

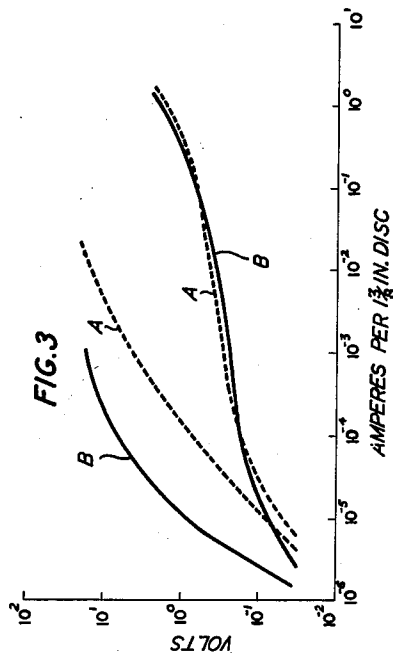
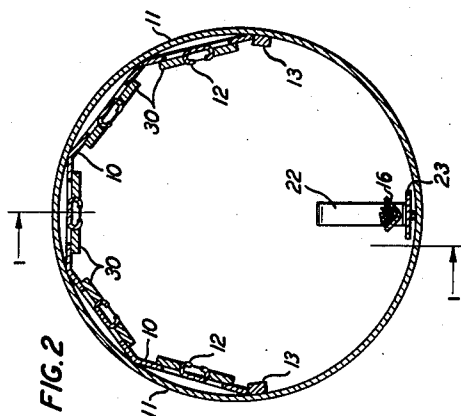
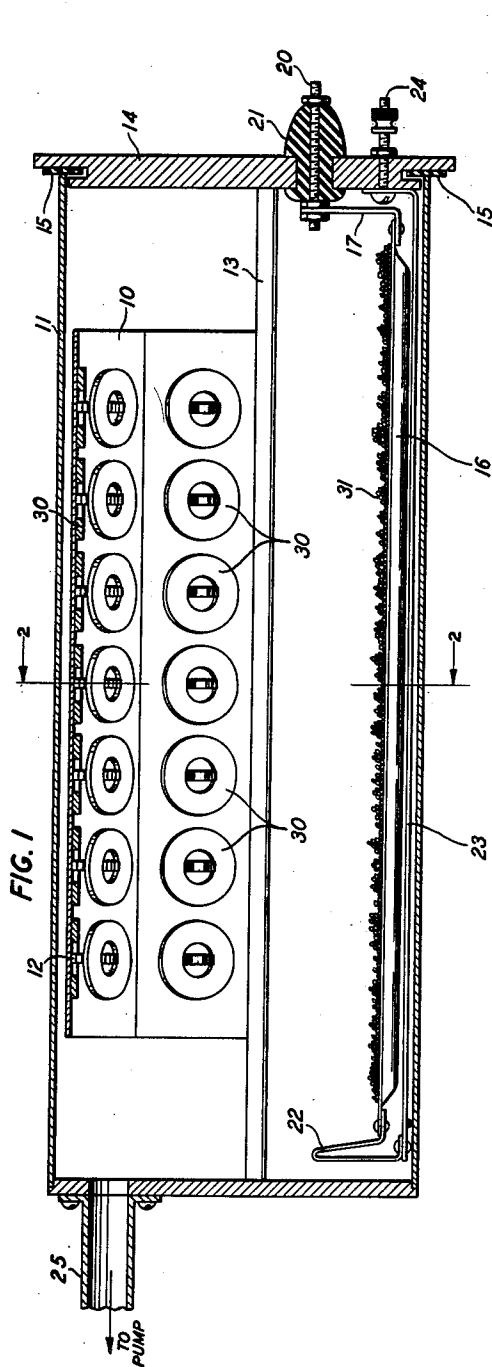
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SELENIUM RECTIFIER AND METHOD OF MAKING IT

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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 making such rectifiers.

