

Oct. 16, 1956

T. E. LE LOUP ET AL
TITANIUM DIOXIDE RECTIFIER

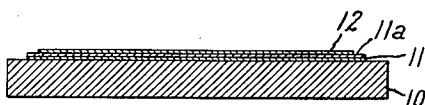
2,766,509

Filed May 22, 1952

Fig. 1.



Fig. 2.



Inventors:
Theodore E. LeLoup,
John C. Marinace,
by *Paul A. Frank*
Their Attorney.

1

2,766,509

TITANIUM DIOXIDE RECTIFIER

Theodore E. Le Loup and John C. Marinace, Schenectady, N. Y., assignors to General Electric Company, a corporation of New York

Application May 22, 1952, Serial No. 289,247

3 Claims. (Cl. 29—25.3)

The present invention relates to an improved alternating current rectifying device and method for producing such a device; more particularly, the invention relates to a rectifying device employing titanium dioxide as the rectifying medium.

Plate rectifiers of the copper oxide and selenium type have been known for many years. Other substances which are good semi-conductors have been known but in general their use for rectification purposes has not measured up in quality to plate rectifiers utilizing copper oxide or selenium.

It is an object of this invention to provide a titanium dioxide alternating current rectifier of the plate type which has a high degree of temperature stability and in other respects compares favorably with rectifiers utilizing copper oxide and selenium.

Briefly stated, in accordance with one embodiment of this invention, a rectifier comprises a base electrode composed of titanium which has a layer of titanium dioxide in which titanium metal is incorporated, overlying at least a portion of the titanium surface, and a metal electrode of high work function or one having a higher work function than the titanium dioxide overlying the layer of titanium dioxide.

In the drawing Fig. 1 is a sectional view showing the layers of a rectifier produced in accordance with this invention. Fig. 2 is a sectional view of an alternative embodiment of the invention. In Fig. 1, a base electrode 10, composed of titanium metal, is subjected to a treatment which produces a partially-reduced oxide layer 11 over all, or a portion of, its surface. Overlying the layer 11 is a counterelectrode layer 12 composed of a metal or alloy having a higher work function than layer 11.

The base electrode 10 is made thick enough to provide structural rigidity for the rectifier. The thickness of the layers 11 and 12 is greatly exaggerated in the drawing in order to achieve clarity of illustration. In actual practice these layers may be less than a thousandth of an inch in thickness. For example, the layer 11 may have a thickness of about 0.0005".

In Fig. 2, the base electrode 10, partially reduced oxide layer 11, and counterelectrode 12 are the same as in Fig. 1. However, Fig. 2 includes a blocking layer 11a which is applied to the partially reduced oxide layer 11. The layer 11a may be composed of a semiconducting oxide such as an oxide of germanium, silicon, or titanium. These oxides may be applied by vapor deposition in a vacuum. The layer 11a may also be produced by further oxidation of the surface portion of the partially reduced oxide layer 11 as by heating the layer 11 in the presence of free oxygen.

In fabricating the rectifier, the titanium plate forming the base electrode 10 is provided with a clean surface. This may be accomplished by an abrasive process or by immersing the plate in an acid cleaning solution. A solution of 80% nitric acid and 20% hydrofluoric acid is satisfactory for this purpose. After the base electrode 10 has been provided with a clean surface, it is subjected

2

to a heat treatment in an atmosphere containing oxygen in order to produce the thin layer 11 of titanium dioxide. While the layer 11 is shown as covering only a portion of one surface of the base electrode 10, it is frequently easier in actual practice to cover the entire surface of the electrode 10 with the oxide layer. Titanium has a very high melting point and consequently the oxidation step may be carried out at a high temperature in order to promote rapid oxidation. I prefer temperatures in excess of 600° C. for this purpose and preferably within the range of 600° C. to 800° C. However, there is nothing critical about this temperature range. Lower temperatures may be used but the time of treatment to produce a satisfactory oxide layer must be increased. Temperatures above 800° C. may also be used but in this event the rate of oxidation is fairly rapid, and it is difficult to maintain close control over the thickness of the oxide layer. At temperatures above 800° C. treatment for just a few minutes is sufficient to provide an oxide layer of the necessary thickness while at temperatures below 600° C. the time of treatment may run to many, many hours. Within the range 600° C. to 800° C. oxidation in air for a period of 2 to 4 hours is sufficient.

