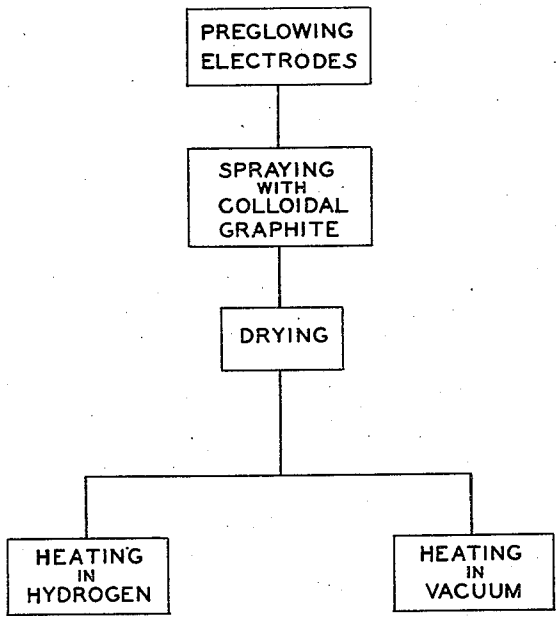
Nov. 20, 1934. G. E. LONG 1,981,652

METHOD OF COATING ELECTRODES

Filed April 28, 1931



INVENTOR
G. E. LONG

BY Walter C. Kiesel
ATTORNEY

Patented Nov. 20, 1934 1,981,652

UNITED STATES PATENT OFFICE

1,981,652

METHOD OF COATING ELECTRODES

George E. Long, Orange, N. J., assignor to Bell Telephone Laboratories, Incorporated, New York, N. Y., a corporation of New York

Application April 28, 1931, Serial No. 533,577

3 Claims. (Cl. 250—27.5)

This invention relates to a method of coating electrodes for use in connection with electron emitting electrodes of electron discharge devices.

In high power electron discharge devices, particularly of the oscillator type, the use of high anode and grid voltages results in pronounced heating of the refractory metallic electrodes. Usually the cathode associated with the anode and grid is provided with a highly thermionic material either combined with the core or uncombined in the form of a coating. Under such temperature condition, the grid or control electrode becomes an emitter of electrons. When the grid emits electrons, a phenomenon known as "blocking effect" occurs, thereby paralyzing the continued operation of the device. The grid emission generally falls into two distinct classes and may be defined as primary emission, due to particles of thermionic material being thrown off the cathode and deposited on the hot grid where they form a source of electrons, and secondary emission, due to the high temperature of the grid and the velocity of the impinging electrons causing the emission of secondary electrons from the grid. Naturally, this adverse condition of the grid should be overcome if the grid is to perform its normal function of controlling the flow of electrons from the cathode to the anode.

However, when attempts are made to overcome emission from the grid by coating this electrode with a black substance to maintain the grid cooler and also to combine with thermionic material so as to form inactive compounds, the characteristics of the device are changed due to the difference in the diameter of the lateral wires of the grid and the spacing between adjacent wires. Furthermore, the thick black coatings usually in the form of oxides of the metal of the grid practically insulate the grid from the other electrodes and it does not assume its normal function until the insulating properties of the coating are broken down by heating. Similarly, some metals, such as molybdenum, do not react favorably when coated with an oxide of the metal of the grid to prevent emission therefrom.

The principal object of this invention is to prevent primary and secondary emission from the grid in electron discharge devices.

Another object of the invention is to form a protective coating on the grid which will not affect the electrical characteristics of the device.

A further object of the invention is to form a protective coating on an electrode, such as an anode, the coating having a high black body constant to dissipate the heat generated in the device.

In accordance with this invention the electrodes, namely, the grid and the anode, are coated by a method which forms a coalescent hard film of carbon on the grid or the anode. The carbon coating having a high black body constant serves to dissipate the heat generated in the electrodes thereby rendering these electrodes cooler and overcoming to a great extent secondary emission from the grid electrode. When particles of thermionic material are deposited on the grid from the cathode, these particles are prevented from introducing primary emission effects, due presumably to the formation of carbides which are not thermionically active and are sufficiently stable at the operating temperatures encountered in the device so as not to affect the operation of the device. Furthermore, the carbon film, while in effect a high resistance coating, does not detract from the proper functioning of the wire grid as a control electrode in the flow of electrons from the cathode to the anode.