Although various different directions have been given from time to time for the making of selenium rectifiers, successful commercial production thereof up to the present time, having in mind uniformity and reproducibility, appears to have required rather strict adherence to a particular series of process steps, which may be described as being substantially as follows:

The selenium because of its physical characteristics must, when used in a thin layer, be supported on a backing member. The backing member should be relatively rigid, capable of conducting current easily, and composed of a material that does not react unfavorably with selenium. The metals nickel and iron appear to be particularly suitable, and the former is favored. A nickel surface is sometimes presented to the selenium by coating one face of an iron disc or plate with nickel. In preparation for coating with selenium, a surface of the electrode is roughened, and the electrode is then immersed in a cleaning solution, rinsed, and dried. This cleaning treatment may for example comprise boiling in sodium hydroxide solution, washing in acetone, rinsing in ether, and drying.

The selenium, usually in powdered form, although it may be in tablets, is deposited in measured quantity on the prepared backing member, e. g., a disc or washer, the latter being much used because of the convenience of handling and assembly afforded by its central orifice. The temperature of the disc or washer is then raised above the melting point of selenium by any suitable means. A temperature of 250° C. is satisfactory. A "hot plate" with temperature control is preferred. When the selenium has melted, it is spread over the surface of the washer as evenly as possible, all surface bubbles being broken. The spreading tool must be clean and of a material that will not contaminate the selenium. A glass or porcelain rod is suitable. This step is handwork, which requires a reasonable degree of skill.

The coated washers are then cooled to solidify the selenium. The selenium at this stage is in the amorphous state and has a resistance much too high for rectifier purposes. Conversion of the selenium to its crystalline state in which it is relatively conducting, is by heat treatment in two steps, the first at about 110° C. and the second at 217° C. During the first step the selenium softens enough to be easily deformable and is partially converted to the crystalline state. Advan-

tage is taken of the softening to smooth and level the selenium surface and to make the coating more uniform in thickness. This may be done by the application of suitable pressure. A convenient and usual way of doing this is to stack a plurality of selenium coated washers on a mandrel or bolt with smooth surfaced washers interleaved between adjacent units. The interleaving washers must be clean and of a material that will not contaminate the selenium. Washers of mica or chromium may be employed. The pressure on the units is controlled by some means such as a calibrated spring. The 110° C. treatment may be done in an oven or furnace and usually lasts for about four hours. The stacks are then disassembled and the units are ready for the treatment at 217° C.

During the second heat treatment only slight deviation from the 217° temperature is allowable if satisfactory units are to be produced in a reasonable time by this process. The selenium must not be allowed to reach the melting point of selenium, i. e., 218° C. nor should it go below 216° C. For this reason only a small number of units are treated at a time. The time of treatment is about twenty minutes and may be divided into two ten-minute periods, the latter being preferred.

The next step is the application of a selenium dioxide film to the selenium face of each unit. Each unit is held, selenium face down, for a few seconds, in the rising vapor of selenium dioxide, which may be obtained by heating selenious acid in a crucible. A fume hood or other protective means must be employed to protect the operator because the selenium dioxide fumes are poisonous. The purpose of the selenium dioxide film is to improve the blocking layer and increase the reverse resistance of the completed rectifier. Omission of this step in the process now being described sometimes results in an inferior product.

The units are now provided with an outer contact, which may be a soft metal washer, but which is preferably of the adherent type. Spray-deposited low melting point metals or alloys are suitable. Several units may be masked at their edges and sprayed at the same time with a coating of tin, a tin-bismuth-cadmium alloy, or the like.

The rectifier element is now mechanically complete but requires "forming" to increase its reverse resistance. The "forming" is accomplished by passing current through the unit in the high resistance direction at gradually increasing voltages from about 12 to 20 or 24 volts, over a period of about two or three hours.

Although the above-described process will produce reasonably good rectifiers, it is nevertheless subject to certain disadvantages. Each unit must be given individual attention to spread the selenium and remove gas bubbles. The selenium which has been applied by melting requires pressure during the 110° C. treatment to smooth its surface, etc. The assembly in the pressure applying apparatus takes time and involves danger of contamination from parts of the apparatus. Since selenium dioxide is poisonous, the treatment therewith involves a health hazard. For best results it has heretofore appeared necessary to maintain the second heat treating temperature close to the melting point of selenium.

An object of this invention is to obviate the above-enumerated difficulties while at the same time to produce a rectifier of equal or better electrical characteristics.

A feature of this invention resides in the simultaneous vapor deposition of selenium on the surfaces of a plurality of suitable electrodes or backing members.

