

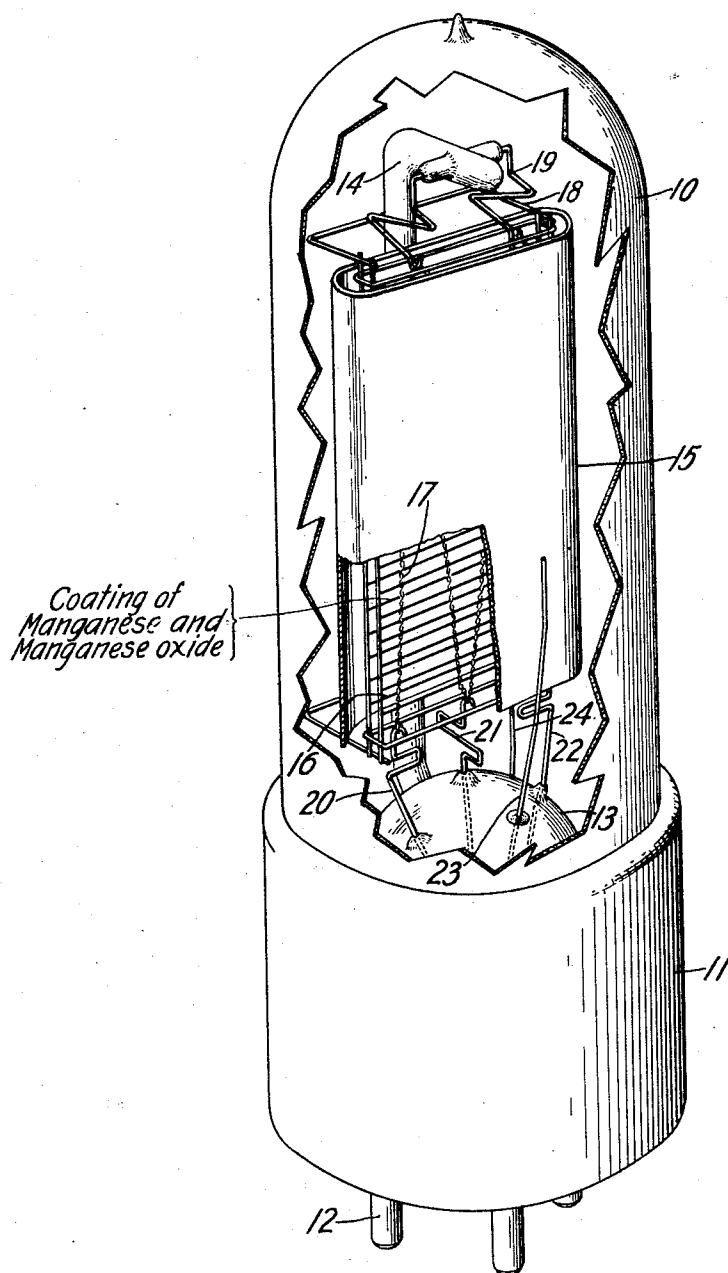
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ELECTRON DISCHARGE DEVICE

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UNITED STATES PATENT OFFICE

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ELECTRON DISCHARGE DEVICE

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An object of the invention is to improve the operating characteristics of electron discharge devices.

When electron discharge devices having thermionically active cathodes are operated at high temperatures, there is a tendency for particles of the active material with which the cathodes are coated to deposit on the control electrodes or grids. Such deposit prevents the proper operation of the device, since the grid becomes a secondary emitter of electrons and causes a blocking effect on the electron stream from the cathode to the anode.

A method for reducing this blocking or paralyzing effect by coating the grid with nickel oxide by oxidation at a suitable temperature is disclosed in M. J. Kelly, Patent 1,432,867, issued October 24, 1922. A similar result is obtained by calorizing the metal grids with aluminum and aluminum oxide, to provide a coating which combines with the active materials emitted from the cathode to form stable compounds, and thereby prevent secondary emission from the grid. This method is disclosed in Patent No. 1,722,121, issued July 23, 1929 to J. R. Wilson. It is also known that the use of a nickel-chromium alloy grid structure, as disclosed in J. E. Harris Patent 1,601,066, issued September 28, 1926, prevents secondary emission from the grid due to the chromic oxide combining with the basic oxides emitted by the filament to form chromites which are stable compounds.

