SELENIUM RECTIFIER, INCLUDING TELLURIUM AND METHOD OF MAKING IT

Filed Aug. 17, 1949 2 SHEETS—SHEET 1

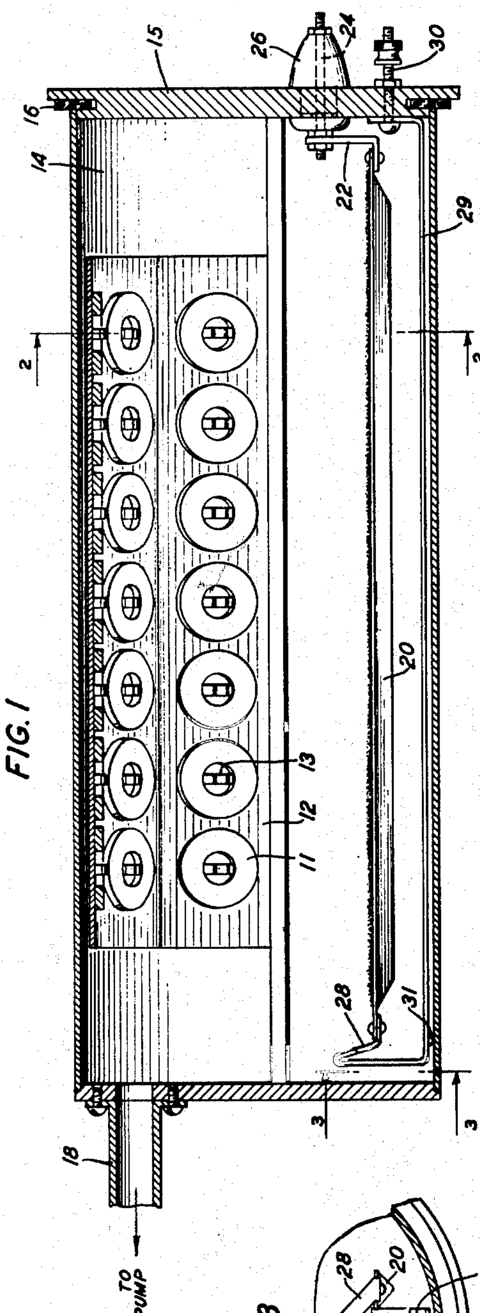

FIG. 1

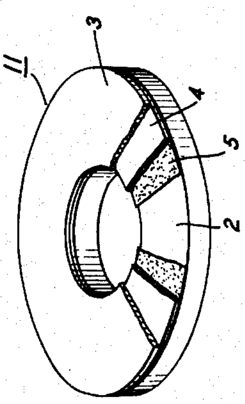

FIG. 8

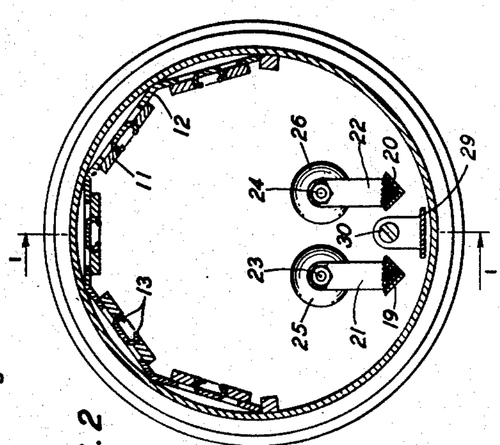

FIG. 2

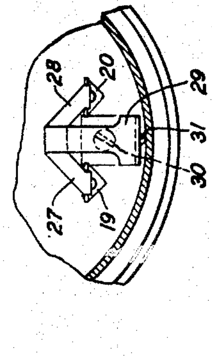

FIG. 3

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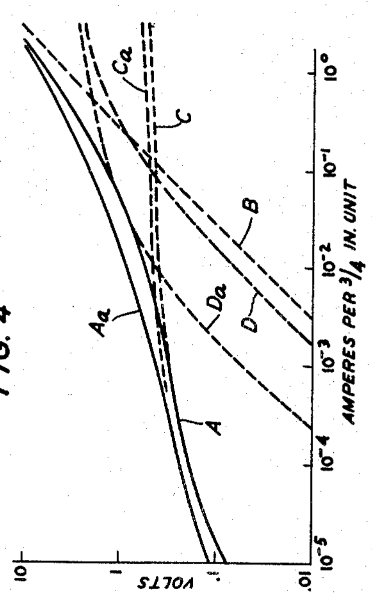

