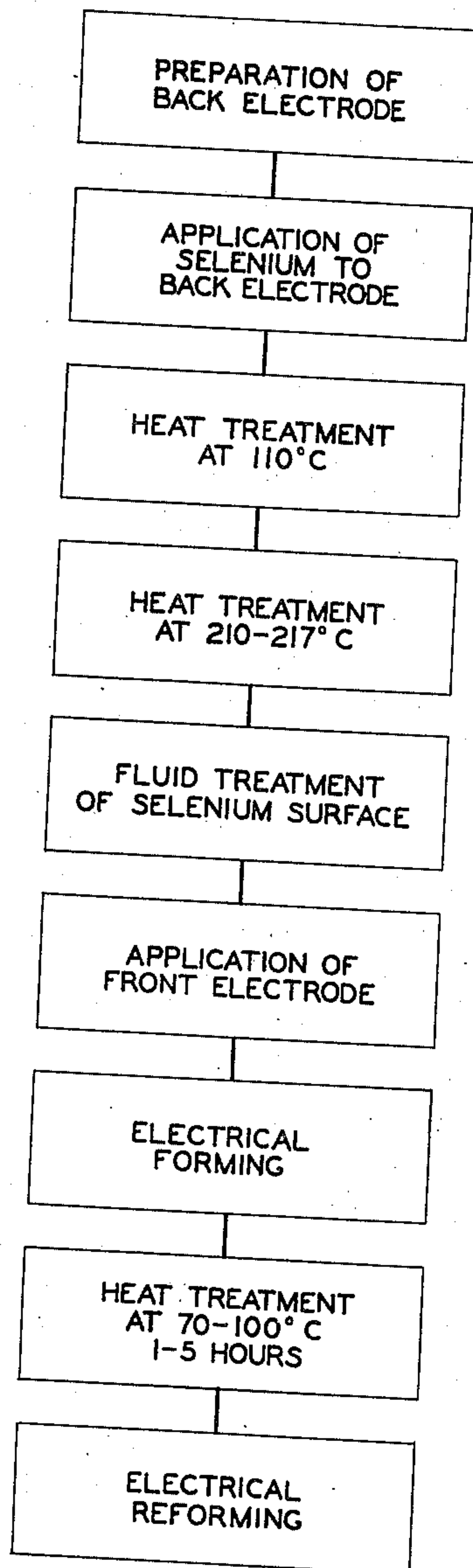


Feb. 19, 1946.

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METHOD OF MAKING DRY RECTIFIERS
Filed Oct. 24, 1942

2,395,259



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Patented Feb. 19, 1946

2,395,259

UNITED STATES PATENT OFFICE

2,395,259

METHOD OF MAKING DRY RECTIFIERS

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Application October 24, 1942, Serial No. 463,258

5 Claims. (Cl. 175—366)

This invention relates to so-called dry rectifiers and more particularly to selenium rectifiers and to methods of improving the rectification ratio of such rectifiers.

Selenium rectifier units may be made by applying a relatively thin layer of selenium to a suitable backing member. Discs of nickel, nickel-iron duplex, i. e., a layer each of nickel and iron rolled together, or some other material that will not react unfavorably with the selenium may be used for the backing member or electrode. The selenium may be applied to a suitably prepared surface of an electrode by melting a measured quantity of selenium powder on the electrode surface. This may be done by placing the electrode disc on a hot plate, applying the selenium powder and raising the temperature of the disc to about 300° C. When the selenium is melted, it 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 make 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 suitable heat treatment. The usual method of performing the heat treatment is divided into two stages. The first stage comprises heating the unit to about 110° C. while under mechanical pressure. At this temperature the selenium is somewhat softened and the pressure tends to make the selenium layer more uniform and to smooth its surface. This stage of the process may be carried out by stacking a plurality of discs on a mandrel with a smooth plate or disc in contact with each selenium surface. The plates in contact with the selenium may be made of mica or some smooth surface metal that will not react with the selenium. Pressure may be applied to the stack by various means, for example, a suitably calibrated spring may be employed. During this stage the selenium is partly converted to the crystalline state and its resistance is reduced appreciably.

The second stage of heat treatment is performed at a temperature slightly below the melting point (218° C.) of the selenium, e. g., between 210 and 217° C. After the heat treatment the surface of the selenium may be treated by exposing it for a short time to a vapor of selenium dioxide, one of the alkaline halides or other suitable fluid. This treatment is to improve the rectifier function characteristic, but may in some cases be omitted. The rectifier unit may then

be 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 rectifier 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 units in the high resistance or reverse direction. The "forming" current should be limited in order to avoid "burning out" of the unit. As the reverse resistance gradually increases during the forming, the voltage may be increased up to about 20 to 24 volts per unit. The term "forming" as used in this specification and the appended claims is intended to cover only the step of applying voltage in the reverse direction to an otherwise completed rectifier to increase the value of the rectification ratio by increasing the reverse resistance. This is believed to be in accordance with the usual nomenclature applied to the making of selenium rectifiers. Careful performance of the various steps of this process will produce a unit having a relatively good ratio of reverse to forward resistance.

An object of this invention is to increase the reverse resistance of a selenium rectifier unit without appreciably affecting the forward resistance to thereby increase the rectification ratio.

Another object of the invention is to make selenium rectifier units more stable, that is, prevent appreciable variation of their resistance characteristics after completion.

