Jan. 11, 1955 R. G. BRECKENRIDGE 2,699,522

TITANIUM DIOXIDE RECTIFIER

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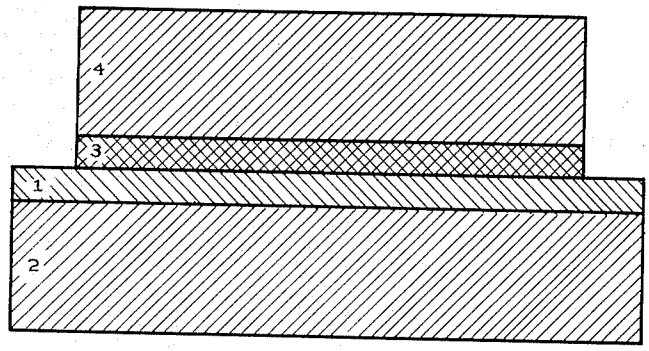


FIG. 1

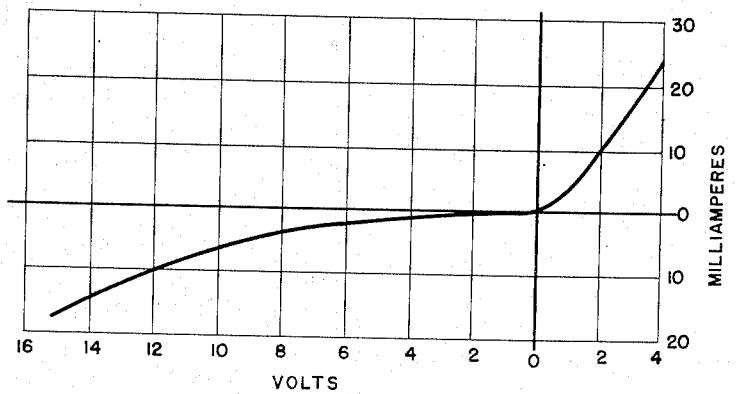


FIG. 2

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TITANIUM DIOXIDE RECTIFIER

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4 Claims. (Cl. 317—238)

(Granted under Title 35, U. S. Code (1952), sec. 266)

The invention described herein may be manufactured and used by or for the Government of the United States for governmental purposes without the payment to me of any royalty thereon in accordance with the provisions of the act of March 3, 1883, as amended (45 Stat. 467; 35 U. S. C. 45).

This invention relates to metal or plate rectifiers for electric current and has particular reference to the production of such a rectifier employing a layer of titanium metal in contact with a layer of titanium dioxide containing a small amount of excess titanium as an essential impurity.

Metal or plate rectifiers as known usually comprise a stack of elements each of which consists of a metal base plate, a superposed layer of a semiconducting material and a further layer of metal as a counter-electrode, the last layer being usually of a different material from the base plate. Graphite is sometimes used as the counter-electrode. The semiconductors chiefly employed in presently known rectifiers are selenium, cuprous oxide, and magnesium-cupric sulphide. Recently germanium rectifiers have come into widespread use, although perhaps these latter are more correctly classed among the crystal detectors. While the known rectifiers have found considerable use and have attained great commercial importance, they are nevertheless subject to a number of very serious limitations which restrict their utility. Some of these rectifiers for example, cuprous oxide and selenium are restricted in the temperature range at which they can be operated. Heating above the range of 50 degrees C. and 90 degrees C., respectively, will seriously impair or destroy their rectifying action. This imposes a serious limitation in the design of compact apparatus employing such rectifiers and also limits the power which they can handle and dissipate. Some types, for example, selenium rectifiers, require substantial amounts of expensive material. The most important commercial types require extreme care in their manufacture and often do not give consistent results, being very sensitive to changes in the manufacturing techniques, so much so that it is very difficult to achieve completely uniform output. The actual manufacture of these items tends to be an empirical art rather than a science. For many of these materials there is no laboratory test by means of which the raw material can be selected. At present the only possible method of trial is by the actual production of a rectifier. The presence of even the most minute quantities of undesirable impurities may have an adverse effect on the reverse resistance of the rectifier as may also the absence of certain essential impurities. The temperature control during manufacture, for example, of copper oxide rectifiers, is exceedingly critical, while often closely controlled annealing and quenching techniques are necessary to produce satisfactory results.

The present invention obviates most, if not all, of the above difficulties and permits the production of a rectifier having very satisfactory electrical characteristics.