Another feature of this invention lies in the omission of the selenium dioxide coating step without loss of the desirable electrical characteristics which this step sometimes imparts to selenium rectifiers in which the selenium is applied by melting.

Still another feature of this invention resides in the smoothness and uniformity of the vapor-deposited selenium layer which do away with the need for application of pressure and its attendant extra labor during the 110° C. treatment.

Another feature of this invention lies in the reduction of the time and temperature sensitivity of the high temperature heat treatment.

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 drawing in which:

Fig. 1 is a longitudinal section of a vaporizing apparatus suitable for carrying out one step of the invention;

Fig. 2 is a section taken on line 2—2 of Fig. 1; and

Fig. 3 is a plot of voltage versus current on logarithmic scales for (A) a rectifier unit made in accordance with the older processes previously described and (B) for a rectifier unit made in accordance with the process of this invention. Some of the smaller dimensions, such as thickness, have been somewhat exaggerated in parts of Figs. 1 and 2 in the interest of clarity of illustration.

The improved process according to the present invention is similar in some respects to the one previously described, and differs in others as is more fully pointed out in the following detailed description:

The backing members or electrodes, which may be of nickel, nickel-coated iron, or the like, as in the other process, may be plates, discs, washers or other suitable shapes, e. g., nickel washers. The washers are first given a preliminary cleaning and are roughened by sandblasting or some equivalent mechanical working. The surface to be coated with selenium must be relatively rough to retain the selenium layer during further processing and subsequent use. After removal of the sandblasting grit and any abraded material, the washers should be further cleaned of dirt, grease and like material by suitable washings. This may be done

by dipping the washers 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, then rinsing in ether and drying. The washers 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 preparatory steps may be performed on a large number of washers at the same time.

In this process a relatively large number of washers may be placed in a vaporizing chamber, which is then evacuated, and in which selenium is deposited simultaneously on all of the washers. An apparatus like that disclosed in Figs. 1 and 2 may be employed. The particular apparatus shown will accommodate thirty-five washers. It is believed to be obvious that much larger quantities of units may be coated if larger chambers and racks are employed.

The cleaned units, washers in this illustration, are loaded into a rack 10, which is adapted to fit in a metal cylinder or jacket 11 which may be of steel. The rack 10 may be a sheet of copper or other metal bent to fit within cylinder 11 and to accommodate several rows of washers 30. The washers may be supported in the rack 10 by means of spring clips 12, punched from the metal sheet and bent over as shown in Fig. 2. The rack may be supported in the cylinder 11 by means of rails 13 secured to the cylinder wall.

The cylinder 11 should be provided with a cover such as 14, which is sealably fitted to one end by suitable means, for example the gasket 15. The gasket 15 may be of rubber or other suitable gasket material. The cover, as the cylinder, may be made of steel.

The receptacle for holding the selenium 31 to be vaporized, may comprise a V-shaped trough 16 of a high melting point metal, such as tungsten or the like. The trough 16 may be supported from the cover 14. The end of the trough adjacent the cover may be secured to a bracket 17, which is supported from a terminal stud 20 insulated from the cover by insulator 21. The other end of the trough may be fastened to a support member 22 secured to a return current conductor bar 23. The bar 23 may be secured directly to the cover 14 by means of a terminal bolt 24. Cylinder 11 should be provided with a suitable pump connection such as 25.

After the loaded rack 10 has been placed in the cylinder 11 and the receptacle 16 filled with the proper amount of selenium, the cover 14 is applied to the cylinder and the evacuation started. Due to the evacuation of the cylinder the cover is held in place by external air pressure. The cylinder should be evacuated to a pressure of about 1 x 10⁻⁵ millimeters of mercury. Current is then passed through the receptacle 16 via terminals 20 and 24, in sufficient quantity to vaporize the selenium. The backing washers are sufficiently spaced from the heater to remain cool enough to allow condensation of selenium thereon. The rate of deposition of selenium should be sufficiently rapid to avoid heating of the washers and consequent remelting of the selenium. Since the electrode surface must be relatively rough to retain the selenium layer, the layer must be thick enough to be continuous and present a smooth surface. A layer approximately 2 mils in thickness on a sandblasted surface has been found satisfactory.