FIG. 4

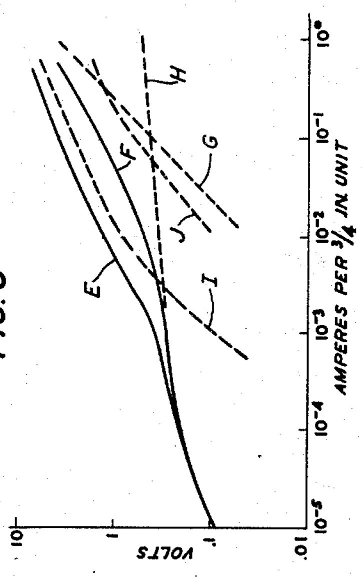

FIG. 5

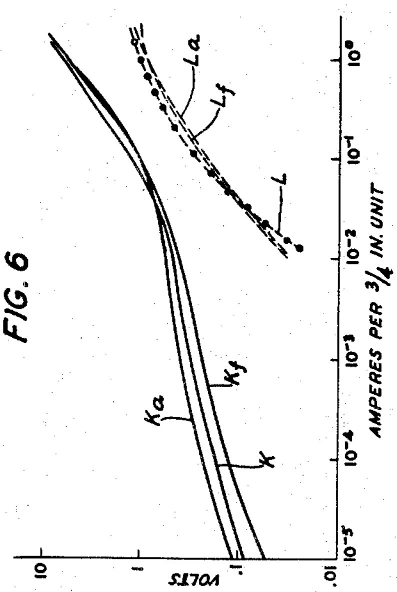

FIG. 6

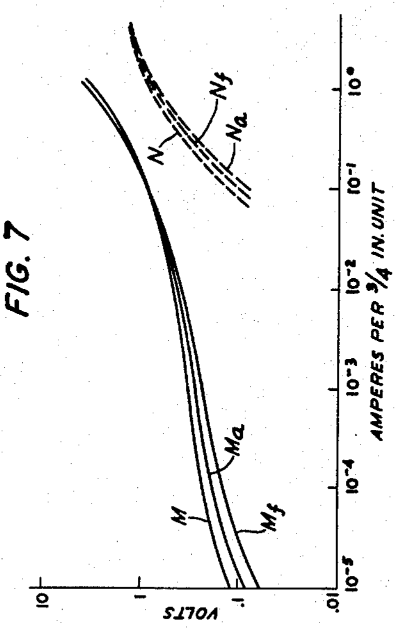

FIG. 7

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UNITED STATES PATENT OFFICE

2,608,611

SELENIUM RECTIFIER INCLUDING TELLURIUM AND METHOD OF MAKING IT

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11 Claims. (Cl. 175—366)

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This invention relates to selenium rectifiers and to methods of making them.

Devices of the type to which this invention pertains comprise, in general, a metallic backing member or electrode, for example of nickel or aluminum, a layer of selenium upon one face of the backing member, and a front electrode, for example of a metal, such as tin, or an alloy, such as of tin, bismuth and cadmium, upon the outer face of the selenium layer. The electrical characteristics of such devices, in the forward or conducting direction, are dependent upon three components namely the main rectifying barrier between the selenium and the front electrode, the selenium layer and the barrier between the selenium and the backing member or electrode. Desirably, of course, the resistance in the forward direction should be low and the operating characteristics should be stable.

