July 28, 1942. P. H. DOWLING 2,291,592

ELECTRICAL RECTIFIER

Filed Aug. 10, 1940

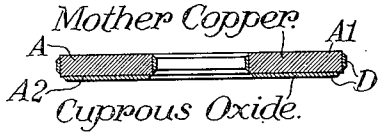

Fig. 1.

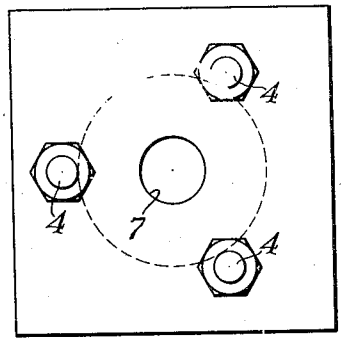

Fig. 4.

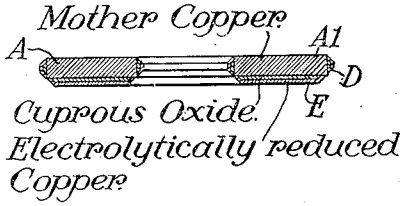

Fig. 2.

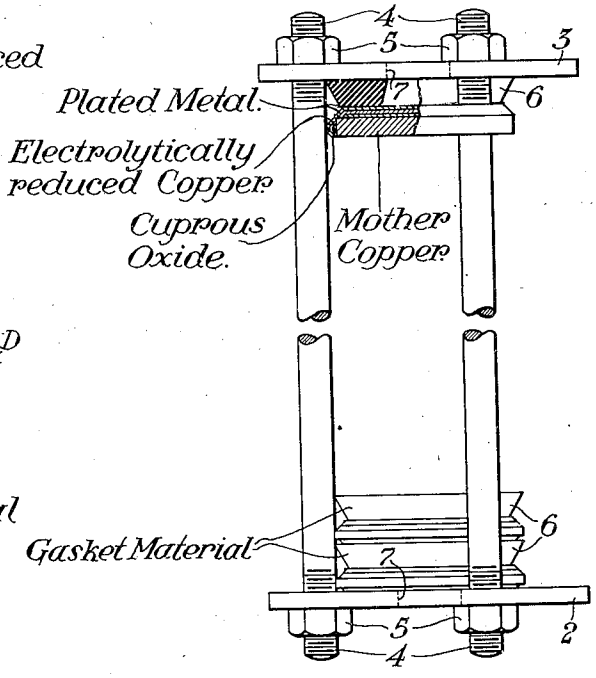

Fig. 5.

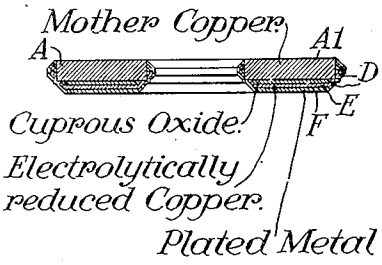

Fig. 3.

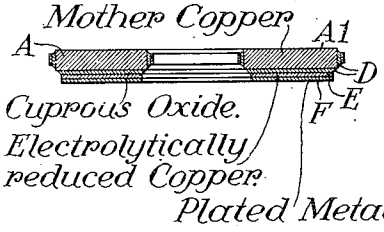

Fig. 6.

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2,291,592

ELECTRICAL RECTIFIER

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Application August 10, 1940, Serial No. 352,150

13 Claims. (Cl. 175—366)

My invention relates to electrical rectifiers, and particularly to electrical rectifiers of the well-known copper oxide variety. More particularly, my present invention relates to copper oxide rectifiers in which both electrolytically reduced and electroplated metal is employed to facilitate making contact with the cuprous oxide layer.

In rectifiers of the type described it is necessary that either of the contact metals should not make contact with the mother copper at any point because if either does, the elements will be short circuited. The only place that the contact metals are likely to make contact with the mother copper is at the edges of the elements, and heretofore in manufacturing the rectifiers it has been customary to prevent both the electrolytically reduced and the electroplated metal from making contact with the mother copper at the edges of the elements either by coating the edges of the elements with a non-conducting paint, lacquer, or the like, or by encasing the elements in rubber masks so that only the portions of the elements with which it is desired to make contact are exposed to the action of the electrolyte.

This method of manufacturing the elements is entirely satisfactory for many types of elements, but for some sizes of the elements it is somewhat more cumbersome and expensive than is to be desired.

One object of my present invention is to provide an improved method for manufacturing copper oxide rectifier elements of the type described, which method will permit the smaller sizes of elements to be manufactured more satisfactorily and more cheaply than has heretofore been possible. It should be understood, however, that my invention is not limited to use with the smaller sizes of elements.