The layer 11 of titanium dioxide must be partially reduced. This reduction may be carried out by maintaining the temperature at the same level that was used for oxidation but changing the atmosphere to a reducing atmosphere, preferably provided by hydrogen. Continuing the heat treatment for four to eight hours in a hydrogen atmosphere is normally sufficient to bring about the partial reduction of the oxide layer 11.

Air oxidation is satisfactory for the purposes of this invention but we prefer to have the oxidation take place in an atmosphere of steam. Treatment in a steam atmosphere at a temperature of about 650° C. for about 4 hours is sufficient to produce a partially reduced oxide layer having a thickness of approximately 0.005", which is satisfactory for our purposes.

Two methods of treatment with reference to the layer 11 have been described. On the one hand, the layer is applied by heat treatment in an atmosphere of air followed by heat treatment in an atmosphere of hydrogen. On the other hand, the layer is applied by heat treatment in an atmosphere of steam. Both treatments produce a layer 11 which has a certain amount of reduced titanium metal in it. In the case of the steam treatment, this is brought about by the fact that the breakdown of the water vapor molecule to provide the oxygen for oxidation results in the production of a hydrogen molecule which has a reducing effect. Rectification requires that the layer 11 contain some titanium in the reduced state.

The counterelectrode 12 is composed of a metal having a work function greater than that of layer 11 such as bismuth, nickel, or platinum. Metals having a work function lower than that of layer 11, such as cadmium, zinc, tin, aluminum, and magnesium, are not satisfactory counterelectrodes as the resulting rectifier would have inferior rectification properties.

The partially reduced oxide layer is an "n" type semiconductor and, as previously explained, the free titanium associated with the layer 11 contributes the electron conduction. The counterelectrodes of bismuth, nickel, or platinum all having missing electrons in their "d" shells which contribute holes for "p" type conduction. Counterelectrodes of materials having these characteristics are satisfactory for our purpose. Accordingly, the term "metals of high work function" is intended to include metals which have missing electrons in their "d" shells and which have "p" type conduction.

The counterelectrode 12 may be applied by any method which insures a "union" between the layers 11 (or 11a) and 12. Application from the molten state will accom-

3

plish this if carefully performed and vapor deposition is also satisfactory. Bismuth lends itself readily to vapor deposition and for this reason we prefer to utilize this metal as a counterelectrode.

Rectifiers made in accordance with our teaching possess excellent stability under high temperature conditions and in other respects, such as current loading and voltage rating, are on a par with selenium rectifiers.

While the present invention has been described with reference to particular embodiments thereof, it will be understood that numerous modifications may be made by those skilled in the art without actually departing from the invention. Therefore, we aim in the appended claims to cover all such equivalent variations as come within the true spirit and scope of the foregoing disclosure.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. The method of preparing a titanium dioxide rectifier which comprises oxidizing at least one surface of a titanium plate by heating it in air for from four hours at 600° C. to two hours at 800° C., reducing the resulting oxide surface by heating said plate in a hydrogen atmosphere for from eight hours at 600° C. to four hours at 800° C. and coating said reduced surface layer with a counterelectrode metal of work function greater than that of said reduced surface layer, said counterelectrode metal being selected from the group consisting of bismuth, platinum and nickel.

2. The method of preparing a titanium dioxide recti-

4

fier which comprises partially oxidizing at least one surface of a titanium plate in a steam atmosphere for about four hours at about 600° C. and coating the partially oxidized surface with a counterelectrode metal of work function greater than that of said partially oxidized surface, said counterelectrode metal being selected from the group consisting of bismuth, platinum and nickel.

3. The method of preparing a titanium dioxide rectifier which comprises oxidizing a surface of a titanium plate by heating said plate in air for from four hours at 600° C. to two hours at 800° C., reducing the surface of the resulting oxide layer by heating said plate in a hydrogen atmosphere for a period of from four to eight hours at a temperature of about 600° C. and coating the reduced surface of said oxide layer with a counterelectrode metal having a work function greater than that of said reduced surface, said counterelectrode metal being selected from the group consisting of bismuth, platinum and nickel.

References Cited in the file of this patent

UNITED STATES PATENTS

2,721,966 Jenkins et al. ----- Oct. 25, 1955

FOREIGN PATENTS

483,088 Great Britain ----- Apr. 12, 1938

OTHER REFERENCES

Electronic Engineering, October 1946, pp. 313-315.