The barrier between the selenium and the backing member, commonly referred to as the secondary barrier, has a direction of rectification opposite to that of the main barrier, that is the one between the selenium and the front electrode. Thus, it adds to the forward resistance. Further, it has been found that in presently known devices whereas the resistance of the selenium layer remains substantially constant and the resistance of the main barrier increases but slightly with time, the resistance of the secondary barrier increases substantially. This results in degradation of the performance of such devices, particularly in a substantial increase in the forward resistance.

Prior attempts to reduce the secondary barrier resistance have involved the addition of a halogen, notably iodine, to the selenium or, particularly in the case of aluminum back electrodes, the provision of a layer of bismuth between the selenium and the aluminum. Although these effect some improvement in decreasing the secondary barrier resistance, this resistance still is subject to increase with age. Further, other undesirable properties may be introduced thereby. For example, the halogen addition increases the sensitivity of the rectifier to atmospheric moisture and renders the rectifier more difficult to form.

One general object of this invention is to improve the performance characteristics of selenium rectifiers.

More specifically, objects of this invention are to reduce the secondary barrier resistance in selenium rectifiers, to minimize variations in this resistance with time and to realize these desiderata concomitantly without the introduction of undesirable properties in the rectifiers.

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Another object of this invention is to enable and facilitate the economic mass production of selenium rectifiers having stable and low secondary barrier resistance.

In accordance with one feature of this invention, in a selenium rectifier of the general construction described hereinabove, a layer or film of tellurium is provided between the selenium layer and the backing member. Such an interposed layer or film, it has been found, results not only in a very low secondary barrier resistance but also such a resistance which is stable with time. Furthermore, rectifiers including such layers are readily formed and substantially unaffected by atmospheric conditions.

A more specific feature of this invention resides in the method of manufacturing a selenium rectifier which comprises roughing and cleaning an element of a material suitable for a back electrode, vapor depositing a thin layer of tellurium on the roughened surface and a layer of selenium on the tellurium in a vacuum, then heat treating the unit to convert the selenium from the amorphous to the crystalline state, mounting a front contact on the selenium surface, and electrically forming a rectifying barrier between the front contact and the selenium.

The foregoing and other objects and features of the invention will be understood more fully and clearly from the following detailed description of an illustrative embodiment thereof taken in connection with the appended drawings in which:

Fig. 1 is a longitudinal section of a vaporizing apparatus suitable for practicing a method in accordance with this invention;

Fig. 2 is a cross-sectional view of the apparatus of Fig. 1 taken along the line 2—2;

Fig. 3 is a partial cross-section of the apparatus of Fig. 1 taken along the line 3—3;

Fig. 4 is a plot of voltage versus current on a logarithmic scale showing a typical forward characteristic of a nickel-backed selenium unit, and its development during aging, curves A and A_a respectively, the subscript (a) being employed throughout this specification to identify the aged characteristics, including the three component resistances which make up the overall characteristic: the resistance of the ohmic body curve B, the resistance of the main barrier, curves C and C_a, and that of the secondary barrier, curves D and D_a;

Fig. 5 is a logarithmic plot of voltage versus current showing the forward characteristic of a typical selenium unit made with an aluminum backing, curve E and with an interlayer of bismuth, curve F and the characteristics of the components including the common ohmic body, curve G, and main barrier, curve H, and the individual aluminum-selenium secondary barrier, curve I, and the aluminum bismuth-selenium secondary barrier, curve J;

Fig. 6 is a logarithmic plot of voltage versus current to the same scale as the curves of Figs. 4 and 5 showing the forward characteristics and secondary barrier effects of a unit of this invention comprising a selenium film with a tellurium interlayer on a backing of nickel before forming, curves K_f and L_f respectively, the subscript "f" being employed hereafter to identify the characteristics of a unit which has not yet been formed, after forming, curves K and L, and after aging, curves K_a and L_a;

Fig. 7 shows a logarithmic plot of the overall characteristics and that of the secondary aluminum-tellurium-selenium barrier of a unit constructed in accordance with this invention and comprising a selenium film having an aluminum backing and a tellurium interlayer before forming curves M_f and N_f, after forming curves M and N, and after aging, curves M_a and N_a; and

Fig. 8 is a perspective view of a selenium rectifier embodying this invention with portions thereof broken away.