The present invention relates to a coating for electrodes which will not readily decompose and also to a method of coating electrodes.

As an electrode coating the invention has its specific embodiment in a grid of an electron discharge device coated with manganese oxide.

As a method the invention is embodied specifically, in an electrolytic deposition process whereby a highly electro-negative metallic coating is obtained by electro-deposition from an aqueous salt solution. Such coating may then be oxidized to form a coalescent acidic oxide coating. In the application of this process, an improved electrode coating is produced by electro-deposition.

The term "electro-negative" is used throughout the specification to designate the metals above hydrogen in the electro-motive series of metals as defined on page 1565, Standard handbook of electrical engineers, 1915, which assume a negative potential in an electrolytic solution.

The coating or plating is produced on the electrode preferably by immersing it in an electrolytic bath containing an electro-negative material in the form of a salt, such as manganese sulphate or chloride, together with a good conducting salt, such as ammonium sulphate or chloride, and an acidifying agent, such as sulphuric acid. The anodic element of the bath consists of an inert material which is immersed in the bath surrounded by a cylinder of refractory material to prevent excessive oxidation of the bath, and also to form a partition for the anolyte and catholyte. The material to be electrolyzed, namely, the electrode, forms the cathodic element of the bath and is immersed in the catholyte surrounding the refractory cylinder. The bath is maintained at a low temperature and a relatively high current density to form a continuous coalescent surface on the cathodic element. Upon removal from the bath the electrode readily oxidizes upon coming into contact with the air to a degree depending on the conditions of the electro-deposition which may be varied to obtain any desirable amount of oxidation. The coating on the electrode is comparable with nickel plating and forms a hard, continuous and adherent surface which will not flake. Furthermore, when mounted in an electron discharge device and heated by bombardment, the oxidized surface of the electrode will not decompose nor will the surface become brittle. In fact, more of the metallic manganese is changed to the oxide to provide a sufficient amount of manganese oxide to react with the thermionically active particles emitted from the cathode to form inactive compounds which are stable.

A satisfactory bath may consist of 600 grams of manganese chloride, $MnCl_2$, $4H_2O$; 40 grams ammonium chloride, NH_4Cl ; 2.5 grams of sulphuric acid; and

water for each liter of solution. This bath is preferably contained in a non-conducting vessel such as a glass jar. An anode of inert material, such as graphite, is inserted in the bath and is surrounded by a porous non-conducting cylinder, preferably of alundum. This cylinder prevents excessive oxidation of the bath and forms a partition wall between the anolyte surrounding the anode and the catholyte surrounding the cylinder.

The electrode to be electrolyzed is inserted in the catholyte and forms the cathode element of the electrolytic bath. The cathode and anode are connected together by an external source of voltage of approximately 4 volts. The bath is maintained at a low temperature of from 5 to 10 degrees centigrade, and a current density of between 70 and 125 amperes per square decimeter. The low temperature and high current density governs the electrolytic action of the bath, whereby the nature of the deposit can be more easily controlled and the coating will be continuous and adherent on the metal electrode which is being plated.

The process of obtaining a continuous and coalescent acidic oxide coating on the electrode is as follows: Before the electrode is inserted in the electrolyte hereinbefore mentioned, it is cleansed in an alkali bath which may consist of a solution of sodium hydroxide or other alkali salts. After this preliminary cleaning, the electrode is immersed in a dilute nitric acid solution, consisting of one part water and one part of nitric acid, to thoroughly clean the metallic surface of the electrode. The electrode is then immersed in the electrolytic bath of the electro-negative substance for a period of from 10 to 30 minutes. By this process there is formed a continuous coating of metallic manganese on the electrode which is comparable with nickel plating. Upon removal from the bath the electrolyzed electrode slowly oxidizes in the air to form a superficial coating of manganese oxide which is an acidic oxide and is light gray in color. The amount of oxide coating which may be formed on the electro-plated surface depends on the controlling factors of temperature and current density at which the bath is maintained during the electrolytic process. For instance, at lower current densities, other than those given above, the deposit is nearly black in color with a heavy coating of oxide.

