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SELENIUM RECTIFIER ELEMENT AND METHOD OF MANUFACTURING SAME

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6 Claims. (Cl. 175—366)

If a selenium rectifier element is subjected to a reasonably high voltage in the blocking direction, the leakage current will at the first instant be very high but will gradually sink to a low and nearly constant value. If then the voltage is raised by a certain amount, the leakage current is suddenly increased to a high value but subsequently sinks again to a new constant value, somewhat higher than the former one. The element may in this way, by a step by step or continuously raised voltage in the blocking direction, be "trained" to stand a considerable blocking voltage, which may be a direct or alternating current voltage. This process is generally called "forming."

If the element, after such a forming, has been out of operation for some time, it has been necessary to subject it to a new forming before it can stand the same high blocking voltage as before, but the forming process then goes many times more rapidly than the first time, and the more rapidly the shorter is the time during which it has been out of operation.

It would be reasonable to expect that an element which, after forming, has been subjected to a comparatively low blocking voltage, lower than that used in the forming, would better retain its state of being formed than if it were completely out of operation. This is, however, not the case. On the contrary, the surprising observation has been made, that if in the former case, the blocking voltage is suddenly changed to a higher value (while still lower than that employed in the forming), then the leakage current will rise to a higher value and sink more slowly to its final value than when the same element is directly subjected to the higher voltage after having been out of operation. The cause of this phenomenon is still unknown.

According to the present invention, the selenium rectifier elements are subjected during manufacturing to a treatment which largely eliminates the aforesaid weakness, so that the elements can be formed much more rapidly after the said treatment. Moreover, the ready-formed elements can endure higher blocking voltages than heretofore.

In the manufacture of a selenium rectifier element, a selenium layer is applied to a metal base plate and is then subjected to a combined pressure and heat treatment in order to be transformed into the well-conducting modification. Subsequently, a counter-electrode is applied to the free selenium surface, usually by spraying a liquid metal alloy having a low fusing point

thereto, but in another modification by applying a solid counter-electrode only under pressure. The treatment according to the present invention consists in supplying to the selenium surface adjacent to the counter-electrode small quantities of thorium or zirconium or of a kindred metal or of a compound containing some of these metals.

The said metals may be supplied to the selenium surface by condensing their vapors or by cathode sputtering before the counter-electrode is applied. It is also possible to apply a metal by alloying it with the counter-electrode, if the latter is intended to be applied by spraying, but not by mixing it into the selenium, since it seems necessary for a good result of the treatment that the addition of the metal is limited to the layer of the selenium immediately adjacent to the counter-electrode.

A simple and efficient method of supplying a compound of the aforesaid metals is to dissolve the compound into a solvent and to treat the selenium surface with the solution. The solvent should be evaporated before the application of the counter-electrode. Although water may be used as a solvent, it has not been found especially appropriate, first because the selenium surface is only with a certain difficulty moistened thereby and also because the water is comparatively slowly evaporated and probably has an unfavorable action in the meantime. Alcohols and other organic solvents have been found more appropriate for these reasons. The compound applied should of course be soluble in the solvent employed and should further not contain, besides the desired metal, substances which may have a noisome influence. Good results have been obtained with nitrates of thorium and zirconium, probably because of their acid component being easily decomposed. Other compounds suitable from this standpoint are nitrites and certain organic compounds, as thorium-ethyl-acetonate. Halogen compounds are not suitable. It is possible that in certain compounds, the negative component has a real favorable influence.

The treatment described influences the current-voltage characteristic of the selenium element in the blocking direction in a very favorable way as regards its operating properties, as has been proved by cathode ray oscillograms. In a rectifier element which has not been treated according to the invention, the leakage current is rather low up to a certain blocking voltage but is then so rapidly increased that the characteristic curve is practically parallel to the current axis. In an element treated according to the present invention, on the contrary, the leakage current rises considerably slower for high blocking voltages. This property together with that of a more rapid forming enables selenium rectifier elements according to the present invention to be employed for higher blocking voltages and makes them less sensitive to incidental overvoltages than elements which have not been treated in the aforesaid manner.

Besides with thorium or zirconium, a similar action is also obtained with the kindred metals hafnium and titanium.

As a modification of selenium rectifier elements, blocking layer photoelectric cells containing selenium may be regarded. These differ in construction from rectifier elements substantially only in that the counter-electrode is translucent or transparent. The invention is also applicable to the manufacture of such photoelectric cells.

I claim as my invention:

1. In the manufacture of selenium rectifier elements in which a selenium layer is applied onto a metallic base, such layer is converted into an electrically conducting state, and a metallic counter-electrode applied over such layer, the step of treating the converted layer before the counter-electrode is applied with a compound of at least one of the metals of the group consisting of zirconium, thorium, hafnium and titanium.

2. A method as claimed in claim 1 in which said metal compound is applied by vaporization or cathode sputtering.

3. A method as claimed in claim 1 in which said metal compound is applied in solution and the solvent is evaporated before the counter-electrode is applied.

4. A method as claimed in claim 3 in which the solvent is organic.

5. A process as claimed in claim 1 in which said metal compound has an easily decomposed acid component.

6. In a selenium rectifier having a base plate, an electrically conducting selenium layer thereon, and a metallic counter-electrode over said layer, said layer having been treated before application of the counter-electrode with a compound of at least one metal selected from the group consisting of zirconium, thorium, hafnium and titanium.

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