According to my invention, the elements after being oxidized and treated to remove the excess oxide in the usual and well-known manner are subjected without the use of masking means of any kind to suitable reducing and plating steps which cause both the reduced and the plated metal to make contact with the desired portions of the elements, and also with the mother copper at the edges of the elements, whereupon the elements are then subjected to a chemical treatment which removes all of those portions of the contact metals which make contact with the edges of the mother copper.

The process disclosed herein is an improvement upon that described and claimed in my copending application for Letters Patent of the United States, Serial No. 291,052, filed on August 19, 1939, for Electrical rectifiers.

I shall describe two processes of rectifier manufacture embodying my invention, and shall then point out the novel features thereof in claims.

In the accompanying drawing, Fig. 1 is a vertical sectional view showing a rectifier element ready to be treated in accordance with the process embodying my invention. Figs. 2 and 3 are views similar to Fig. 1 showing the element as it appears during different steps in the process of manufacture embodying my invention. Figs. 4 and 5 are top plan and side elevational views, respectively, showing a clamp employed in one step of the process embodying my invention. Fig. 6 is a view similar to Figs. 1, 2 and 3 showing a completed rectifier element manufactured in accordance with my invention.

Similar reference characters refer to similar parts in each of the several views.

In the practice of my invention, a copper blank, usually in the form of a copper washer, is first oxidized on one side and is then treated to remove the excess oxide formed during the oxidizing process. This portion of the process is well known, and may, for example, be carried out in accordance with the teachings of my prior Patent No. 2,094,642, granted to me on October 5, 1937, for the Manufacture of electrical rectifiers. Following this portion of the process, the rectifier element will appear as shown in Fig. 1 in which A designates the mother copper and D designates the layer of cuprous oxide remaining on the inner and outer edges and on one face A2 of the element, it being noted that the face A1 is substantially free from oxide, and that there is a clear cut discontinuity between the mother copper and the cuprous oxide at both the inside and outside edges of the element.

The element is next treated to reduce the outer surface of the cuprous oxide coating to metallic copper. This reduction may be accomplished in a variety of ways, but I prefer to accomplish it by immersing the element in a dilute solution of ammonium hydroxide and passing a current through this bath to the element from an insoluble anode such as carbon or platinum. The ammonium hydroxide solution may, for example, consist of .2% by volume of NH_4OH in distilled water at room temperature, and with a current density of about 12 amperes per square foot, the desired reduction can be accomplished in a period of from 3 to 8 minutes. During this reduction all parts of the element are exposed to the

reducing solution, and this step differs from that described in my prior application, Serial No. 291,052, filed on October 19, 1939, for Electrical rectifiers in this respect since in my prior application the inside and outside edges of the element were masked to prevent a narrow band of the oxide adjacent the edges of the element from becoming reduced. The fact that it is unnecessary to mask the edges of the element in accordance with the teachings of my present process enables this step to be performed more speedily and hence more cheaply than when a mask is used. Upon the completion of this step the element will appear as shown in Fig. 2, from which it will be noted that the outer surface of the cuprous oxide layer is covered by a layer of electrolytically reduced copper. It will also be noted that this reduced layer extends to the mother copper at the edges of the element, and hence short circuits the element. The relative thicknesses of the cuprous oxide and reduced copper layers have been exaggerated somewhat in the drawing for the sake of clearness.

Following the reduction of the outer surface of the element to metallic copper, the reduced surface is plated with another metal to improve the aging characteristics of the element. One metal which is suitable for this purpose is nickel, and this plating may be accomplished by making the element the cathode in a standard nickel plating solution and passing a current through the solution to the element. One well-known nickel plating solution which may be used may, for example, comprise $NlSO_4.7H_2O$, 27 ounces per gallon; boric acid, 6 ounces per gallon; $NiCl_2.6H_2O$, 4 ounces per gallon. With this solution maintained at a pH value of between 5 and 5.2 an excellent coating of nickel will be obtained with a current density of about 12 amperes per square foot maintained for about 3 minutes. During this plating, all portions of the element are exposed to the action of the electrolyte, but the element is turned with the reduced copper surface facing the nickel electrode so that a substantially uniform layer of nickel is formed on the front of the element, but that very little nickel is deposited on the back of the element. This step differs from the corresponding step disclosed in my prior application, Serial No. 291,052, referred to hereinbefore only by the fact that no mask is used during this step. The fact that no mask is used, however, decreases handling costs, and is of considerable advantage for this reason.

Following this step, the element will appear as shown in Fig. 3, from which it will be noted that all of the reduced copper layer, as well as the edges of the mother copper, are now covered with nickel. The fact that the contact metals are in contact with the mother copper at the edges of the element causes the element to be short circuited, and before the element can be used for its intended purpose it is necessary to remove a sufficient amount of both the reduced copper and the plated metal at the edges of the element to form a clear cut discontinuity between the mother copper and both the reduced copper and plated metal layers.

