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METHOD OF MANUFACTURING RECTIFIER ELEMENTS

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The invention refers to a method of manufacturing rectifier elements, particularly those which can withstand a very high reverse voltage.

It is, therefore, the main object of the present invention to provide a method which will enable the rectifier element to withstand up to more than five times the normal reverse voltage.

It is very well known that in the manufacturing process of rectifier elements a base plate is covered with a rectifying layer of selenium, the latter converted into its metallic state, whereupon various known means are used to enable the rectifier elements to withstand higher reverse voltage by providing barrier layers between the selenium and the counter-electrode layer. Such means comprise the application of insulating lacquers or oxidizing agents to the metallic selenium surface. Finally, a counter-electrode layer is applied in order to finish the manufacturing process.

The object of the present invention is achieved by substituting the mentioned application of insulating lacquers or oxidizing agents to the metallic selenium surface by an electrolytic process to which the rectifier disc is subjected, after the selenium layer has been converted into its metallic state, in which process the rectifier disc is used as the cathode.

The purpose of the electrolytic process is the application of a barrier layer comprising a metal organic polyselenide and, preferably, a cadmium organic polyselenide or a tin organic polyselenide, respectively, depending on the use of cadmium or tin in the electrolyte or in the counter-electrode, or even in both. Yet any metal forming a basic plating solution can be used in the electrolytic process, the same metal which is to be plated being used as the anode.

In accordance with the present invention two modifications of the method can be used in order to achieve the insulating layer consisting of a cadmium or tin organic polyselenide.

According to the first modification, an aqueous solution containing an alkaline hydroxide or alkaline salt e. g. NaOH, KCl, ammonium hydroxide, or ammonium salts in addition to an organic agent, the nature of which is to be disclosed later, is used as the electrolyte in the electrolytic process. Some relatively inert material, preferably platinum, serves as the anode in this process. The applied current may vary from 2.5 ma. per cm.^{2} up to 50 ma. per cm.^{2} of selenium layer surface. The duration of the process varies from about 7½ seconds to about 150 seconds and is mainly inversely as the current applied in order to attain similar rectifying characteristics. After the electrolytic process is performed, the cathode, namely the selenium disc, is then dried either at room temperature or in an oven at a temperature below 100° C., preferably 60° C. Finally, preferably a cadmium alloy or a cadmium-tin alloy is sprayed on the disc as the counter-electrode and thereby a layer of an alkaline organic polyselenide has been formed on the surface of the selenium layer which compound is not very stable. Upon spraying the cadmium or cadmium-tin counter-electrode alloy on the disc the mentioned compound is transformed into a more stable cadmium organic polyselenide. It can be seen, therefore, that according to the thus described first method an alkaline organic polyselenide is formed first which, after providing the counter-electrode, is transformed into a cadmium organic polyselenide.

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According to the second modification which is to be considered as preferable, a cadmium, tin or any other metal as a lead anode capable of forming a basic plating solution is provided in the electrolytic process and a corresponding commercial cadmium plating solution

$$(CdO+NaOH+NaCN)$$

a commercial tin plating solution

$$(Na_2SnO_3+NaOH+NaC_2H_3O_2)$$

or any other basic plating solution which is, therefore, again an alkaline hydroxide or an alkaline salt in addition to an organic agent, is used as the electrolyte. As a result of this electrolytic process a layer of cadmium, tin or other metal organic polyselenide which is a stable compound will be formed on the surface of the selenium layer, immediately in one step upon application of the electrolytic process. Thus it can be seen that the layer of cadmium, tin or other metal organic polyselenide is here achieved as a result of the electrolytic process in one step even before providing the counter-electrode alloy, whereas according to the first mentioned method two steps are necessary, namely the electrolytic process and the forming of the counter-electrode layer.

Besides the above mentioned metals, namely cadmium, tin and lead, also silver, gold, zinc, copper, brass and others can be used as anode with the corresponding plating solution.

The concentration of the electrolyte may be as low as necessary to merely maintain the conductivity of the solution, say about .001 normal, whereas the maximum concentration to be used

will be at the saturation point at room temperature.

While there is a marked difference in results when the electrolyte concentration is varied, since the increase in both the forward and reverse resistances is proportional to the concentration of the electrolyte, it can be seen that the grade of concentration of the electrolyte provides some means to control the results to be achieved.

It has been stated before that the electrolyte in the first as well as in the second modification of the method comprises in addition to the aqueous solution an organic agent. Principally all organic agents which are soluble in water can be used as addition to the electrolyte. Therefore, alcohols, aldehydes, ketones, acids, phenols, and the like can be used or also more than one of the mentioned products at the same time. The concentration of the organic agents will be at least 5% and any higher concentration than the minimum value will yield high voltage rectifiers provided that the solution is still electrically conductive at said particular concentration.