It has been appreciated for some time that titanium dioxide has at least theoretical possibilities as a rectifier material. H. K. Henish in his recent book "Metal Rectifiers," Oxford University Press, 1949, pp. 127–130, discusses the possibility of producing such a rectifier from thin sheets of titanium dioxide powder prepared with a binder and fired in a reducing atmosphere (usually hydrogen) at temperatures between 1500° C. and 1700° C. for several hours. However, none of the suggested techniques are capable of producing successful rectifiers. The mechanical properties of this arrangement are very poor.

According to the present invention commercially pure titanium metal is first oxidized by heating to a temperature of about 700° C. in oxygen gas to produce a film of titanium dioxide and subsequently partially reducing the layer of titanium dioxide at a temperature of about 700° C. in hydrogen gas.

Reference will now be made to the appended drawings in which Figure 1 is a cross section through a single element of a rectifier made in accordance with the present invention. Figure 2 is a graph showing the current-voltage characteristic of such a rectifier.

Referring to Figure 1, a plate or disk **1** of titanium metal may be supported by and maintained in good electrical contact with a base plate **2** of any other suitable material. The titanium metal is treated as above described to produce a nonporous adherent film of reduced titanium dioxide **3**, which is a semi-conducting material. The titanium disk **1** is used as the base electrode, electrical contact being made either directly or through the base plate **2**. The counter-electrode **4** is made of any suitable metal which may be applied to the titanium dioxide layer **3** by any known process, such as evaporation in a vacuum, metal spraying, electrodeposition, et cetera. The unit so prepared shows a rectifying action; that is, the measured resistance of the unit depends on the direction of current flow and it is nonlinear as shown by the graph of Figure 2.

It will be seen that according to this invention an electrically satisfactory rectifier is produced, having the advantages previously indicated. It is prepared from nontoxic materials of high melting point, which in addition to the advantages previously stated also give a high burnout resistance. The oxide layer is preferably made at a temperature of 700 degrees C. maintained for one hour in an oxygen atmosphere, followed by the reducing step which is maintained in a hydrogen atmosphere for about 5 minutes at the same temperature to produce a desirable amount of the trivalent titanium ion that is believed to act as an essential impurity in producing rectification. The reaction may be produced in a temperature range of from 600 degrees C. to 900 degrees C. and a time range of from ½ to 2 hours, the lower temperatures requiring longer times to complete the reaction. The reducing step will require from 1 to 15 minutes depending upon the temperature maintained during the reducing step, the lower temperatures requiring longer times. At the upper range of temperatures the oxide layer tends to have poor physical properties and to crack up. It has been found that the preferred procedure produces a layer in the order of 0.00025 to 0.0013 inch thick, which appears to give the best result. The oxidizing reaction produces the quadrivalent titanium oxide and the reducing reaction produces the trivalent titanium ion which is the essential impurity in this rectifier.

It will be apparent that the embodiments shown are only exemplary and that various modifications in construction and arrangement can be made within the scope of my invention as defined in the appended claims.

I claim:

1. A dry disk rectifier comprising a base electrode of titanium, a semiconductor of titanium dioxide containing trivalent titanium ions formed directly on said titanium, and a counter-electrode, said semiconductor being formed by heating the titanium base electrode in oxygen at 700 degrees C. for one hour and then reducing the oxide in hydrogen at 700 degrees C. for 5 minutes.

2. A dry disk rectifier comprising a base electrode of titanium, a semiconductor of titanium dioxide containing trivalent titanium ions, and a counter-electrode, said semiconductor being formed by heating the titanium base electrode in oxygen for from 2 hours at 600° C. to one-half hour at 900° C. and then reducing the oxide in hydrogen for from 15 minutes at 600° C. to one minute at 900° C.

3. A titanium dioxide dry disc rectifier comprising a base electrode of titanium, a semi-conducting film of blue titanium dioxide formed on and directly from said titanium base electrode and a counterelectrode applied to said semi-conducting film, said rectifier having a maxi-

mum forward resistance at one volt of approximately two hundred and fifty ohms and a minimum backward resistance at ten volts of approximately fourteen hundred ohms.

4. A titanium dioxide dry disc rectifier comprising a base electrode of titanium, a semi-conducting film of blue titanium dioxide formed on and directly from said titanium base electrode and a counterelectrode applied to said semi-conducting film, said rectifier passing a minimum forward current of approximately four milliamperes at one volt, passing a maximum backward current of approximately seven milliamperes at ten volts, and having a maximum forward resistance of approximately two hundred and fifty ohms at one volt.

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