It is noted that the curves which are shown are for an average of a number of three-quarter inch diameter washer units of the general construction shown in Fig. 8 having a non-iodized selenium layer.

Referring now to the drawings, the device of Fig. 8 is illustrative of those to which this invention pertains. It comprises a washer **1** having a roughened surface **2** of some material such as nickel which provides the back electrode and support for the remainder of the elements, a front electrode **3** and a selenium layer **4**. It may include also an intermediate layer **5** between the selenium and the back electrode. The front electrode **3** is of some material such as an alloy of tin, bismuth and cadmium applied to the unit in intimate contact with the underlying layer of selenium **4** to form at the interface between the two the main rectifying barrier. The secondary rectifying barrier in prior art devices is generally formed between the selenium and the back contact **2**. Such barrier is substantially eliminated in accordance with this invention by making the layer **5** of tellurium as hereinafter described.

As evidenced by the curves of Fig. 4, the secondary barrier contributes a considerable portion of the resistance in the characteristic of the prior art selenium-nickel units. This secondary barrier, curves D and D_a, is an undesirable part of the rectifier because it adds unwanted resistance to the unit. Furthermore, the continued development of this secondary barrier during its use is largely responsible for the progressive increase in the forward resistance of the rectifier known as aging. Curves D and D_a show how this secondary barrier develops during aging and how its development is reflected in an increased forward resistance for the rectifier characteristic curve A_a. During aging the ohmic body resistance remains substantially unchanged, curve B and the main barrier, curves C and C_a, increases only slightly in resistance. The greatest change is in the reverse characteristic of the secondary barrier and the resulting increase in resistance of the measured characteristic is such as to reduce the forward current at one volt, (the usual operating voltage) from 60 milliamps to 15 milliamps for the particular unit described.

The aluminum-selenium units also exhibit a large secondary barrier loss, curves I and J of Fig. 5, which seriously impairs the operation of the device.

In order to more closely approach an ideal rectifier it is desirable to reduce the secondary barrier to an intimate, zero resistance, time stable contact between the selenium and the backing plate. Several methods have been employed in an attempt to reduce the undesirable secondary barrier effects. One is to employ small quantities of iodine added to the selenium in the fabrication of the nickel-backed unit, and while this decreases, somewhat, both the magnitude of the secondary nickel-selenium barrier and the rapidity with which it changes with time, these units are sensitive to atmospheric moisture, and are difficult to form. Where aluminum backings are employed, the surface of the plate is covered with an evaporated coating of bismuth before applying the selenium layer in order to reduce the secondary barrier effects. Curve J of Fig. 5 shows the characteristic with the bismuth inner layer. However, this still results in a rather large magnitude secondary barrier which has a tendency to age in about the manner of the nickel-selenium barrier.

In accordance with this invention, extremely desirable characteristics, including a greatly reduced secondary barrier resistance which is substantially independent of the support plate material, has a stable value and unusually low aging, and eliminates the need of adding halogen to the selenium, thus permitting the units to form more rapidly and making the units more stable against short-circuiting in damp weather, are obtained by placing a film of tellurium indicated at **5** in Fig. 1 and advantageously deposited by vacuum evaporation, on the surface of the backing plate before the application of the selenium layer.

Fig. 6 shows the average forward characteristics of a number of typical nickel-backed units with the tellurium interlayer. Curves are shown for the unit before forming, after forming, and after aging. The body resistance and main barrier components of the overall resistance have not been included in these curves since the body resistance changes very little and the main barrier ages in about the same way as does that for the standard unit shown in Fig 4. The secondary barrier characteristic is of lower resistance than for units not having the tellurium layer, and it does not change substantially in resistance during forming and aging. These two features result in a composite characteristic which is of low resistance in the one volt region and which does not exhibit substantial increase in resistance during aging. The advantages realized by the use of the tellurium protective layer on the nickel backing are evident when these characteristics are compared with those of Fig. 4, wherein the current at one volt after aging is about one-fifth of that for the tellurium film unit.

