

Oct. 31, 1950

M. ARDITI ET AL
NONEMISSIVE ELECTRODE FOR USE
IN ELECTRON DISCHARGE DEVICES
Filed Aug. 19, 1947

2,527,513

Fig. 1.

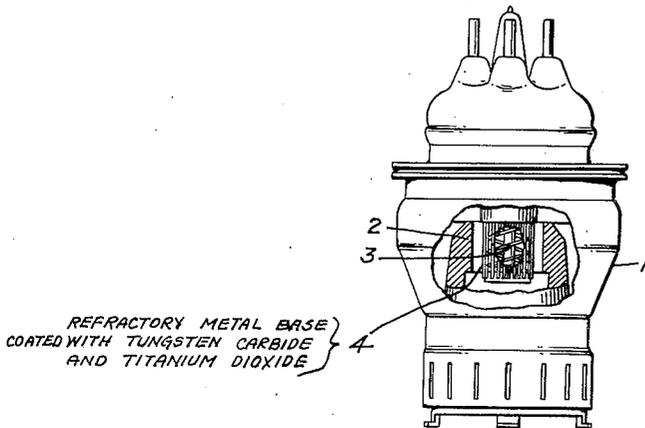
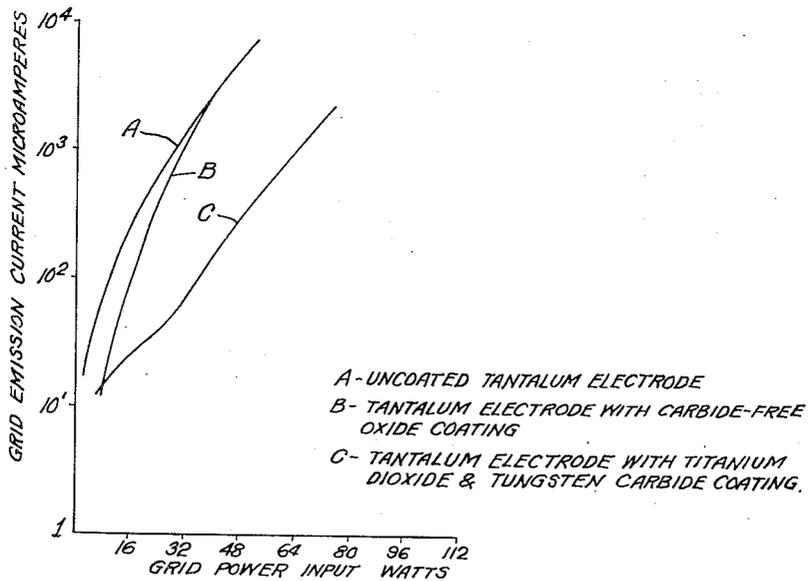


Fig. 2.



INVENTORS
MAURICE ARDITI
VINCENT J. DE SANTIS
BY
Thomas J. Foley
ATTORNEY

UNITED STATES PATENT OFFICE

2,527,513

NONEMISSIVE ELECTRODE FOR USE IN ELECTRON DISCHARGE DEVICES

Maurice Arditi, New York, N. Y., and Vincent J. De Santis, Chatham, N. J., assignors to International Standard Electric Corporation, New York, N. Y., a corporation of Delaware

Application August 19, 1947, Serial No. 769,329

9 Claims. (Cl. 250-177)

1

This invention relates to improvements in electron tubes, particularly in electrodes suitable for use in electron discharge devices, especially an improved type of electrode characterized by primary and secondary electron emission.

In electron discharge devices a stream of electrons passes from the cathode or emitter electrode to the anode or receiver electrode, and characteristics of the stream are affected or controlled by one or more grid electrodes interposed in the stream or placed adjacent thereto. The grid electrodes usually are biased at potential levels above the cathode but below the anode potentials with the result that inevitably during the course of operation of the device certain electrons from the electron stream bombard and are retained by the grid electrodes. When thus bombarded many types of grid electrodes emit electrons, the ratio between the number of electrons bombarding the surface and the number of electrons emitted being determinative of the coefficient of secondary emission of the substance from which the surface is formed. Inasmuch as secondary emission is generally an undesirable phenomenon in the operation of an electron discharge device, various expedients have been utilized from time to time in an effort to minimize this secondary emission.

Present day electronic research has resulted in the development of devices functioning at ever increasingly high frequencies ranging upward into thousands of megacycles per second. In electron discharge devices used at these high frequencies the electrodes are exceedingly minute and inter-electrode spaces are very small. Inasmuch as the primary or thermionic electron emissivity of metallic surfaces is enhanced by increase in the temperature of the surfaces, it is obvious that the control of the primary and secondary emission of electrodes in electron discharge devices operated at high frequencies presents unique design problems because the grid electrodes are disposed in such close proximity to the cathode electrodes that they are thereby heated resulting normally in primary emission, and the bombardment by electrons from the cathode additionally causes high secondary emission at the grid electrodes unless extraordinary measures are taken to prevent the same.