The drawing shows diagrammatically the process steps required to obtain the results of this invention.

The method of coating the electrode with a film of carbon consists in pre-glowing by heating the grid or anode in a vacuum or reducing atmosphere to completely free the electrode of occluded gases and deleterious substances. The electrode is then coated with a colloidal solution of graphite, known commercially as "Aquadag" and finally the carbon is fixed to the electrode surface in a vacuum or reducing atmosphere of hydrogen. The film of carbon formed on the electrode surface by this fixing method is relatively thin, hard and smooth and is firmly adherent to the surface. Furthermore, the diameter of the wire grid is not materially increased as to affect the static and dynamic characteristics of the device in which it is associated with a cathode and an anode.

In accordance with this invention the anode or grid is first deoxidized by heating the metallic body in a reducing gas, such as hydrogen, or in a vacuum to remove occluded gases and oxygen forming compounds which may deleteriously affect the carbonizing process. This step produces a clean and bright surface on the electrode which is then ready for the carbonizing treatment. The carbonizing of the wire grid or the anode consists in spraying or otherwise coating the surface of the grid or anode with a concentrated,

slightly ammoniacal solution of colloidal graphite commercially known as "Aquadag". The sprayed electrodes are allowed to dry and are then subjected to a "fixing" treatment in order to insure complete coalescence between the carbon coating and the surface of the electrode. This "fixing" process may be carried out by either of two methods of heat treatment.

In the first method the sprayed electrode is placed in a reducing oven and heated to a temperature from 500 to 800° C. while hydrogen or other reducing gas is injected into the oven. The "fixing" process may also be carried out in a high vacuum at a temperature from 600 to 900° C. In either "fixing" process the colloidal graphite coating on the electrode is formed into a closely adherent film on the electrode which film is very difficult to remove even by abrasion methods.

A major advantage of this method is that while the coating is of sufficient thickness to accomplish the desired result of considerably lowering primary and secondary emission, it is thin enough that it does not in any manner change the electrical characteristics of the devices. The controlling of the dimensions of the grid structure is a primary requisite in electron discharge technique since a change in diameter of the grid wire of 0.002 inch will materially affect the dynamic and electrostatic characteristics of the device. For this reason a large number of carbon producing compounds are objectionable since they result in a relatively thick coating of carbon on the grid and therefore cause variations in the spacing between the wires of the grid electrode.

While the "fixed" coating of carbon applied to an anode surface is relatively thin, its black body constant is relatively high so that it serves as an efficient heat radiator to dissipate the heat generated in the anode. While the carbonizing and "fixing" process has been found particularly advantageous in coating highly refractory metals such as molybdenum, the invention may also be applied to other metals, for instance, nickel electrodes which are usually associated with low temperature coated filaments.

The pre-glow treatment of the electrodes in accordance with this invention, prior to the carbonizing and "fixing" treatments prevents alteration of the carbon film on the electrodes during the "fixing" treatment and subsequent exposure to air prior to inserting the electrodes within an evacuated vessel. Furthermore, the pre-glowed carbonized electrode insures freedom from oxygen forming compounds which may combine with thermionically active material under electronic action of the cathode and deleteriously affect the cathode coating material.

It is of course understood that other metals such as iron and alloy metals generally employed as electrodes in electron discharge devices may be carbonized by the process as herein described. Therefore, the invention is only to be limited within the scope of the appended claims.

What is claimed is:

1. The method of carbonizing an electrode for an electron discharge device which comprises preglowing the electrode to remove occluded gases, coating the electrode with a colloidal graphite solution, and heating the electrode at temperatures from 500 to 900° C.

2. The method of carbonizing an electrode which comprises heating the electrode in a reducing atmosphere to remove occluded gases, coating the electrode with colloidal graphite, fixing the graphite coating in a reducing atmosphere, and heating the electrode at a temperature from 500 to 800° C. while in the reducing atmosphere.

3. The method of carbonizing an electrode which comprises heating the electrode in a vacuum to remove occluded gases, spraying the electrode with a concentrated ammoniacal solution of colloidal graphite, drying in air, and finally heating the electrode in an evacuated vessel within a range of temperatures from 600 to 900° C. to fix the carbon to the electrode surface.

GEORGE E. LONG.