A feature of this invention resides in subjecting the formed rectifier units to an additional heat treatment at from 70 to 100° C. for from 1 to 5 hours and then reforming the units.

The invention and the foregoing and other objects and features thereof 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 the single figure is a schematic representation of the improved process of this invention.

After the selenium rectifier units are made and formed by a suitable process such as the one previously described, the additional heat treatment is applied. The formed units are heated at from 70 to 100° C. for from 1 to 5 hours. This may be done by distributing a plu-

rality of units on a suitable carrier such as a metal plate and inserting them in an oven, which has been brought up to the required temperature. The temperature is maintained at the value chosen, for the whole time of treatment and then the units are removed and allowed to cool. Since the effect of this treatment appears to be a function of both time and temperature, a general rule is that a longer time is employed for the lower temperatures and a shorter time for the higher temperatures. Improvement, that is, increased, in the reverse resistance may be obtained over the whole of the given temperature range for time periods up to and including 5 hours. At the higher temperatures, i. e., 95° C. and above, if the time is extended beyond about 3 hours, the forward resistance may increase so much that there is no net improvement in rectification ratio. In the temperature range from 75 to 85° C., the increase in forward resistance is relatively slight and this coupled with a considerable increase in reverse resistance gives an improved rectification ratio. For these lower temperatures the improvement is greater if the time is extended beyond 3 hours up to and including 5 hours. A full 5-hour treatment at 75° C. appears to have practically no effect on the forward resistance while increasing the reverse resistance considerably. At temperatures above about 95° C., care must be taken to avoid reaction between the selenium and the front contact. This is particularly true where the front contact is an adherent coating of low melting point metal or alloy. For example, with a tin-bismuth-cadmium alloy, adherent contact, which melts at about 102° C., the treatment could be carried up to 100° C. without melting the contact but there is danger of reaction between the contact alloy and the selenium when the melting point is approached.

After this additional heat treatment, the rectifier units are again subjected to the electrical forming treatment, by passing current through them in the reverse direction at controlled voltages. A reforming for about 20 minutes at about 20 volts in the reverse direction has been found to give satisfactory results.

As an example of the results obtainable by this method, a treatment at from 90 to 95° C. for 1 3/4 hours followed by reforming at about 20 volts increased the rectification ratio in the order of 90 per cent with a reduction of less than 10 per cent in the value of forward current. Treatment at 175° C. for about 5 hours with a subsequent 20-volt reforming increased the rectification ratio by about 70 per cent with no noticeable reduction in forward current. It is thus seen that this process may be performed to produce a very large increase in rectification ratio with very little loss in forward current or a somewhat smaller but nevertheless marked increase in rectification ratio with no loss of forward current.

In addition to the effect on the absolute values of the forward and reverse resistances, it has been found that selenium rectifiers given a heat treatment and then reformed in accordance with this invention are more stable than units prepared in the ordinary manner. That is, there appears to be less drift with time for both forward and reverse characteristics.

Although this invention has been disclosed by means of illustrative embodiments thereof, it is not intended that it be limited thereby, but by the scope of the appended claims only.

What is claimed is:

1. The method of making a selenium rectifier unit with a high reverse resistance and large rectification ratio that comprises applying amorphous selenium to a suitable electrode, heat treating to convert the amorphous selenium to crystalline selenium, providing the unit with an outer contact, forming the unit by application thereto of a voltage in the reverse direction, then further heat treating the unit at a temperature of from 70 to 100° C. for a period of from 1 to 5 hours, and then reforming the unit by further application thereto of a voltage in the reverse direction.

2. The method of making a selenium rectifier unit having a high reverse resistance and large rectification ratio, that comprises applying amorphous selenium to a suitable electrode, heat treating to convert the amorphous selenium to crystalline selenium, providing the unit with an outer contact, forming the unit by application thereto of a voltage in the reverse direction, then further heat treating the unit at a temperature of from 90 to 95° C. for a period of from 1 to 3 hours, and then reforming the unit by further application thereto of a voltage in the reverse direction.

3. The method of making a selenium rectifier unit having a high reverse resistance and large rectification ratio that comprises applying amorphous selenium to a suitable electrode, heat treating to convert the amorphous selenium to crystalline selenium, providing the unit with an outer contact, forming the unit by application thereto of a voltage in the reverse direction, then further heat treating the unit at a temperature of about 75° C. for a period of about 5 hours and then reforming the unit by further application thereto of a voltage in the reverse direction.

4. The method of improving the rectification ratio of selenium rectifier units by increasing the reverse resistance thereof without appreciably changing the forward resistance, that comprises subjecting completely formed rectifier units to a temperature of from 70 to 100° C. for a period of from 1 to 5 hours, and then reforming the units by further application thereto of a voltage in the reverse direction, the time period within the indicated range being short for the higher temperatures and long for the lower temperatures.

5. The method of making a selenium rectifier unit with a high reverse resistance and large rectification ratio that comprises applying amorphous selenium to a suitable electrode, heat treating to convert the amorphous selenium to crystalline selenium, providing the unit with an outer contact, forming the unit by application thereto of a voltage in the reverse direction, then further heat treating the unit at approximately 95° C. for a period of about 1 3/4 hours, and then reforming the unit by passing current therethrough in the reverse direction under a pressure of about 20 volts for about 20 minutes.

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