While the object of the present invention, viewed in its broader aspects, is to provide an electron discharge device including means for controlling and inhibiting both primary and secondary emission from the electrodes of the device, the principles of the invention are particularly

2

applicable to the control of primary emission in electron discharge devices of the type used in generating high-power very-high-frequency radiation.

Another object of the invention is to provide an electrode structure which is characterized by substantially no primary or secondary emission even when operated at very high temperatures and which permanently maintains this characteristic at a stable level.

The further object of the present invention is to provide an electrode structure which can be utilized in controlling an electron stream emanating from a thoriated tungsten emitter without either primary or secondary emission from the control electrode and which does not develop emissive properties not even as a result of deposit thereon of thorium from the emitter.

In the accompanying drawings Fig. 1 illustrates a typical electron discharge device including an electrode according to this invention; and

Fig. 2 is a graphic representation of properties of such an electrode contrasted with properties of prior art electrodes.

Regarding certain of its broader aspects, the novel non-emissive electrode structure according to this invention comprises a refractory metal base element carrying a tenaciously adherent continuous coating that comprises an essentially homogeneous mixture of tungsten carbide and titanium dioxide. When operated in an electron discharge device in conjunction with a thoriated tungsten cathode and at temperatures within the range of 1300° C. to 1600° C. This electrode is substantially free of both primary and secondary emission, thus making it ideally suited for use in high-power high-frequency electron discharge devices.

Viewed in a more particular sense, the electrode according to this invention comprises a base element, preferably formed from tantalum, columbium, tungsten or, less desirably, from molybdenum, provided with a substantially continuous coating consisting of tungsten carbide in the proportion of 40% to 60% based on total weight of mixture, the remainder being titanium dioxide. The coating is composed of these substances homogeneously mixed and in finely divided state, say particles having a size of about 4 microns or less, and the coating being approximately 12 microns thick. It has been found by experience that coatings produced by using particles exceeding about 4 microns in size are not wholly satisfactory for the purposes of this in-

vention because such coatings are usually porous and in some instances discontinuous.

A novel non-emitting electrode embodying the principles of this invention can be produced by forming an essentially homogeneous suspension of tungsten carbide and titanium dioxide, in the proportions and the particle size above mentioned, in an organic or inorganic binding agent of the type commonly used in the manufacture of coated electrodes, applying this suspension to a refractory metal electrode element and consolidating the coating upon the element by drying, either at atmospheric or elevated temperatures, the latter being preferable. Pyroxylin solution is an example of the type of organic binder which can be used in the practice of this invention and when this binding agent is used, the coated electrode is fired in vacuo at a temperature of about 800° C. or higher. Silicate binders are examples of the type of inorganic binding agent that can be used satisfactorily in practicing this invention and of these binders the alkyl silicates, e. g. tetraethylorthosilicate, are particularly preferred. When silicate binders are used the coated electrodes are fired at temperatures in the vicinity of 1000° C. for about 4 to 5 minutes.

In the accompanying drawings Fig. 1 illustrates a typical electron discharge device including an electrode according to this invention. The device comprises a gas tight envelope 1 within which are mounted an anode 2 and cathode 3 between which is positioned a control electrode 4 bearing a non-emissive coating according to this invention. In Fig. 2 of the drawings, characteristics of electrodes according to this invention are depicted in contrast with corresponding properties of other electrodes not according to this invention. It will be noted that in this graph grid emission is plotted against grid input power and the temperature of operation of the grid is proportional to the electrical energy or power dissipated in that electrode. The curve A reflects data obtained by testing an uncoated electrode formed from tantalum. Curve B relates data obtained by testing a typical so-called "non-emissive" electrode according to the prior art. In this instance the electrode consisted of tantalum bearing a coating of metallic oxides free from metallic carbides. Curve C depicts correlated data obtained by testing an electrode embodying the principles of this invention, namely, a tantalum electrode bearing an adherent continuous coating comprising tungsten carbide and titanium dioxide. It is to be understood that these data are based on tests conducted subsequent to the usual ageing of the electrodes by operation for a short period under the conditions of intended use.

