

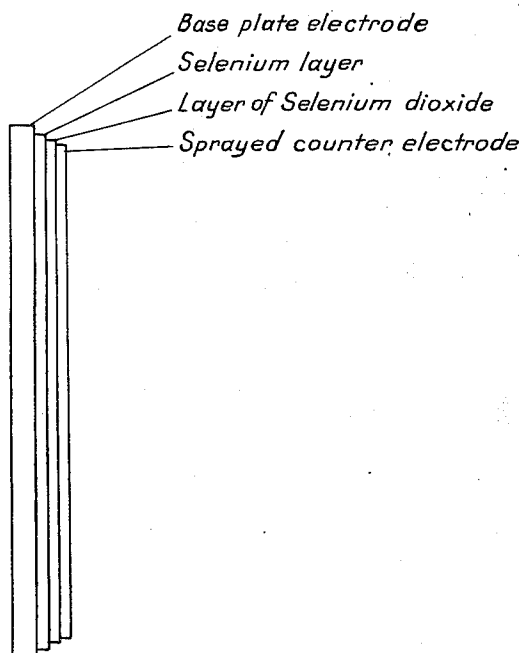
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SELENIUM RECTIFIER AND METHOD OF PRODUCING SAME

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## UNITED STATES PATENT OFFICE

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SELENIUM RECTIFIER AND METHOD OF  
PRODUCING SAME

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6 Claims. (Cl. 175—366)

The present invention briefly relates to rectified devices, and more particularly to selenium rectifiers and methods of producing same.

It is a known fact to those skilled in the art that not only the blocking resistance but also the disruptive strength of a blocking layer formed on the upper surface of a selenium layer forming part of a selenium rectifier may be considerably improved in an electric formation process. Although the nature of this blocking layer has not yet been fully investigated, it is believed to be either an extremely thin film of a compound of the selenium with the metal applied thereon as a counter electrode by spraying, or even a thin layer of amorphous selenium.

It belongs to common technical knowledge to apply an artificial blocking layer of a material which stands in no genetic relation to the adjacent electrodes, e. g., a thin coating of lacquer, on the selenium layer of a selenium rectifier. It is also a known expedient to apply by evaporation a second very thin film of selenium on the first selenium layer of a rectifier valve.

The object of our invention is to produce a selenium rectifier in which the blocking layer formed on the selenium layer of such device involves superior properties over the blocking layers heretofore known in the art. This is achieved in accordance with the method proposed by this invention by depositing on the layer of selenium forming part of a selenium rectifier a thin film of selenium dioxide by evaporation before the electrode overlying the selenium layer is applied in a spraying operation.

A still superior improvement upon the blocking layer will be obtained according to a further feature of this invention when in addition to the deposition of the selenium dioxide also aqueous vapour is applied to the superficies of the selenium.

As one specific embodiment of our process of manufacturing selenium rectifiers, we will hereinafter describe the procedure employed in applying a selenium dioxide film overlying the selenium layer of a selenium rectifier.

The accompanying drawing shows in an exaggerated scale a side elevation of a selenium rectifier produced in accordance with the rules disclosed in this invention.

A layer of selenium intimately united with a nickel-plated base member of iron in any manner well known in the art and subsequently converted into its grey crystalline state in a heat treatment is held, either manually or by the agency of a supporting device, at a given space

from a source of selenium dioxide vapour. The selenium dioxide is then deposited in the form of a thin film on the free surface of the selenium, whereupon this film is coated by spraying thereon a metal forming the counter electrode of the rectifier device. The so prepared rectifier cell or valve is thereafter treated in an electric formation during the course of which the formation voltage applied across the cell or valve is gradually increased to approximately 20 volts proportional to the decreasing back current in response to the progressive improvement of the blocking layer during the formation.

This electric formation process is assumed to be the equivalency of an electrolysis which constitutes a selenium compound or even a layer of amorphous selenium involving the same properties as a blocking layer.

We have discovered that the properties of a rectified blocking layer may be still more improved when aqueous vapour is applied to the selenium layer simultaneously with the deposition of the selenium dioxide on the free surface thereof. These two elements or constituents form a selenic acid which is easily split under the influence of the electric current active during the formation process.