According to my present invention, I accomplish this result by chemical means, as follows: A number of the elements are stacked alternately between masking discs of rubber or other gasket material of such size and shape that the edges of the elements are left exposed, but that a central annular area of the nickel layer is covered by the discs, and the elements are then subjected to a reagent which will dissolve the contact metals from the unmasked portions of the elements without otherwise impairing the electrical characteristics of the elements.

To facilitate stacking the elements a clamp such as shown in Figs. 4 and 5 may be conveniently employed. Referring to Figs. 4 and 5, this clamp comprises two end plates 2 and 3 secured together in parallel spaced relation by means of three or more rods 4 passing through clearance holes in the plates and threaded at their ends into nuts 5. The nuts 5 associated with one plate may, if desired, be secured thereto to facilitate handling, but the nuts associated with the other plate must, of course, be separate from the plate to enable assembly and disassembly of the parts. All parts of the clamp must be made of a material which is unaffected by the reagent used. When the plated metal is nickel, this reagent may, for example, comprise nitric acid, in which case the parts of the clamp may be made of stainless steel or stainless iron.

The masking discs may be shaped similar to the discs 6 shown in Fig. 5, which discs it will be noted are frusto-conical in cross section, the one base having outside and inside diameters which are the same as those of the unplated side of the rectifier elements and the other base having outside and inside diameters which are somewhat smaller and larger, respectively, than the outside and inside diameters of the elements. With the discs constructed in this manner, it will be seen that the discs completely cover the unplated faces of the elements, but only cover a central annular area of the plated faces of the elements.

The rods 4 are preferably so spaced that they will automatically position both the elements and the masking discs. For elements of the type shown which are in the form of washers, the end plates 2 and 3 are provided with holes 7 which align with the holes in the elements to permit the dissolving reagent to reach the inside edges of the elements.

If the elements are not in the form of washers, the central holes in the masking discs, as well as the holes in the end plates will, of course, be unnecessary and can be omitted.

The concentration of the nitric acid solution is not critical, but a solution containing more than 50% by volume of nitric acid in water should not be used and a solution containing much less than 35% by volume will leave undissolved finely divided copper which is troublesome to remove.

The elements may be immersed in the nitric acid for a time which is somewhat longer than necessary to remove the unwanted metal. This is particularly true with nitric acid as the dissolving reagent since this acid has beneficial effects in cleaning up the edges of the cuprous oxide at the junction with the mother metal, as is well known.

Upon the removal of the elements from the nitric acid bath they are washed and dried, whereupon they will appear as shown in Fig. 6, from which it will be seen that a portion of the mother copper is now exposed at both the outside and inside edges of the elements.

As a modification of the above described process, the elements immediately after they are subjected to the oxidizing treatment and before the excess cupric oxide is removed may be subjected to the reducing and plating steps described hereinbefore, and may then be subjected to the action of dilute nitric acid in the manner also described

hereinbefore to remove the excess nickel. In this event, after the unwanted metal has been removed, the rectifier elements will preferably be further treated by first subjecting them to the action of a solution consisting of approximately .2% by volume of sulphuric acid and .1% by volume of hydrochloric acid in distilled water, and then subjecting them to the action of concentrated nitric acid, as set forth in my prior Patent No. 2,094,642, granted on October 5, 1937, for the Manufacture of electrical rectifiers. The purpose of these last two mentioned steps is to clean up the edges of the cuprous oxide to cause the rectifier elements to have better reverse current characteristics.

Although I have herein shown and described only two processes of rectifier manufacture embodying my invention, it is understood that various changes and modifications may be made therein within the scope of the appended claims without departing from the spirit and scope of my invention.

Having thus described my invention, what I claim is:

1. The process for making contact with the copper oxide layer of a copper oxide rectifier element which consists in reducing the outer surface of the copper oxide layer to metallic copper, plating the reduced surface with another metal by subjecting the entire element to the action of the plating solution, whereby the element becomes short circuited, and then chemically removing that portion of the contact metals which causes the element to be short circuited.

2. The process for preparing an electrical rectifier which consists in oxidizing a copper blank to form a layer of cuprous oxide thereon, electrolytically reducing the outer surface of said oxide layer to metallic copper to make electrical contact therewith, plating another metal onto said element by immersing the element in an electrolyte and passing a current through said electrolyte to said element in such manner that a portion of said other metal makes contact with both the reduced copper and the mother copper, and then dissolving those portions of the contact metals which make contact with the mother copper by means of a reagent which is a solvent for such metals.