In order to facilitate a better understanding of the matter of the present invention and how the same may be practiced, certain specific examples herewith follow, which, it is to be understood, are provided by way of illustration and not by way of limitation of the invention:

Example one

About 25 grams of tungsten carbide and about 25 grams of titanium dioxide are ground in a ball mill until a homogeneous mixture having an average particle size of 4 microns or less is obtained. A solution of 25 cc. of tetraethylorthosilicate is formed in about 15 cc. of alcohol (denatured alcohol may be used satisfactorily for this purpose) and about 0.5 cc. of 10% hydrochloric

acid aqueous solution is added to the mixture to produce the binding agent. A homogeneous mixture is formed of about 60 cc. of this binding agent and about 50 grams of the mixed titanium dioxide tungsten carbide powder to be used as a coating composition. A grid electrode element is formed of tantalum and the above described coating composition is applied to this element by spraying, dipping or other operations conventional in the art of applying coating compositions to articles. After coating, the coated electrode is fired in vacuo at about 1000° C. for approximately 4 to 5 minutes. Under these conditions volatile components of the coating composition are volatilized and a tenaciously adherent coating of the consolidated oxide-carbide mixture is produced upon the electrode element. This electrode exhibits substantially no emission when operated at a temperature in the range of 1300° C. to 1600° C. and this characteristic of non-emissivity remains permanently unaltered even when the electrode is used in conjunction with a thoriated tungsten cathode.

Example two

The operations described in Example 1 are repeated except that 60 parts by weight of tungsten carbide are milled with 40 parts by weight of titanium dioxide. The coated electrode so produced possesses substantially the same electrical characteristics as the electrode obtained in accordance with Example 1.

Example three

The operations described in Example 1 are repeated with the modification that about 40 parts by weight of tungsten carbide are mixed with about 60 parts by weight of titanium dioxide, instead of mixing these substances in the proportions in Example 1. The electrode so produced has electrical properties comparable to those of the electrodes produced as described in Example 1.

Example four

The operations described in Example 1 are repeated except that instead of the binder therein described the following binding composition is used:

Concentrated pyroxylin solution.....	cc. 30
Amylacetate	200

The pulverized titanium dioxide tungsten carbide mixture is incorporated in this binder in the same manner and proportions as set forth in Example 1 concerning the silicate binder and the electrode after coating is fired at a temperature of 800° C. or higher. The coated electrode obtained by these operations possesses electrical properties substantially the same as electrodes prepared as described in Example 1. In similar manner the operations described in Examples 2 and 3 can be repeated substituting the pyroxylin binder for the silicate binder therein and the electrodes so obtained are substantially identical in electrical properties to the electrodes obtained by the process described in Examples 2 and 3.

It is to be clearly understood that any of the methods conventional in the coating art can be utilized in applying the dioxide-carbide coating composition to the electrode elements as herein described. The application of the coating by spraying has been found entirely satisfactory and likewise application of the coatings by dipping.

After application of the coatings, the electrodes can be incorporated in any desired type of electron discharge device. It will be found that during operation of the electron discharge device under conditions such that the coated electrodes operate at a temperature in the range of 1300° C.-1600° C., the coated electrodes are substantially free from both primary and secondary electron emission.

It will of course be clearly understood that although the principles of this invention have been disclosed with particular reference to the fabrication and grid electrodes, the principles are equally applicable to the fabrication of other types of electrodes wherein primary and secondary emission is undesirable.

It is to be understood that in the following claims the term "non-emissive electrode" means an electrode substantially free from primary and secondary electron emission when operating at a temperature of about 1300° C. to 1600° C. subsequent to an initial ageing consisting of operation of the electrode after a period of time under the conditions of intended use. This absence of substantial secondary emission characteristic of electrodes according to the present invention is observed in grid electrodes at potentials as high as 20 volts or higher voltages.

What is claimed is:

1. A thermally stable non-emissive electrode for use in an electron discharge device, that comprises a refractory metal element carrying an adherent coating comprising tungsten carbide and titanium dioxide.

2. An electrode as defined in claim 1, wherein the tungsten carbide constitutes 40% to 60% of the coating based on weight.

3. A thermally stable non-emissive electrode for use in an electron discharge device, that comprises a base element formed from a metal selected from the class consisting of tantalum, columbium, tungsten and molybdenum, carry-

ing an adherent coating comprising tungsten carbide and titanium dioxide.

4. An electrode as defined in claim 3 wherein the tungsten carbide constitutes 40% to 60% of the coating based on weight.

5. A non-emissive electrode for use in an electron discharge device, that comprises a tantalum base element carrying an adherent coating comprising tungsten carbide and titanium dioxide.

6. An electrode as defined in claim 5, wherein the tungsten carbide constitutes 40% to 60% of the coating based on weight.

7. An electron discharge device including an electrode formed of a refractory metal carrying a coating that comprises an essentially homogeneous mixture of tungsten carbide and titanium dioxide.

8. An electron discharge device including an electrode formed of a refractory metal carrying a coating that comprises an essentially homogeneous mixture of tungsten carbide and titanium dioxide, the tungsten carbide being present in said composition in the proportion of forty per cent to sixty per cent based on total weight.

9. An electron discharge device including an electrode formed of a refractory metal carrying a coating that comprises an essentially homogeneous mixture of tungsten carbide and titanium dioxide, said substances being present in the coating in substantially equal proportions based on weight.

MAURICE ARDITI.
VINCENT J. DE SANTIS.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,417,461	Becker	Mar. 18, 1947