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SELENIUM RECTIFIER AND METHOD OF ITS PRODUCTION

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FIG. 1

PERFORMANCE TESTS ON NICKEL MATRIX AND NICKEL CLAD SELENIUM RECTIFIER CELLS 1 1/2" CELLS									
TYPE	D.C. FORWARD IN MA. AT IV. OR IN VOLTS FOR 1000 MA.			PEAK REVERSE I IN MA. FOR 18V. R.M.S. APPLIED					
	LOW	HIGH	AVG.	LOW	HIGH	AVG.			
PAINTED MATRIX SINTERED AT 850°C SPRAYED MATRIX SINTERED AT 1000°C PAINTED MATRIX SINTERED AT 925°C SPRAYED MATRIX SINTERED AT 925°C	.98V	.90V	.93V	2.5	6	4.7			
	.97V	.90V	.94V	4	16	8.8			
	.90V	.85V	.88V	10	11	10.5			
	.87V	.87V	.87V	6.5	9	7.8			
CONTROL CELLS NICKEL CLAD CONTROL CELLS NICKEL CLAD	MILLIAMPERES FOR 1 VOLT								
	520	835	658	2	9.5	5.1			
	505	.95V	860	2	27	8.5			

FIG. 2



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1

This invention relates generally to methods of making asymmetrical devices and more particularly to methods for making selenium rectifiers having a nickel interface.

In order to reduce the adverse effects on the electrical characteristics of selenium rectifiers which would occur if the selenium were deposited directly on a metal backing of steel or a member of the iron group, it is customary to interpose some other element, for example nickel, or other metal selected from the iron group between the steel backing and the selenium, the nickel or other metals selected from the iron group are particularly advantageous since they generally do not form any chemical compounds with the selenium subsequently applied thereon as the semiconductor layer of the rectifier, and if such compounds would be formed, they occur as highly conductive selenides offering very small ohmic resistances in the current transfer direction so that the ohmic losses may be reduced to a low value.

It has been found that the physical properties of the surface of the nickel layer have a very important effect on the electrical characteristics of the finished product. In the prior art, this nickel layer has been applied to the steel backing by cladding plating or by electrolytic deposition. Since a surface having a certain degree of roughness is desirable it has been found necessary to produce such a surface on the nickel by some means such as etching or sand-blasting. This entails an extra operation in the manufacture of selenium rectifiers.

One of the objects of this invention is to simplify the method of making selenium rectifiers by forming in one step a nickel interface matrix having the desirable degree of roughness.

Another object of the invention is to produce a selenium rectifier having performance and electrical characteristics superior to those of selenium rectifiers made by other methods.

A further object is to produce a selenium rectifier that with a given applied voltage has a forward current approximately one and a half times as large as that of selenium rectifiers produced by other methods.

Another object is the improvement of methods of making selenium rectifiers generally.

Features of the invention comprise forming a nickel interface on a metallic backing member on which the selenium is to be deposited by spraying or painting a suspension of finely divided high purity nickel particles in a nitrocellulose solution on the metallic backing mem-

2

ber and heating the coated member for approximately fifteen minutes in a hydrogen atmosphere at a temperature between 850° C. and 1000° C. to drive off the temporary nitrocellulose binder and sinter the parts to the backing member.

The above-mentioned and other objects and features of the invention will be more fully understood and appreciated from the following detailed description of the method of manufacturing and the drawing in which:

Fig. 1 shows in the form of a chart the electrical characteristics of selenium rectifiers made by this invention as compared with selenium rectifiers using a cold rolled nickel interface, designated as "Control Cells Nickel Clad"; and

Fig. 2 shows the selenium rectifier wherein the metal backing element is designated as element 10, the nickel layer as element 11, the selenium layer as element 12, and the counter-electrode as element 13.

In general, the method comprises the following steps: First, the backing discs which may be of iron or steel are examined for grease or oil films which may be present thereon. If such films are found it is necessary to degrease the discs in some solution such as trichlorethylene or other suitable solvent. Also, if there is an appreciable amount of rust on the discs it may be found necessary to remove the rust by some method such as a pickling process in a one to one hydrochloric acid solution, for example. The disc is then ready for the application of the nickel matrix which may be applied either by painting or by spraying with a prepared suspension containing nickel, which will be described in more detail later. Following the application of the nickel coating by either painting or spraying, the discs are sintered in a hydrogen atmosphere at temperatures of from 850° C. to 1000° C. for approximately fifteen minutes.

It is to be noted that the degreasing of the discs and the pickling processes may be omitted if the discs are reasonably clean. This is a matter of some discretion and can be easily determined by visual observation after a few tests.

