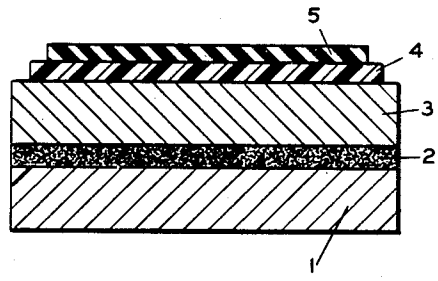
April 26, 1949. W. C. VAN GEEL ET AL 2,468,527

BLOCKING-LAYER CELL

Filed April 10, 1946



WILLEM CHRISTIAAN VAN GEEL
LUDOVICUS AUGUSTINUS LAMBERTUS ESSELING
INVENTORS

BY E. J. Wendrich

ATTORNEY

Patented Apr. 26, 1949 2,468,527

UNITED STATES PATENT OFFICE

2,468,527

BLOCKING-LAYER CELL

Willem Christiaan van Geel and Ludovicus Augustinus Lambertus Esseling, Eindhoven, Netherlands, assignors, by mesne assignments, to Hartford National Bank and Trust Company, Hartford, Conn., as trustee

Application April 10, 1946, Serial No. 661,022
In the Netherlands August 8, 1944

Section 1, Public Law 690, August 8, 1946
Patent expires August 8, 1964

7 Claims. (Cl. 175—366)

1

This invention relates to a method of applying a blocking layer, more particularly consisting of selenium, onto an electrode for a blocking layer cell, and to a blocking layer cell comprising such a blocking layer.

Various methods of applying a blocking layer have already been proposed. Thus, for instance, non-genetic blocking layers have come to be known, which consist of a synthetic resin and were precipitated from a solution on to the surface to be coated. Such a method, however, has first of all the drawback that only those materials can be provided that are soluble in a suitable medium. Secondly, it appears that such layers are not always very homogeneous of composition and thickness in regard to the blocking effect.

Furthermore it has already been proposed to precipitate, by vaporisation, materials such as quartz, magnesium—or beryllium oxide. Particularly if the materials have a low vapour pressure it is difficult to apply them, since in this case very high temperatures have to be used. In addition these layers are not sufficiently homogeneous for the required effect.

Again it is known to vaporise sulphur on to selenium electrodes. This took place by means of a thermal treatment, during which the selenium was converted into the conducting crystalline modification. Such a method is complicated and expensive.

The present invention has for its object to avoid the aforesaid drawbacks and to obtain other advantages. It is characterized in that the blocking layer material is applied by disintegration, through ion bombardment, of the material to be applied (sputtering) and is precipitated on the carrier for the blocking layer.

A blocking layer applied by means of the method according to the invention is very homogeneous. This is visible even with the naked eye when observing a plate carrying a blocking layer thus established under an inclined beam of light. In this case one definite interference colour is observed. Another advantage, which is more particularly inherent to a selenium blocking layer, consists in that the selenium thus applied is highly resistant to chemical attack. At variance with selenium layers provided in the usual way, which are attacked even at a normal temperature by various substances, notably nitric acid, a layer applied by means of the method according to the invention only dissolves at a high temperature in nitric acid.

All of the selenium layers applied in a known manner have the drawback of contracting on being heated above their melting point. The novel layer perfectly retains its coherence upon heating.

2

It appears that the last-mentioned two advantages are obtained more particularly if the sputtering takes place in the air. When providing the blocking layer by vaporisation, it often appears, at variance with disintegration, that a film forms under these conditions, which is liable to chemical attack. Consequently, these drawbacks, are also inherent to the vaporisation of sulphur or selenium.

It has turned out that according to the invention blocking layer cells can be obtained which have a high and well reproducible breakdown voltage which is to be ascribed to the high homogeneity and compactness of the layer; in addition the forward current has a suitable value.

In an extremely suitable example of the method according to the invention, used for the manufacture of a blocking layer cell in which one of the electrodes consists of selenium, first of all a blocking layer is formed by making a liquid act upon the surface of the selenium layer, followed by another blocking-layer forming treatment according to the aforesaid method of disintegration.

By making a liquid act upon the surface of a selenium layer a blocking layer or at least a layer having a very low conductivity is obtained, it is true, but it appears that when providing a counter-electrode on such a blocking layer, for instance by spraying of an alloy having a low melting point, the alloy material and the liquid residue left on the blocking layer form an insulating compound. Owing to the presence of a layer of this compound the forward current decreases after formation of a blocking layer cell. If, however, after a blocking-layer forming treatment by the action of a liquid, another treatment is used, in which the blocking layer material is applied by disintegration thereof through ion bombardment on to the available insulating layer, it is not feasible for the alloy to combine with the liquid residue, this residue being separated from the alloy material by the blocking layer applied by disintegration.

It is advantageous to carry out the aforesaid first treatment for the formation of a blocking layer by means of a liquid from which a layer of a resin is formed which is precipitated on the surface of the selenium layer. In fact, this yields a more or less coherent blocking layer.