Several examples are given which show the choice of materials and their concentration as preferable choice for different purposes in accordance with the mentioned modifications of the methods:

Example 1 (in accordance with the first modification)

Solution:
9 parts by vol. .006 normal NaOH in water
1 part by vol. C. P. acetone
Anode: Platinum
Cathode: Metallic selenium on nickel plated steel or on aluminum base plate
Current: 12½ ma. per cm.² of selenium surface
Time: 30 seconds

Example 2 (in accordance with the first modification)

Solution:
7 parts by vol. 1 normal KCl in water
3 parts by vol. methyl alcohol
Anode: Platinum
Cathode: Metallic selenium on nickel plated steel or on aluminum base plate
Current: 12½ ma. per cm.² of selenium surface
Time: 30 seconds

Example 3 (in accordance with the second modification)

Solution: 25 g. CdO dissolved per liter of 2.2 normal NaCN
Anode: Cadmium
Cathode: Metallic selenium on nickel plated base plate
Current: 6 ma. per cm.²
Time: 1 minute

Example 4 (in accordance with the second modification)

Solution:
5 parts by vol. 1.7 normal Na_2SnO_3 in water
5 parts by vol. 0.75 normal NaOH in water
1 part 1% by vol. H_2O_2 in water
5 parts by vol. 0.7 normal $NaC_2H_3O_2$
Anode: Tin
Cathode: Metallic selenium on nickel plated base plate
Current: 6 ma. per cm.² of selenium surface
Time: 1 minute

Example 5 (in accordance with the second modification)

Solution:
1 part by vol. 10 normal NaOH in water
1 part by vol. 0.4 normal $PbC_2H_3O_2.3H_2O$
Anode: Lead
Cathode: Metallic selenium on nickel plated base
Current: 6 ma. per cm.² of selenium surface
Time: 30 seconds

The two examples cited in accordance with the first mentioned method yield rectifier units of different electrical characteristics. Specifically, units subjected to an electrolytic process as given in Example 1 may be electroformed to withstand 60 volts in about five minutes. For a direct current output of 6 ma. per cm.² a voltage of more than 40 volts D. C. is maintained. The reverse leakage is very low, namely approximately .02 ma. ac per cm.².

Units subjected to the electrolytic process as given in Example 2 will withstand more than 100 volts A. C. in the reverse direction. The forward resistance will be relatively high and, therefore, it is not advisable to use such units for power rectification. However, these units may be used in such applications where high D. C. voltages must be maintained while no current is drawn from the power supply, e. g. in maintaining electrostatic fields.

In Example 1 where hydroxide has been used as the electrolyte the organic agent was 10% by volume whereas the hydroxide solution was 90% by volume. In Example 2 where a salt solution is used as the electrolyte only 70% by volume of the salt is used, whereas the organic agent rises to 30% by volume. However, if in Example 1 the organic concentration is reduced to 5% instead of 10, or in Example 2 to 20% instead of 30, still higher than normal voltages can be recognized.

The Examples 3 and 4 which are to be used in accordance with the second mentioned modification, will yield high voltage rectifiers which are suitable for low power operation. Changes in the concentration of the electrolyte will provide similar changes in the electrical characteristics of the discs produced in such a solution in the same manner as outlined before for the electrolytes in accordance with the first mentioned modification.

The counter-electrode alloy will preferably always contain cadmium, though in the case of using a cadmium anode and a cadmium plating solution in the electrolytic process a counter-electrode alloy can be used, which does not contain cadmium.

The currents used in both mentioned modifications can vary from 2½ ma. up to 50 ma. and the time within which the electrolytic process has to be performed is varied inversely as the current is used in attaining the same quality rectification and correspondingly the times varies from 150 seconds down to 7½ seconds. By increasing the time in which the process is performed or by increasing the current for even both high voltage discs with reduced power rectification efficiency will be attained.

While I have disclosed the principles of my invention in connection with several different embodiments, it will be understood that these embodiments are given by way of example only and not as limiting the scope of the invention as set forth in the objects and the appended claims.

What I claim is:

1. In a process for the manufacture of selenium rectifier elements wherein a base plate is provided with a coating of metallic selenium upon which an overlying counter-electrode is thereafter applied, the improvement that comprises, prior to application of the counter-electrode, making the selenium coated base plate the cathode during electrolysis of an alkaline aqueous electrolyte, the anode used in the electrolysis being a metal selected from the class consisting of tin and cadmium and the electrolyte comprising a solution for electroplating the metal of which the anode is formed and also including an organic substance selected from the class consisting of water soluble alcohols, water soluble aldehydes, water soluble ketones, water soluble organic acids, water soluble phenols.

2. The process as defined in claim 1 wherein the anode used in the electrolysis is tin.

3. The process as defined in claim 1 wherein the anode used in the electrolysis is cadmium.

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