The effect of using the tellurium protective layer technique with aluminum backing is shown in Fig. 7. The curves for the average forward characteristics of typical units before forming, after forming and after aging show again the low resistance secondary barrier characteristic and the resulting low resistance composite characteristic in the one volt operating region. They show also, as was the case for units made with the tellurium coated nickel backings, that the characteristics in the operating region change only slightly with time.

Rectifiers may be constructed in accordance with this invention on a backing member of some suitable material such as nickel, nickel coated iron, aluminum, or magnesium which may be in any convenient form, for example a disc or washer. The preliminary step in the treatment of the backing member is to roughen the surface by sandblasting or an equivalent mechanical working so that the selenium layer is provided with a surface to which it will adhere during the subsequent processing and use. The residue from the roughening process is then removed by a preliminary washing after which the backing member is thoroughly cleaned of all dirt and grease. This may be done by dipping the washer in hydrochloric acid for about ten seconds, then washing in water, dipping in nitric acid for about ten seconds and again washing in water, rinsing in acetone and then rinsing in ether and drying. The backing members may then be degassed and cleaned of residual grease and dirt, if any, by heating them in a vacuum of about 10^{-5} millimeters of mercury at 600 or 700° C. for about thirty minutes. All of the foregoing preliminary steps may be performed on a large number of washers at the same time.

The cleaned units, washers **11** in Figs. 1 and 2 of the drawing, are then mounted on a holder, for example, the rack **12** having the spring fingers **13** depending therefrom and engaging the central apertures of the washers **11**. The holder **12** and the mounted washers **11** are then placed within a vacuum chamber **14**. The chamber **14** is then sealed by placing the cover **15** thereon with the gasket **16** intermediate the cover and chamber wall. Atmospheric pressure on the exterior of the cover **15** forces it against the end of the chamber wall and compresses the gasket **16** to form an airtight joint when the chamber **14** is evacuated through the exhaust tube **18**.

A pair of troughs **19** and **20** are attached to the cover **15** and extend along the bottom of the chamber **14** below the mounted discs. These troughs are supported from the cover at one end by metal straps **21** and **22** which are connected to the terminal bolts **23** and **24** secured in insulating bushings **25** and **26** on the cover. The opposite ends of the troughs are supported by metal arms **27** and **28** depending from the off-set end of the bar **29** which is connected to the terminal **30** extending through the cover **15**. Additional support is provided for the troughs by the insulating bead **31** secured to the bar **29** and functioning as a leg therefor resting on the bottom wall of the chamber.

The troughs **19** and **20** are filled with the proper amount of tellurium and selenium, respectively, prior to mounting cover **15**. After the chamber **14** has been evacuated to a pressure of about 10^{-5} millimeters of mercury, a coating of tellurium having a thickness of about 2 milligrams per square inch is vapor deposited on the washers by passing a sufficient current between the terminals **23** and **30** to cause the trough **19** to heat up to the temperature at which tellurium vaporizes. When a sufficient layer of tellurium has been deposited upon the washers the current is removed from the trough **19** and applied to trough **20** to vaporize the selenium therein. The backing washers are sufficiently spaced from the trough heaters to remain cool enough to allow condensation of the vaporized metals thereon. The rate of deposition of the metals should be sufficiently rapid to avoid heating of the washers and consequently melting of the condensed metals. Since the electrode surface must be relatively rough to retain the selenium layer, the tellurium layer must coat the backing member without smoothing the roughened surface, therefore, this layer is only about .0005 millimeter in thickness, while the layer of deposited selenium must be thick enough to be continuous and present a smooth surface. A selenium layer approximately two mils in thickness has been found satisfactory.