The aqueous vapour may be added to the surface of the selenium layer in a variety of different manners. The simplest method which has been found satisfactory in many cases comprises heating an amount of selenium dioxide in a flame whose products of combustion include a large quantity of aqueous vapour, and so exposing the selenium layer to the resultant gases that the aqueous vapour and the vapour of selenium dioxide are simultaneously deposited on the superficies of the selenium layer. It is on the other hand likewise possible to place selenium dioxide in one receptacle and to provide a second receptacle containing water, either about or in the central portion of the first mentioned receptacle and to concurrently cause the contents thereof to evaporate. Still a further alternative process of imparting the necessary amount of aqueous vapour to a selenium dioxide film applied to a selenium layer overlying the base plate electrode is to store the prepared unit in a room which is maintained at a desired degree of moisture. The selenium dioxide on account of its hygroscopic nature will then absorb the required quantity of aqueous vapour proportional to the time of such storage.

The percentage of the constituents selenium dioxide and aqueous vapour to which a selenium

layer is to be exposed is determined by the time during which the evaporation is effective, by the space between the selenium layer and the receptacles containing the elements subject to evaporation and likewise by the intensity thereof. Even if the quantitative amount of evaporation might be raised in response to a temperature augment of the ambient medium, the proper relation of aqueous vapour to the selenium dioxide vapour will be maintained in each and every instant since the former is subjected to a corresponding increase.

In cases that the aqueous vapour is absorbed by the hygroscopic selenium dioxide from the moist atmosphere in a room being maintained at a desired degree of wetness, the proper amount of vapour absorption is given by the time during which the prepared rectifier unit is stored in a room of a predetermined degree of humidity.

The period of time required for depositing the selenium dioxide with or without adding aqueous vapour is equal to few seconds.

The metallic counter electrode which is preferably sprayed onto the preparatorily finished rectifier is suitably applied immediately after the selenium dioxide and the additional aqueous vapour have been deposited on the superficies of the selenium layer in order to sustain the proper content of moisture imparted to the selenium dioxide during the process as described in the foregoing.

What is claimed is:

1. The method of producing selenium rectifiers which comprises the steps of: forming a layer of selenium on one major surface of a nickel-plated iron member, converting the selenium into its grey crystalline state in a heat treatment, depositing a thin film of selenium dioxide on the superficies of the layer of selenium, spraying a layer of metal onto the film of selenium dioxide overlying the selenium, and subjecting the resultant unit to an electric formation process.

2. The method of producing selenium rectifiers which comprises the steps of: forming a layer of selenium on one major surface of a nickel-plated iron member, converting the selenium into its grey crystalline state in a heat treatment, depositing a thin film of selenium dioxide on the superficies of the layer of selenium while simultaneously adding aqueous vapour to the selenium dioxide, immediately spraying a layer of metal onto the film of selenium dioxide of given humidity overlying the selenium, and subjecting the resultant unit to an electric formation process.

3. The method of producing selenium rectifiers which comprises the steps of: forming a layer of selenium on one major surface of a nickel-plated iron member, converting the selenium into its grey crystalline state in a heat treatment, evaporizing a quantity of selenium dioxide in a flame the combustion products of which contain a substantial percentage of aqueous vapour, exposing the grey crystalline selenium layer to the composite mixture of resulting selenium dioxide vapour and aqueous vapour for concurrently depositing the constituents of the mixture on the selenium layer in the shape of a thin film, immediately spraying a layer of metal onto the film of selenium dioxide of given humidity overlying the selenium, and subjecting the resultant unit to an electric formation process.

4. The method of producing selenium rectifiers which comprises the steps of: forming a layer of selenium on one major surface of a nickel-plated iron member, converting the selenium into its grey crystalline state in a heat treatment, depositing a thin film of selenium dioxide on the grey crystalline surface of the selenium, imparting the proper percentage of humidity to the selenium dioxide by storing during a predetermined period of time the selenium dioxide film overlying the selenium layer formed on the base member in a room maintained at a given degree of moisture, removing the unit from the storage room, immediately spraying a layer of metal onto the film of selenium dioxide of given humidity, and subjecting the resultant unit to an electric formation process.

5. As a product of manufacture, a selenium rectifier comprising a nickel-plated base member of iron acting as an electrode, a grey crystalline layer of selenium formed on the said base member, a thin film of selenium dioxide overlying said layer of selenium, and a layer of metal applied on the said film of selenium dioxide as the counter electrode of said product.

6. As a product of manufacture, a selenium rectifier comprising a nickel-plated base member of iron acting as an electrode, a grey crystalline layer of selenium formed on the said base member, a thin film of selenium dioxide of a predetermined percentage of moisture overlying said layer of selenium, and a layer of metal applied on the said film of selenium dioxide as the counter electrode of said product.

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