A typical nickel coating mixture may have the proportionate composition of 400 grams of a 325-mesh size nickel powder in 200 milliliters of a 2-per cent solution of nitrocellulose solution in amyl acetate. This is ground with riddled flint pebbles of the order of 1/4 inch diameter for about 100 hours at which time there is added 50 milliliters of amyl acetate and 50 milliliters of butyl cellosolve. The mixture is then rolled for approximately one hour and strained through a

standard 200-mesh sieve. Preferably using an automatic machine, the cleansed discs are then sprayed with the plasticized mixture so that approximately 3 milligrams of nickel per square centimeter of disc surface are deposited. The spraying conditions are adjusted to give a wet coating of uniform coverage.

The nickel coated discs are then placed in a furnace having a hydrogen atmosphere with the furnace temperature between 805° C. and 1000° C. This heat treatment is continued for approximately fifteen minutes during which time the nickel is sintered to the iron backing disc, thus producing a matrix-like finish of desired roughness. A selenium layer can then be applied to the nickel coating in any one of several well-known manners such as for example evaporating iodized selenium onto the coating.

After the selenium coating has been applied to the nickel matrix, a counter electrode is applied to said selenium coating. This counter-electrode may be applied in well-known manners and can be any one of a number of materials such as antimony, thallium, tin-cadmium-thallium alloy, tin-bismuth-cadmium alloy, or other suitable, well-known materials.

The superior electrical characteristic of selenium rectifiers produced by the method of this invention over selenium rectifiers produced by other methods is shown in the drawing wherein a selenium disc having a cold-rolled nickel interface has been chosen for comparison. It is to be noted that from .87 volt to .98 volt is required to pass 1000 milliamperes through a selenium rectifier made by the processes described herein whereas one volt applied across the selenium rectifier having a cold-rolled interface will only produce from 520 to 860 milliamperes.

It is to be understood that the above-described method of producing selenium rectifiers is but a preferred example of the same and that various changes can be made in materials, and heat treatment time and temperatures without departing from the scope and spirit of the invention.

What is claimed is:

1. The method of making a dry rectifier which comprises the steps of mixing nickel powder in a nitrocellulose solution, grinding said solution for approximately 100 hours, adding amyl acetate, adding butyl cellosolve, rolling for approximately one hour, straining through a sieve, applying the strained product to a metallic backing element, sintering said backing element at a temperature of from 850° C. to 1000° C. for approximately 15 minutes in a hydrogen atmosphere, applying a layer of selenium on the nickel coating, and applying a counter-electrode on said selenium layer.

2. The method of making a dry rectifier which comprises the mixing of 400 grams of nickel powder with 200 milliliters of nitrocellulose solution, grinding said mixture with riddled flint pebbles for approximately 100 hours, adding 50 milli-

liters of amyl acetate, adding 50 milliliters of butyl cellosolve, rolling the mixture for approximately one hour, then straining said mixture through a 200-mesh sieve, applying 3 to 6 milligrams of nickel from the strained suspension to each square centimeter of a backing element, sintering said coated backing element at a temperature of from 850° C. to 1000° C. in a hydrogen atmosphere for approximately 15 minutes, applying a layer of selenium on the nickel coating, and applying a counter-electrode on said selenium layer.

3. The method of making a dry rectifier which comprises mixing nickel powder in a nitrocellulose solution, grinding said suspension with riddled flint pebbles for approximately 100 hours, adding amyl acetate, adding butyl cellosolve, rolling the suspension for approximately one hour, applying from 3 to 6 milligrams of the nickel to each square centimeter of a backing element of a member of the iron group, wetting the coated backing elements with amyl acetate, sintering the dried coated backing elements in a hydrogen atmosphere at a temperature of from 850° C. to 1000° C. for about 15 minutes, evaporating in a vacuum a layer of selenium of the resultant nickel coating, and applying a counterelectrode on said selenium layer.

4. A dry rectifier comprising a base plate electrode, a coating of finely divided particles of a metal of the iron group sintered to said base plate electrode, a selenium layer overlying said metal coating, and a counter-electrode on said selenium layer.

5. A dry rectifier comprising a base plate electrode, a thin matrix coating of finely divided particles sintered to said base plate, said coating consisting essentially of from 3 to 6 milligrams of nickel per square centimeter, a selenium layer overlying said coating, and a counter-electrode on said selenium layer.

6. A dry rectifier comprising a ferrous base plate electrode, a thin matrix coating of finely divided nickel particles sintered to said base plate, a selenium layer overlying said nickel coating, and a counter-electrode on said selenium layer.

7. A dry rectifier comprising an iron base plate electrode, a uniformly thin matrix coating of finely divided nickel particles sintered to said base plate, said nickel coating consisting of from 3 to 6 milligrams of nickel per square centimeter, a selenium layer overlying said coating, and a counter-electrode on said selenium layer.

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