

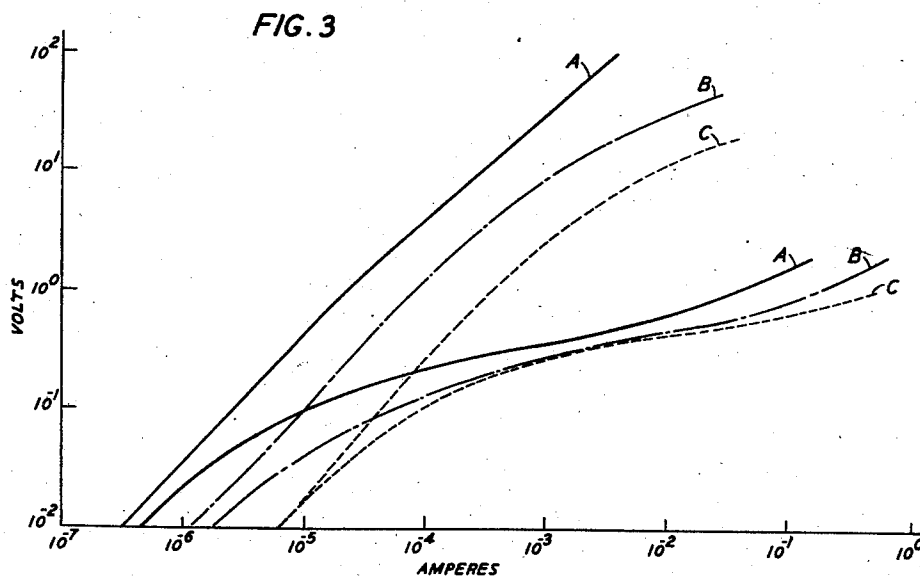
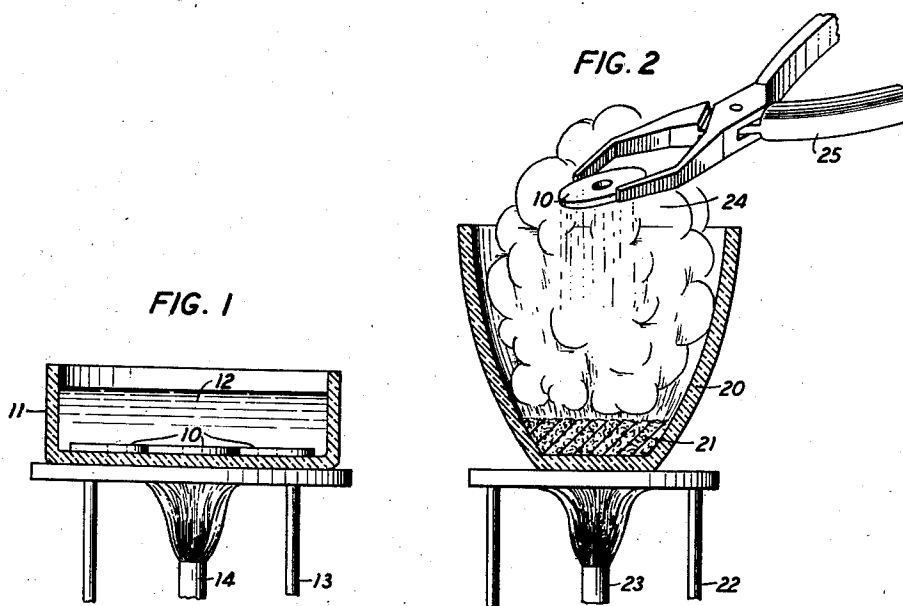
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SELENIUM RECTIFIER AND METHODS OF MAKING IT

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SELENIUM RECTIFIER AND METHOD OF MAKING IT

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This invention relates to selenium rectifiers and more particularly to methods of and means for improving the resistance characteristics of such rectifiers.

Selenium rectifier units may be made by applying a relatively thin layer of selenium to a backing member or electrode of nickel, nickel-iron or some other material that will not react unfavorably with the selenium. One way of applying the selenium is to place a measured amount of powdered selenium on the backing member, e. g., a nickel disc and then heat the disc and selenium to a temperature above the melting point of selenium. A suitable temperature is about 300 C. The selenium when melted is spread evenly over the surface of the disc. This assembly is then allowed to cool, solidifying the selenium coating. At this stage the selenium is in the relatively non-conductive amorphous state. In order to render the selenium usable for rectifier purposes, the non-conducting selenium must be converted to the relatively conductive crystalline form. This may be done by the application of heat treatment to the unit. The usual method of performing the heat treatment is divided into two steps. The first step comprises heating the unit to about 110° C. while under mechanical pressure. The pressure may be applied by stacking a plurality of units with a smooth plate or disc in contact with each selenium surface. These interleaving discs may be made of mica or some smooth surfaced metal that will not react with the selenium. Pressure may be applied to the ends of the stack by any suitable clamping means. The selenium is softened during this heat treatment and the effect of the pressure is to render the selenium layer more uniform and to smooth its surface. During this step the selenium is partly converted to the crystalline state and its resistance is reduced appreciably.

