metal on the surface of the carbon, although it is advantageous that such surface layer of the noble metal should not be so thick as to impair seriously the dark color of the carbon and its high black body radiation constant. As a further result of the application of the solution of the compound of the noble metal from the exterior of the carbon layer, it is probable that, as shown in Figs. 2 and 3, the particles 10 of noble metal are in a greater concentration at the outer surface of the composite layer than in the interior thereof.

More specifically, Fig. 2 represents to a greatly enlarged scale a portion of an anode embodying the invention, the base metal 11 of molybdenum or other suitable metal having firmly adhering to it the composite layer 12 comprising carbon 9 having dispersed therein the finely divided particles 10 of a noble metal. Fig. 3 similarly represents to a greatly enlarged scale a grid wire embodying the invention and comprising a wire 13 of molybdenum or other suitable base metal having firmly adhering to its exterior surface a composite coating 14 embodying the invention.

In the manufacture of coated metal electrodes embodying the invention, the carbon layer which is advantageously first formed on the base metal of the electrode may be applied in any one of various ways. Thus, the surface of the base metal may be coated with a paste of carbon or graphite in a suitable liquid or binder and the coated member heated in a suitable atmosphere to form an adherent layer of carbon. Or, the base metal may be coated with a layer of finely divided carbon the particles of which are firmly held in place by a binder of silica, as described in Patent 2,348,045, issued May 2, 1944, to L. A. Wooten, which coating is advantageously prepared by hydrolyzing an organic silicate to form a solution of colloidal silica, adding finely divided carbon to form a suspension of carbon particles and colloidal silica in a volatile liquid, applying

the suspension to the desired surface, and evaporating the suspending liquid by air drying or heating to form the desired coating of carbon. If the base metal is a metal such as nickel which in the form of the metal or in the form of its oxide is readily carbonizable by cracking of a hydrocarbon, it may be carbonized in the conventional manner by heating it in the presence of a suitable hydrocarbon gas such as methane, acetylene, or the like, to a sufficiently high temperature to cause the gas to crack and deposit carbon upon the surface of the metal. If the base metal is one which can be carbonized only with difficulty, if at all, such as molybdenum, tungsten, stainless steel, or the like, the carbonization procedure described in copending application Serial No. 425,374 filed January 1, 1942 by E. A. Thurber and L. A. Wooten may be employed to advantage. According to the carbonization procedure described in said application, the base metal is first coated with an applied oxide of a metal of the iron family, such as nickel oxide, as by spraying of a suspension of the oxide in a suitable liquid. The oxide coated surface of the metal is then exposed to a carbonization treatment according to which the coated metal is heated in the presence of a suitable hydrocarbon gas, such as methane, acetylene, or the like, to a temperature sufficient to crack the gas and deposit carbon on the metal. A hard, adherent layer of graphitic carbon is thus obtained. As is described in said application, the nickel metal in the carbon layer resulting from reduction of the metal oxide may be removed, leaving a layer of substantially pure carbon. The carbon layers produced in such manners have sufficient porosity to permit ready penetration of the solution of the compound of the noble metal.

It is advantageous to employ a chloride of the desired noble metal dissolved in a volatile solvent, such as an alcohol, and to impregnate the resulting solution into the carbon coating by dipping the carbon coating into the solution or by spraying the solution on the carbon coating. The chloride may be decomposed to the metal and the volatile solvent and decomposition reaction by-products removed by suitably heating the impregnated coating. The cycle of impregnating with the solution and heating to decompose the metal may be performed as often as is desired to obtain a composite coating having the desired density of metallic particles.

Such a procedure usually results in a greater density of the particles at the outer surface of the carbon layer. By such a procedure it is also possible to obtain a metallic layer on the carbon. Under some circumstances it may be advantageous to coat the metal impregnated layer of carbon thus prepared with another layer of carbon, which in general can be readily accomplished by heating the composite layer to a sufficiently high temperature in the presence of a hydrocarbon gas.