Hereinafter an example is given of the method according to the invention, the advantages ob-

tained by the invention appearing from the measuring results.

A layer of selenium 3 is applied on to an aluminium carrier plate 1 which is roughened and furnished with a layer of carbon 2. To the selenium is added, for increasing its conductivity, a volatile halide e. g. tin chloride. The selenium surface is smoothed by means of a press, the surface of the pressing plate having previously been coated with a resin-forming liquid e. g. quinoline. After this the plate is heated in a furnace at about 200° C., the selenium being converted into the conducting crystalline modification. At the same time a resin forming liquid, for instance triethanolamine, is sprayed on to the selenium surface, thus forming a layer of resin 4 having a thickness of several tenths of a micron. The assembly is placed in a space in front of a plate-shaped selenium electrode (cathode), the latter being connected to the negative side of a source of potential of several kilovolts, whereas another plate-shaped electrode is connected to the positive side of the same source. The selenium-coated plate is now placed in the field between the two electrodes, the free selenium side of the plate 1, 2 facing the cathode. The space is exhausted down to a pressure of about 100 units. The current amounts to several times ten ma. The thickness of the selenium layer disintegrated by ion bombardment (denoted by 5 in the drawing) depends on the time during which the distintegration is effected. As a rule, the disintegration is continued until the thickness amounts to several tenths of a micron. This thickness may be adjusted in accordance with the purpose for which the plate is to be used. During the process oxygen is consumed. The voltage and the current may be kept constant by carefully admitting air.

The selenium electrode thus furnished with a blocking layer is now covered with a counter-electrode consisting of an alloy having a low melting point. On measuring, cells thus established yielded the following values in regard to the outgoing current and back electromotive force.

On the left are stated the data for non-formed cells, on the right those of cells after formation.

Before formation		After formation	
Forward current	Reverse voltage [1]	Forward current	Reverse voltage [1]
Amperes	*Volts*	*Amperes*	*Volts*
5	8	5,7	23
7	9	9	24
6,5	8	7,2	20

[1] The reverse voltage is the voltage to be applied to make a current of 100 ma. flow in the blocking direction. All measurements have been made on cells having a diameter of 45 mm. It is remarkable that, in contradistinction to hitherto manufactured blocking layer cells, which after formation exhibit, it is true, a higher reverse voltage but a reduced forward current, cells made by means of the method according to the invention exhibit an increased forward current after formation. Furthermore, it has been found that cells established by means of the method according to the invention retain their electrical properties during operation.

For applying by distintegration a different material, for instance surphur, the process is the same.

What we claim is:

1. A method of manufacturing a blocking layer cell comprising the steps of ionically disintegrating an element selected from the group consisting of selenium and sulfur, and precipitating said disintegrated element on a selenium electrode to form a blocking layer thereon.

2. A method of manufacturing a blocking layer cell which comprises the steps of ionically disintegrating an element from the group consisting of selenium and sulfur in air, and precipitating said disintegrated element on a selenium electrode to form a blocking layer thereon.

3. A method of manufacturing a blocking layer cell which comprises the steps of forming a layer of selenium on a base, converting the selenium into a conducting crystalline modification, ionically disintegrating selenium, and precipitating said disintegrated selenium on said selenium layer.

4. A method of manufacturing a blocking layer cell which comprises the steps of forming a layer of selenium on a base, converting the selenium into a conducting crystalline modification, applying a liquid to said selenium layer to form a blocking layer thereon, ionically disintegrating selenium, and precipitating said disintegrated selenium on said selenium layer to form a blocking layer thereon.

5. A method of manufacturing a blocking layer cell which comprises the steps of forming a layer of selenium on a base, converting the selenium into a conducting crystalline modification, applying a resin-forming liquid to said selenium layer to form a layer of resin, ionically disintegrating selenium, and precipitating said disintegrated selenium on said resinous layer to form a blocking layer thereon.

6. A method of manufacturing a blocking layer cell which comprises the steps of forming a layer of selenium on a base, converting the selenium into a conducting crystalline modification, applying a resin-forming liquid to said selenium layer to form a layer of resin, ionically disintegrating sulfur, and precipitating said disintegrated sulfur on said selenium layer to form a blocking layer thereon.

7. A method of manufacturing a blocking layer cell which comprises the steps of forming a layer of selenium on a base, applying quinoline to said selenium layer, heating said selenium layer to convert the selenium to the conducting crystalline modification thereof, applying triethanolamine to said selenium layer to form a resinous layer, ionically disintegrating selenium, and precipitating said disintegrated selenium on said resinous layer to form a blocking layer thereon.

WILLEM CHRISTIAAN VAN GEEL.
LUDOVICUS AUGUSTINUS
LAMBERTUS ESSELING.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,221,596	Lorenz	Nov. 12, 1940
2,223,203	Brunke	Nov. 26, 1940
2,303,522	Addink et al	Dec. 1, 1942