3. The process for preparing a copper oxide rectifier element which consists in plating onto the element a layer of nickel which short circuits the element, and then dissolving a sufficient amount of the nickel to remove the short circuit.

4. The process for preparing a copper oxide rectifier element which consists in electrolytically depositing onto the element a layer of nickel a part of which makes contact with the oxide and another part with the mother copper, and chemically dissolving that part of the nickel layer which makes contact with the mother copper.

5. The process for preparing a copper oxide rectifier element which consists in oxidizing a copper blank to form an inner layer of cuprous oxide and an outer layer of cupric oxide, chemically treating the element to remove the cupric oxide layer and to form a clear cut discontinuity between the mother copper and the cuprous oxide at the edges of the element, electrolytically reducing the outer surface of the oxide layer to metallic copper, electrolytically depositing onto the element a substantially uniform layer of nickel a part of which makes contact with the reduced copper and another part of which makes contact with the mother copper at the edges of the element, and then dissolving in nitric acid those parts of the reduced copper and plated nickel layers which make contact with the mother copper.

6. The process for preparing a copper oxide rectifier element which consists in oxidizing a copper blank to form an inner layer of cuprous oxide and an outer layer of cupric oxide, chemically treating the element to remove the cupric oxide layer and to form a clear cut discontinuity between the mother copper and the cuprous oxide at the edges of the element, electrolytically reducing the outer surface of the oxide layer to metallic copper, electrolytically depositing onto the element a substantially uniform layer of nickel a part of which makes contact with the reduced copper and another part of which makes contact with the mother copper at the edges of the element, masking the central portion of the nickel layer, and dissolving the unmasked portion as well as any underlying reduced copper.

7. The process of preparing a copper oxide rectifier element which consists in electrolytically depositing onto the element a layer of nickel a part of which makes contact with the oxide and another part of which makes contact with the mother copper, and then dissolving that part which makes contact with the mother copper in a solution of nitric acid consisting of approximately 35 to 50% by volume of concentrated nitric acid in water.

8. The process of preparing a copper oxide rectifier element which consists in electrolytically depositing onto the element a layer of nickel a part of which makes contact with the oxide and another part of which makes contact with the mother copper, and then dissolving that part which makes contact with the mother copper in a solution of nitric acid consisting of approximately 35% by volume of concentrated nitric acid in water.

9. The process for making contact with the oxide layer of a copper oxide rectifier element which consists in electrolytically reducing the outer surface of the oxide layer to metallic copper and plating onto the reduced surface a layer of nickel which contacts the mother copper at the edges of the element and thereby short circuits the element, and then dissolving from the edges of the element sufficient metal to remove the short circuit and to restore the element to its full rectifying efficiency.

10. The process for making contact with the oxide layer of a copper oxide rectifier element which consists in electrolytically reducing the outer surface of the oxide layer to metallic copper and plating onto the reduced surface a layer of nickel which contacts the mother copper at the edges of the element and thereby short circuits the element, masking all of the element but the edges, and then subjecting the element to the action of nitric acid to dissolve any contact metal which is present on the unmasked portions.

11. The process for making contact with the oxide layer of a copper oxide rectifier element which consists in successively subjecting the element while unmasked to the action of a solution for electrolytically reducing the outer surface of the oxide layer to metallic copper and to the action of a solution for plating a layer of nickel onto the reduced copper layer, whereby a portion of the resulting layers makes contact with the mother copper at the edges of the element, masking all but the edges of the element, and then

immersing the element in a dilute solution of nitric acid for a sufficient length of time to dissolve that portion of the contact layers not protected by the mask.

12. The process of preparing a copper oxide rectifier element which consists in oxidizing a copper blank to form an inner layer of cuprous oxide and an outer layer of cupric oxide thereon, electrolytically reducing the cupric oxide layer to metallic copper, plating the reduced copper layer with nickel, masking all but the edges of the element and subjecting it to the action of dilute nitric acid to dissolve the nickel and reduced copper from the edges of the element, subjecting the element to the action of a dilute solution of sulphuric and hydrochloric acid, and then subjecting said element to the action of a concentrated solution of nitric acid.

13. The process for preparing a copper oxide rectifier element which consists in oxidizing a copper blank to form an inner layer of cuprous oxide and an outer layer of cupric oxide, chemically treating the element to remove the cupric oxide layer and to form a clear cut discontinuity between the mother copper and the cuprous oxide at the edges of the element, electrolytically reducing the outer surface of the cuprous oxide layer to copper which contacts the mother copper at said discontinuity between the mother copper and the cuprous oxide, and then chemically dissolving that portion of the reduced copper which is in contact with the mother copper.

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