The following are three examples of processes embodying the invention for producing electrodes embodying the present invention:

Example 1.—A molybdenum grid was carbonized according to the procedure described in the above-mentioned application Serial No. 425,374 by being first sprayed with a suspension of nickel oxide in ethyl alcohol, after which the grid was heated to 750° C.-950° C. in an electric furnace in a non-oxidizing atmosphere of methane diluted with hydrogen in a ratio of 1 to 2 by vol-

ume, for about twenty minutes, or for a period sufficiently long to provide a carbon coating of the desired thickness.

A 2 per cent by weight solution of gold trichloride in ethyl alcohol was then prepared. The grid having the carbonized surface was dipped into the gold trichloride solution and then baked in an oven at approximately 125° C. for fifteen minutes to decompose the gold chloride and remove the ethyl alcohol. This procedure was repeated three times and a suitable density of gold particles dispersed in and upon the carbon layer was obtained. The grid was then built into an electron discharge tube.

Example 2.—A molybdenum grid was carbonized as described in Example 1. To a 2 per cent solution of chloroplatinic acid (platinum chloride) in ethyl alcohol was added from 5 to 10 parts by volume of natural oil of lavender. The carbonized grid was dipped three times in the solution, each dip being followed by a ten-minute bake in a furnace at about 150° C. Baking at this temperature primarily removed the ethyl alcohol solvent. The impregnated carbon coated grid was then heated in an electrically heated furnace for fifteen minutes at about 800° C. in a gas mixture of hydrogen and methane in a ratio of 9 to 1 by volume. This subsequent heating decomposed the chloroplatinic acid to platinum, removed the by-products of the decomposition, and also caused a thin layer of carbon to deposit on the outer surface of the composite layer. The composite coating consisted of very finely divided particles of platinum dispersed in the carbon layer. The resulting electrode was built into an electron discharge device.

Example 3.—A molybdenum anode was carbonized in the same manner as was the grid described in Example 1. A 10 per cent solution of iridium tetrachloride in ethyl alcohol containing by volume 5 to 10 parts of natural oil of lavender was prepared. The carbonized anode was then treated according to the same procedure outlined for the carbonized grid in the preceding example. That is, the carbonized anode was dipped three times in the solution of iridium tetrachloride, each dip being followed by a ten-minute bake in a furnace at about 160° C., after which the anode was heated in a furnace for about fifteen minutes at 800° C. in a gas mixture of hydrogen and methane in a ratio of 9 to 1 by volume. The resulting composite coating consisted of very finely divided particles of iridium dispersed in the carbon layer. The coated anode was built into an electron discharge device in the usual manner.

Each of the coated electrodes prepared as above was a deep black in color, although that prepared according to the first example had a faint metallic sheen.

Operation of vacuum tubes of the type shown in the drawing embodying the electrodes prepared according to the above examples indicated that in each case the coating substantially prevented electronic emission from the electrode coated therewith, and was in this respect more advantageous than when an electrode of the same base metal was coated with the same noble metal alone or with carbon alone. Such operation also revealed that there was no appreciable alloying of the noble metal with the base metal and that the effective life of the coating was much greater than the life of a coating of noble metal applied directly to the base metal.

It is advantageous, particularly in cases where

the coated electrodes are subjected to high outgassing or operating temperatures, to incorporate in the carbon with the noble metal a small amount of silica, preferably in the colloidal form. In such case the silica acts as an absorbent and is a stabilizer for the dispersed particles of metal, thus inhibiting migration and coalescence thereof and retarding vaporization of the metal from the carbon. The silica can be advantageously incorporated by adding to the solution of the heat decomposable compound of the noble metal, such as to the solution of the chloride of such a metal, a small amount of colloidal silica solution, such as that conveniently prepared by hydrolysis of an organic silicate such as ethyl silicate. The resulting solution can be impregnated into the carbon and heated as indicated above. As another example, a small amount of an organic silicate such as ethyl silicate may be added directly to the solution of the chloride or other compound of the noble metal, and be hydrolyzed by said solution, after which the resulting solution may be impregnated and heated as described above. As another example, an electrode having a surface of carbon impregnated with a noble metal may be dipped into, or painted or sprayed with, a solution of colloidal silica in a suitable volatile liquid, which solution can be prepared by hydrolysis of a suitable organic silicate.