The second heat treating step is performed at a temperature slightly below the melting point (218° C.) of selenium. After completion of the heat treatment, the surface of the selenium may be treated by exposing it for a short time to selenium dioxide vapor. This is to improve the rectifier junction characteristic. The rectifier unit is structurally completed by applying a contact to the surface of the selenium. This may be done by pressing a disc or washer of soft metal against the surface by any suitable clamping means. An adherent electrode is often preferred and may be made by the deposition of a low melting point metal or alloy, such as tin or a tin-bismuth-cadmium alloy on the surface of the selenium.

Although at this stage the units have a higher resistance in one direction than in the other, the high resistance may be markedly increased by "forming." This "forming" is accomplished by passing current through the unit in the high resistance or reverse direction. In order to avoid "burning out" of the unit, the "forming" current must be limited. As the reverse resistance gradually increases during the forming, the voltage is increased up to 20 or 24 volts per unit. Since the building up of the reverse resistance is often slow, appreciable time must be taken to obtain a reasonably satisfactory unit. A time of at least two or three hours may be required. However, if this process is properly performed, it will produce units having a fairly good ratio of forward to reverse resistance.

An object of this invention is to increase the reverse resistance of selenium rectifier units without appreciably affecting the forward resistance.

Another object of the invention is to reduce the time necessary to properly form the rectifier units.

One feature of this invention resides in treating the selenium with a halide after its conversion to the relatively conductive, crystalline state, and before application of a second electrode.

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

Fig. 1 shows apparatus illustrative of that which may be used for treatment of the rectifier units with a halide liquid.

Fig. 2 shows illustrative apparatus for treating the units with a gaseous halide; and

Fig. 3 is a plot of voltage vs. current for both forward and reverse current directions to show the resistance characteristics of (A and B) units treated in accordance with this invention and (C) those not so treated.

As has been intimated, it has been found in accordance with this invention that treatment of the crystalline selenium of selenium rectifiers with a halide increases the reverse or high resistance and decreases the time needed to form the rectifier. Alkaline halides have been found particularly suitable for this purpose. Halides which have been successfully used include ammonium chloride, potassium bromide, sodium chloride, potassium chloride, potassium iodide, sodium bromide, sodium iodide, ammonium bromide, ammonium iodide, barium chloride, magnesium chloride and ammonium fluoride. It is

noted that the foregoing group includes the alkali metal halides including the ammonium halides and also alkali earth halides. The term alkali or alkaline halide is intended to include any or all of the above halides. The selenium of the partly completed rectifier may be given the halide treatment by means of a liquid or gas.

The treatment with a halide liquid may be carried out at room temperature, but a more elevated temperature is preferred. Using a solution, for example, of potassium bromide and the apparatus illustrated in Fig. 1, the process may be carried out as follows:

A plurality of units 10 comprising crystalline selenium on a suitable backing may be placed in a container 11 and covered with the potassium bromide solution 12. The container may be placed on a stand 13 over a burner 14 and the solution brought to a boil. Since a relatively short treatment, 30 to 40 seconds produces good results, the solution may be first brought to a boil and the units then immersed therein. Potassium-bromide solutions of concentrations ranging from 1.2 grams to 40 grams per 100 cubic centimeters of water were found to be satisfactory. The stronger solutions appear to give somewhat better results.

After this treatment the units are washed and dried and a front contact applied thereto. An adherent contact comprising a spray deposited alloy of tin, bismuth and cadmium is suitable. The units are then formed by passing current therethrough in the reverse direction by subjecting them to successively increasing voltages up to about 50 volts.

Treatment with halides in vapor form may be applied by means of apparatus such as that illustrated in Fig. 2. A quantity of the halide, e. g. ammonium chloride, is placed in a crucible 20 as at 21. The crucible may be placed on a stand 22 over a suitable burner 23 and heated sufficiently to evolve vapor as indicated at 24. A unit 10 held in suitable means, such as tongs 25, is then passed through the vapor 24. The unit 10 may be cold when passed through the vapor or preferably is heated to about $150^{\circ} \pm 25^{\circ}$ C. before treatment. The time of treatment is relatively short and its end point is indicated by darkening of the selenium surface. Any loose deposit which may be found on the unit after treatment may be removed, for example by means of a blast of compressed air. The unit is then supplied with a front contact as previously indicated and is formed.

Units treated with ammonium chloride vapor were formed at voltages up to 100 volts, the units formed at approximately 100 volts having a higher reverse resistance than those formed at about 50 volts, the forward resistance in each case being about the same.

As indicated in connection with the previous descriptions of processing with potassium bromide or ammonium chloride, the forming voltages run much higher in this process than in the older process described. The time required for forming is also considerably reduced because the reverse resistance builds up very rapidly. After a treatment of about 40 minutes the resistance is considerably higher than in the old process and may be increased still further by continued treatment with voltages ranging up to 50 or 100 volts or higher. Although particularly good results have been obtained with the ammonium chloride and potassium bromide applications specifically described, a considerable increase in reverse re-

sistance and decrease in forming time has been obtained with any of the halides previously noted.