The drawing illustrates one form of an electron discharge device having an electrode or grid made in accordance with this invention, a protective coating on the grid preventing that electrode from becoming a source of secondary electrons.

The discharge device, as illustrated, consists of an evacuated vessel 10 to which the usual base portion 11 supporting the terminals 12 is attached. Within the vessel 10 is

a glass stem 13 from which an arbor or post 14 arises. This arbor 14 provides means for supporting a nickel anode 15, a nickel grid 16, and a cathode 17 coated with thermionically active material preferably basic oxides of the alkaline earth group of metals. The anode, as shown, is in the form of a flattened cylinder and is supported by suitable wires (not shown) extending from the arbor 14. The anode 15 surrounds the grid 16 and the cathode 17. The grid 16 is supported from the arbor 14 by wires 18 and the cathode is supported at one end, from the arbor 14, by wires 19 and at the lower end by means of wires 20, 21 and 22. The wires 20 and 22 also serve as leading-in wires for the current applied to the cathode. Wires 23 and 24 are leading-in wires connecting respectively to the plate and the grid. While the mechanical arrangement of the electrodes within the illustrated tube have been described, it is to be understood that the invention is not limited to this particular type of tube, which is shown merely for the purpose of illustrating one form of an electron discharge device to which this invention is applicable.

In the manufacture and assembly of the electrodes in the evacuated vessel, the electrodes and the vessel are subjected to an evacuation process to remove occluded gases and water vapor. During this process the electrodes are heated to a dull red color to increase the evacuation of gases. This heating may be utilized to further oxidize the metallic manganese plating on the grid and thereby increase the oxide coating so that the oxide content of the grid will be substantially greater than the metallic manganese content. After the evacuation process is completed the tube is sealed at the tip and the device is ready for use. The coating on the grid will be found to be relatively hard and coalescent and will not chip or flake in the operation of the device.

By thus coating the grid electrode in the manner above described, the particles of thermionically active material which may be emitted from the cathode and deposited on the grid, will not render the grid thermionically active since the acidic oxide coating will combine with the basic oxides of the material thrown upon the grid and thereby form inactive stable compounds, presumably manganites. Furthermore, the acidic oxide readily reacts with the thermionic oxides so that the compounds are formed instantaneously upon contact.

While the detailed description of the invention is directed to a method of forming the electro-negative metal and acidic oxide on a base metal such as nickel, the invention is not limited to base metals, since the electrodeposition may be produced on any metallic surface.

What is claimed is:

1. A coating for an electrode of an electron discharge device consisting of a thin layer comprising metallic manganese.
- 5 2. A coating for an electrode of an electron discharge device comprising a surface layer of partially oxidized manganese.
3. An electrode for an electron discharge device having a coalescent coating comprising electro-deposited metallic manganese.
- 10 4. An electrode for an electron discharge device having a coating of electro-deposited metallic manganese at least partially oxidized.
- 15 5. An electron discharge device comprising a thermionically active cathode, and another electrode, said other electrode having an electro-deposited coating consisting of manganese and manganese oxide which combines with particles from said cathode to form stable compounds.
- 20 6. An electron discharge device comprising a cathode having a coating containing a thermionically active basic oxide, and another electrode having a coating of partially oxidized manganese which forms a stable thermionically inactive compound with said basic oxide.
- 25 7. An electron discharge device comprising a cathode, a grid, and an anode, said grid having an electro-deposited coating consisting of manganese and manganese oxide.
- 30 8. An electron discharge device comprising a cathode, a grid and an anode, said grid having a coating comprising manganese oxide.
- 35 9. An electron discharge device comprising a cathode, a grid, and an anode, said grid having a coalescent coating comprising electro-deposited metallic manganese.
- 40 10. An electron discharge device comprising a cathode having a coating containing a thermionically active basic oxide, a grid and an anode, said grid having a coating comprising manganese oxide which forms a stable thermionically inactive compound with said basic oxide.
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In witness whereof, I hereunto subscribe my name this 27th day of July A. D., 1926.

ROBERT M. BURNS.