The washers having been coated with a layer

of selenium which is in the amorphous state, must now be heat treated to convert it to the crystalline form. This treatment is in two stages, one at about 110° C. and the other somewhat below 218° C., the melting point of selenium. Since the vapor-deposited selenium is relatively dense and has a smooth surface, there is no need for applying pressure during the 110° C. treatment. The washers are therefore simply loaded into an oven and left until the treatment is completed. This ordinarily takes about four hours.

The high temperature heat treatment, i. e., that in the neighborhood of 218° C. is the next step. It has been found, that with units prepared by vacuum deposition of the selenium, neither the temperature of this treatment nor the time cycle is as critical as in the previously noted process. A temperature of about 215° C. is apparently as effective as one of 217° C. Also units which are left in the furnace for twenty minutes continuously appear as good, when completed, as those for which this heat treatment is divided into two periods of ten minutes each as in the older process.

What would be the next step in the process previously described, i. e., application of a selenium dioxide film, may be omitted with vapor-deposited selenium units. A study of the characteristics of these units indicates that they suffer no disadvantage ascribable to the omission of this step. Furthermore, doing away with this step makes the use of a fume hood unnecessary and eliminates the individual handling which each disc must receive at this point in the present commercial process.

The units are now provided with a front contact and "formed" as in the older process. As previously indicated, an adherent contact is preferred. This contact may be a spray-deposited layer of soft metal, such as tin, or an alloy such as one of tin, bismuth and cadmium. The "forming" is accomplished by passing current through the unit in the high resistance direction under progressively increasing voltages up to about 24 volts.

The voltage-current plot of Fig. 3 shows curves for current in both the forward and reverse direction. The broken lines and solid lines show respectively the characteristics of representative units made in accordance with (A) the present commercial process as described in this specification and (B) the process of this invention. As may be seen by an inspection of these curves, the resistance ratio for a rectifier made in accordance with this invention (curves B), is in the order of ten times that for a rectifier made by the older process (curves A). Furthermore, since the increase in ratio is due primarily to the much higher reverse resistance of the rectifiers having vapor-deposited selenium, the losses are greatly reduced.

In addition to the marked improvement of the product resulting from the process of this invention, there are definite advantages of the new process itself over the old. As has been noted in connection with the various steps of the two processes, the process of this invention has the following additional advantages: (a) application of selenium by vacuum deposition makes possible the coating of large numbers of units at once; (b) elimination of pressure during the 110° treatment results in a cheaper process and eliminates the possibility of contamination from the holder while applying pressure; (c) reduction of the time and temperature sensitivity of the high temperature treatment reduces the need for

rigid control at this point and thereby simplifies the process; and (d) elimination of the selenium dioxide coating step does away with the need for expensive equipment and eliminates a health hazard.

Although a specific embodiment of this invention has 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 selenium rectifier units by which a plurality of units may be simultaneously processed at each step, that comprises roughening a surface of each of a plurality of electrode elements of suitable metal, cleaning the elements of dirt, grease and other foreign material, by washing and vacuum heating vapor-depositing selenium on the roughened surfaces of said cleaned 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 at approximately 110° C. for four hours, then heat treating said units at 215° to 216° C. for about twenty minutes, applying an adherent electrode to each selenium surface and electrically forming the units.

2. The method of making selenium rectifier units that comprises preparing metal bodies of suitable material and configuration by roughening one surface thereof, cleaning the bodies mechanically and chemically and also by heating them in a vacuum at 600 to 700° C., placing the clean bodies in a vacuum chamber and vapor-depositing in a vacuum, a layer of selenium on the roughened surfaces thereof, removing the bodies from the vacuum chamber, heat treating said bodies by first exposing them to a temperature of 110° C. for about four hours, then to a temperature of 215° to 216° C. for approximately twenty minutes, applying an adherent contact to the surface of the selenium and electrically forming the units by the application of current to each in the high resistance direction.

3. The method of making selenium rectifier units in quantity that comprises, roughening a surface of each of a plurality of backing electrodes for the units, cleaning said electrodes, placing the electrodes in a carrier, inserting the carrier in a chamber, evacuating the chamber to a pressure of about 10^{-5} millimeters of mercury, vaporizing a quantity of selenium sufficient to coat one surface of each electrode, maintaining the electrodes at a temperature that will insure condensation of selenium vapor thereon, removing the coated electrodes from the chamber, placing the units in an oven and subjecting them to a temperature of about 110° C. for approximately four hours, then placing the units in a furnace and subjecting them to a temperature of 215° to 216° C. for about twenty minutes, spray-depositing a second electrode on the surface of the selenium and electrically forming the units by passing current through each in the high resistance direction at gradually increasing voltages up to about 24 volts per unit.