In Fig. 3 are shown curves of voltage-current characteristics in both forward and reverse directions for three representative rectifier units, curves A being for a unit treated with ammonium chloride, curves B for a unit treated with potassium bromide, and curves C for a unit made in accordance with the prior art process previously described in this specification. As may be seen from an inspection of these curves, each of the halide treated rectifiers, as shown by curves A and B, exhibits a reverse resistance which is considerably higher than that of untreated units represented by curves C. Although the forward resistance is somewhat increased by the treatment, it is not increased as much as the reverse resistance. Units made in accordance with this invention, therefore, show a decided increase in rectification ratio, as compared with units made by the older process. The raising of the reverse resistance not only improves the resistance ratio, but it is also responsible for a reduction in losses.

Although specific embodiments of this invention have been shown and described, it will be understood that modifications may be made therein without departing from the scope and spirit of this invention as defined by the appended claims.

What is claimed is:

1. The method of making a selenium rectifier that comprises applying an adherent film of amorphous selenium to a conductive backing member, converting the amorphous selenium to crystalline selenium by heat treatment, exposing the surface of the selenium to a fluid alkaline halide for a short time, applying an electrode to said surface and forming the rectifier by passing current therethrough in the high resistance direction.
2. The method of making a selenium rectifier that comprises applying a film of amorphous selenium to a nickel surfaced disc, heat treating the selenium to convert it to the crystalline form, immersing the filmed disc in a boiling solution of potassium bromide in water, for from 30 to 40 seconds, the concentration being from 1.2 to 40 grams per hundred cubic centimeters, washing and drying the disc, applying an electrode to the surface of the selenium and forming the rectifier by passing current through the disc in the high resistance direction at progressively increasing voltages up to about 50 volts.
3. The method of making a selenium rectifier that comprises applying a film of amorphous selenium to a nickel surfaced disc, heat treating the selenium to convert it to the crystalline form, bringing the filmed disc to a temperature of $150^{\circ} \pm 25^{\circ}$ C., passing the disc through the vapor of heated ammonium chloride until the selenium surface is darkened, applying an electrode to the selenium surface and forming the rectifier by passing current through the disc in the high resistance direction at progressively increasing voltages up to about 100 volts.
4. The method of making a selenium rectifier that comprises preparing a layer of crystalline selenium on a suitable backing, treating the selenium surface with potassium bromide, applying a contact to the treated selenium surface and forming the rectifier by the application thereto of successively increasing voltages up to 50 volts, in the high resistance direction.
5. In the method of making a selenium rectifier that comprises applying a layer of amorphous selenium to an electrode, heat treating to con-

vert the amorphous selenium to a crystalline selenium and applying a contact to the selenium surface, the step of increasing the reverse resistance, that comprises treating the surface of the crystalline selenium, before applying the contact, with an alkaline halide.

6. In a method of making a selenium rectifier by applying a film of amorphous selenium to a conductive backing, converting the selenium to the crystalline form by heat treatment, applying a contact to the surface of the selenium and forming the rectifier by passing current there-through in the high resistance direction, the step that reduces the forming time and comprises subjecting the surface of the crystalline selenium to an alkaline halide before applying the contact.

7. The method of making a selenium rectifier that comprises coating a suitable electrode with amorphous selenium, heat treating to convert the selenium to its crystalline state, treating the selenium with sodium chloride, applying a second electrode to the treated selenium and forming the rectifier by passing current therethrough in the high resistance direction.

8. The method of making a selenium rectifier that comprises coating a suitable electrode with amorphous selenium, heat treating to convert the selenium to its crystalline state, treating the selenium with an alkaline halide and increasing the reverse resistance of the rectifier by passing current therethrough in the high resistance direction at increasing voltages from 10 to 100 volts, the maximum voltage applied depending upon the reverse resistance desired.

9. The method of increasing the reverse resistance and reducing the forming time of a selenium rectifier made by coating a suitable electrode with amorphous selenium, changing the selenium to its crystalline state by heat treatment, applying a second electrode to the selenium surface and forming the rectifier by the application of current thereto in the reverse direction at increasing voltage, that comprises exposing the selenium to an alkaline halide in fluid form prior to the application of the second electrode.

10. A selenium rectifier comprising a backing electrode, a layer of selenium on said electrode, the surface portion only of said layer being alkaline halide treated, and a front electrode on said treated surface.

11. A selenium rectifier comprising a backing electrode, a layer of selenium on said electrode, the surface portion only of said layer being ammonium chloride treated, and a front electrode on said treated surface.

12. A selenium rectifier comprising a backing electrode, a layer of selenium on said electrode, the surface portion only of said layer being potassium bromide treated, and a front electrode on said treated surface.

13. A selenium rectifier comprising a backing electrode, a layer of selenium on said electrode, the surface portion only of said layer being sodium chloride treated, and a front electrode on said treated surface.

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