The selenium as deposited is in the amorphous state which is of too high resistance to be practical for use in rectifiers. Therefore, it must be heat treated to convert it to the crystalline form. This treatment comprises a preliminary heating at about 110° C. for a period of about four hours in air and then a high temperature treatment also in air for about twenty minutes at a temperature in the range of about 214° C. to 217° C. A front contact is now provided for each unit by one of well known methods; for example, the contact may be a spray deposited layer of soft metal such as tin or an alloy such as one of tin, bismuth and cadmium. Forming of the body is next accomplished by passing current through it in the high resistance direction, from the backing member through the selenium to the soft metal front contact, under progressively increasing voltages up to about 24 volts.

The operating characteristics, both initially and over the entire life of a unit constructed in accordance with this invention are considerably better than those of the prior art units as pointed out in the above discussion of the curves of Figs. 4, 5, 6, and 7. The tellurium interlayer enables a wide choice of backing materials to be employed for selenium rectifiers while maintaining a low stable secondary barrier resistance. Further the process of manufacturing these units is amenable to mass production and requires only a minimum of handling of the individual units.

What is claimed is:

1. An asymmetric conducting device comprising a backing electrode, a thin layer of tellurium thereon, a selenium layer on said tellurium layer, and a front electrode contacting said selenium layer.

2. An asymmetric conducting device comprising a backing electrode having a nickel surface, a thin layer of tellurium thereon, a selenium layer on said tellurium layer and a front electrode contacting the surface of said selenium.

3. An asymmetric conducting device comprising a backing electrode having an aluminum surface, a thin layer of tellurium thereon, a selenium layer on said tellurium layer and a front electrode contacting the surface of said selenium.

4. An asymmetric conducting device comprising a backing electrode having a magnesium surface, a thin layer of tellurium thereon, a selenium layer on said tellurium layer and a front electrode contacting the surface of said selenium.

5. An asymmetric conducting device comprising a backing electrode, a layer of tellurium having a thickness of the order of .005 millimeter thereon, a selenium layer on said tellurium layer, and a front electrode contacting the surface of said selenium.

6. An asymmetric conducting device comprising a backing electrode, a vapor deposited layer of tellurium on a portion of said electrode, a seleni-

um layer on said tellurium layer and a front electrode contacting the surface of said selenium.

7. An asymmetric conducting device comprising a backing electrode, a layer of tellurium thereon, a vapor deposited layer of selenium, and a front electrode contacting the surface of said selenium.

8. An asymmetric conducting device comprising a backing electrode, a vapor deposited film of tellurium thereon, a vapor deposited selenium layer on said tellurium layer, and a front electrode contacting the surface of said selenium.

9. The method of making a selenium rectifier having a low, stable secondary rectifying barrier resistance that comprises coating a surface of an electrode element of suitable material with a thin layer of tellurium, coating the tellurium layer with a layer of selenium, heat treating the unit to convert the selenium to the crystalline state, applying a front electrode to the selenium surface and electrically forming the unit.

10. The method of making a selenium rectifier unit which comprises roughening a surface of an electrode element of suitable metal, cleaning the element, applying a thin coating of tellurium to the roughened surface of said element, coating the tellurium layer with a layer of selenium of sufficient thickness to have a relatively smooth external surface, heat treating the unit to convert the selenium to a crystalline state, applying a front electrode to the selenium surface and electrically forming the unit.

11. The method of making selenium rectifier units that comprises roughening a surface of each of a plurality of electrode elements of suitable material, vapor depositing tellurium on the roughened surfaces of said cleaned elements in a vacuum, vapor depositing selenium on the tellurium coating surfaces of said elements in a vacuum, the amount of selenium deposited being sufficient to produce a layer that is thick enough to have a relatively smooth external surface, heat treating the units to convert the selenium to the crystalline state, applying front electrodes to the selenium surface and electrically forming the units.

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