4. The method of making selenium rectifier units in quantity that comprises roughening a surface of each of a plurality of nickel discs, cleaning said discs by washing and by heating the discs in a vacuum at about 650° C., vapor-depositing selenium on the roughened surface of said discs in a vacuum of about 1×10^{-5} mil-

limeters of mercury, heat treating the discs at approximately 110° C. for about four hours, then heat treating said discs at 215° to 216° C. for about twenty minutes, spray-depositing an electrode of soft metal on the selenium surfaces and electrically forming the units by passing current through each in the high resistance direction.

5. The method of making selenium rectifiers having a rectification ratio in the order of 25,000 to 1 at one volt that comprises roughening and cleaning a surface of each of a plurality of electrodes by mechanical abrasion, further cleaning the electrodes by washing them in suitable solvents, drying the electrodes, loading these electrodes into a rack, placing the rack and an amount of selenium sufficient to coat the roughened surface of each electrode, in a chamber, sealing the chamber, reducing the pressure in the chamber to about 10^{-5} millimeters of mercury, heating the selenium to a vapor and allowing the vapor to condense on the electrodes, the rate of heating being sufficiently rapid and the electrodes being sufficiently spaced from the heat source to avoid remelting of the deposited selenium, allowing the chamber pressure to return to atmospheric, removing the electrodes, heat treating the coated electrodes at approximately 110° C. for about four hours, then at 215° to 216° C. for about twenty minutes, applying a front electrode to the selenium surface of each coated electrode and forming the rectifier by passing current therethrough in the high resistance direction at successively increasing voltages up to about 24 volts.

6. The method of making selenium rectifiers to have a rectification ratio in the order of 25,000 to 1 at one volt that comprises roughening and cleaning a surface of each of a plurality of suitable electrodes by mechanical abrasion, further cleaning the electrodes chemically, enclosing said electrodes and a suitable quantity of selenium and subjecting them to a vacuum of about 10^{-5} millimeters of mercury, applying sufficient heat to vaporize the selenium and deposit the vapor on the electrodes, releasing the vacuum, heat treating the coated electrodes at approximately 110° C. for about four hours, then at 215° to 216° C. for about twenty minutes, applying an elec-

trode to each selenium surface and forming the rectifier by passing current therethrough in the high resistance direction at successively increasing voltages.

7. The method of making selenium rectifier units in quantity that comprises cleaning a plurality of electrodes and roughening a surface thereof by mechanical abrasion, further cleaning the electrodes by subjecting them to a temperature of from 600 to 700° C. in a vacuum of about 1×10^{-5} millimeters of mercury for approximately thirty minutes, vapor-depositing selenium on the roughened surface of each electrode in a vacuum of about 1×10^{-5} millimeters of mercury, heat treating the selenium, coating by subjecting it to a temperature of about 100° C. for approximately four hours and then to 215° to 216° C. for about twenty minutes, applying a contact electrode to each selenium surface and increasing the reverse resistance of each unit by passing current therethrough in the reverse direction at successively increasing voltages up to about 24 volts.

8. In a method of making a selenium rectifier that comprises depositing amorphous selenium on a first electrode, changing the amorphous selenium to crystalline selenium by heat treatment, applying a second electrode to the selenium surface and forming the rectifier by passing current therethrough in the high resistance direction, the step whereby said forming produces a reverse resistance in the order of 1×10^4 ohms per square centimeter at about 10 volts, that comprises vapor-depositing the selenium on the first electrode.

9. A selenium rectifier comprising a back electrode having a roughened surface, which electrode has been thoroughly cleaned by washing and vacuum heating, a layer of vapor deposited selenium on the roughened surface of said electrode and a front electrode directly on the surface of said selenium, the ratio of the forward to the reverse resistance being in the order of 1 to 25,000 at one volt and the reverse resistance being about 1×10^4 ohms per square centimeter at 10 volts.

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