Electrodes embodying the invention may be employed to advantage in gas or vapor-filled electron discharge devices, as well as in electron discharge devices of the high vacuum type. In gas-filled devices the gas may be any of the noble gases or any of suitable vapors, such as mercury vapor. One or more gases or vapors, or a combination of one or more gases and one or more vapors may be employed. Indeed, such electrodes may be employed to particular advantage in gas or vapor-filled devices because of their resistance to the emission of electrons despite bombardment of high intensity.

Electrodes embodying the invention may be employed to advantage in electron discharge devices in conjunction with various types of cathodes, such as the pool type cathodes and thermionic emitting electrode type cathodes.

In some cases it is advantageous to coat other parts of electron discharge devices than the electrodes with coatings embodying the invention, although such coatings appear to find their most advantageous employment as coatings on electrodes from which electronic emission is undesired. Moreover, the electrodes or other parts may be entirely formed of metal-impregnated carbon, although it appears that the best advantages are obtained when the metal-impregnated carbon is employed as a coating on a metal electrode body because of the improved strength and electrical conductivity provided by such a construction. Such a coating may be over the entire surface of the electrode or over only a portion of it.

It is apparent that the impregnating metal may be an alloy of two or more metals, and that the impregnated carbon may contain particles of several different suitable metals and even small quantities of other materials. The claims are intended to include such modifications.

Modifications other than those indicated above may be made in the metal-impregnated carbon bodies described above, in the processes of making said bodies described above, and in the devices embodying the invention. The metal im-

pregnated carbon bodies of the invention may be produced by methods other than those indicated above.

It is intended that the patent shall cover by suitable expression in the appended claims whatever features of patentable novelty reside in the invention.

What is claimed is:

1. An electron discharge device comprising a sealed envelope containing a cathode adapted to emit electrons and an electrode which is disposed in the path of electrons emitted from said cathode and from which electron-emission is undesired, said electrode comprising a metal body having a surface in the path of electrons emitted from said cathode coated with a layer comprising carbon impregnated with a noble metal.

2. An electron discharge device comprising electron-emissive means, and a non-emissive electrode comprising a metal body having a portion of its surface coated with a layer comprising carbon impregnated with a noble metal, said noble metal being dispersed in finely divided particles in said carbon.

3. An electron discharge device as claimed in claim 2, in which said noble metal is gold.

4. An electron discharge device as claimed in claim 2, in which said noble metal is platinum.

5. An electron discharge device as claimed in claim 2, in which said noble metal is iridium.

6. A non-emissive electrode for an electron discharge device comprising a metal body having a portion of its surface coated with a layer comprising carbon impregnated with a noble metal and having on the surface of the carbon a layer of noble metal.

7. An electrode for an electron discharge device comprising a mass comprising carbon, silica, and dispersed finely divided particles of a noble metal.

8. The method of making an element for an electron discharge device having a surface coating which inhibits electron-emission comprising impregnating a porous layer of carbon adhering to the surface of a metal element for an electron discharge device with a heat-decomposable compound of a noble metal in liquid form, and heating said element to decompose said compound and deposit noble metal in dispersed finely divided particles in said carbon layer.

9. The method of forming on a surface of an element of an electron discharge device a coating which inhibits electron emission comprising forming on said surface a porous layer of carbon, impregnating said layer with a compound of a noble metal in liquid form, which compound is capable of being decomposed to produce the noble metal, and decomposing said compound to deposit the noble metal in dispersed finely divided particles in said carbon layer.

10. A process of forming a non-emissive electrode for an electron discharge device having a metal body, a portion of its surface being coated with a layer comprising carbon impregnated with a noble metal, which comprises impregnating a previously formed porous mass of carbon with a decomposable compound of the noble metal in liquid form and decomposing the compound to deposit the noble metal in dispersed finely divided particles in said carbon mass.

VIVIAN L. HOLDAWAY.
ELMER A. THURBER.
LELAND A. WOOTEN.