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P. H. DOWLING ET AL

2,197,632

ELECTRICAL RECTIFIER

Filed June 15, 1938

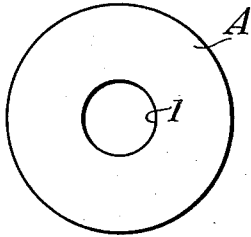


Fig. 1.

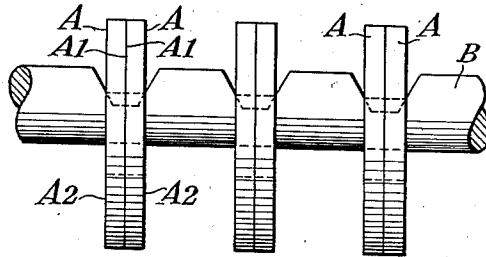


Fig. 2.

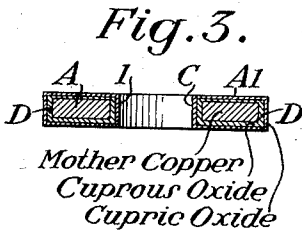


Fig. 3.

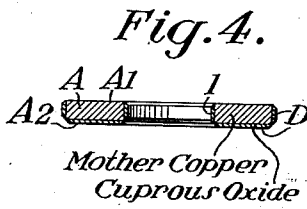


Fig. 4.

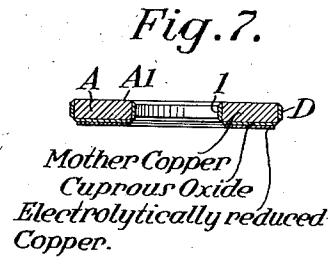


Fig. 7.

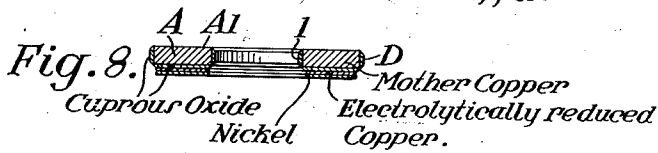


Fig. 8.

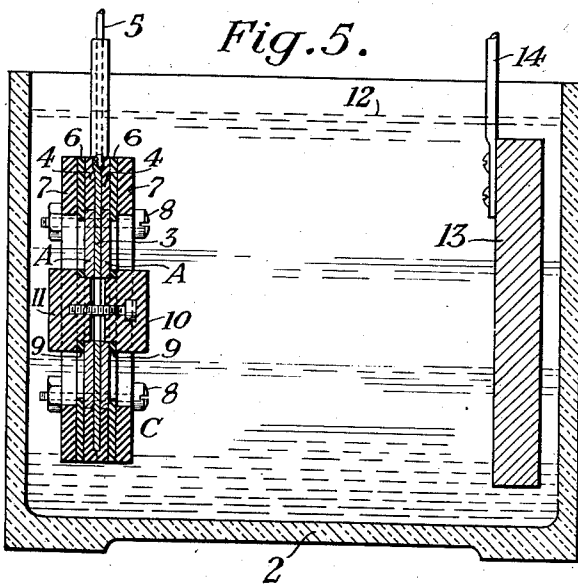


Fig. 5.

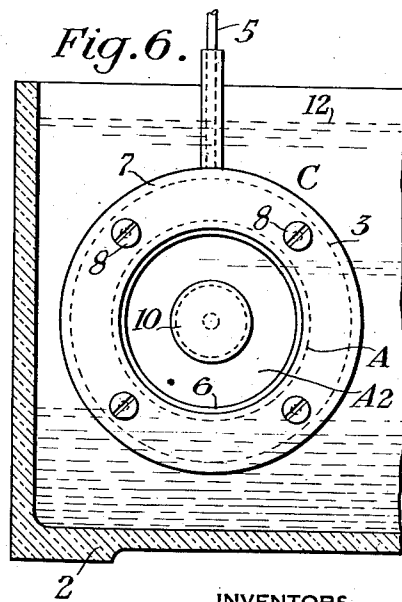


Fig. 6.

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2,197,632

ELECTRICAL RECTIFIER

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Application June 15, 1938, Serial No. 213,876

9 Claims. (Cl. 175—366)

Our invention relates to electrical rectifiers, and particularly to electrical rectifiers of the well-known copper oxide variety.

One object of our invention is to provide a copper oxide rectifier in which good electrical contact is obtained between the oxide surface and an adherent metal such for example as nickel.

Another object of our invention is to provide a process for depositing a metal such as nickel onto the oxide surface of a copper oxide rectifier in a manner which will not impair its rectifying properties and which will insure good electrical and mechanical contact between the metal and the copper oxide surface.

Other objects and characteristic features of our invention will appear as the description proceeds.

We shall describe several forms of rectifiers embodying our invention and several processes for manufacturing said rectifiers, and shall then point out the novel features thereof in claims.

In the accompanying drawing, Fig. 1 is a view showing in elevation one form of blank ready to be prepared as a rectifier element in accordance with one process of manufacture embodying our invention. Fig. 2 is a view showing a number of blanks assembled on a support as they appear during one step in the process of manufacture. Fig. 3 is a vertical sectional view showing, in an exaggerated form, a rectifier element as it appears in another step in the process of manufacture embodying our invention. Fig. 4 is a view showing a rectifier element as it appears in still another step in the process of manufacture embodying our invention. Fig. 5 is a longitudinal sectional view of an electrolytic bath utilized in the process of manufacture embodying our invention. Fig. 6 is a side view of a masking device utilized in connection with the bath shown in Fig. 5 for a purpose which will be made clear in the following specification. Fig. 7 is a vertical sectional view showing a rectifier element as it appears in a further step in the process of manufacture embodying our invention. Fig. 8 is a vertical sectional view similar to Figs. 3, 4 and 7 showing a completed rectifier element constructed in accordance with our invention.

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

Referring to the drawing, the reference character A designates a blank of suitable material such as copper. As here shown, this blank is of circular configuration, and is provided with a central aperture *f*, although this particular form

is not essential to our invention. A number of these blanks are assembled on a suitable support B in pairs in the manner shown in Fig. 2, so that the blanks of each pair have their adjacent faces A1 in contact, and the blanks are then subjected to an oxidizing process, such for example, as the application of heat in an oxidizing atmosphere to form an oxide coating on the blanks.

The oxidizing process is continued until a sufficient deposit of oxide is formed over the exposed surfaces of the blanks. Each blank will then appear as shown in Fig. 3 from which it will be seen that blank A is now covered with an inner coating D of cuprous or red oxide of copper and a thin outer coating C of cupric or black oxide of copper. It will also be seen from an inspection of Fig. 3 that the flat face of the blank which is exposed during the oxidizing process, that is to say, the lower face has a much heavier oxide coating than the upper face.

After the oxidation is completed, the elements are cooled in any suitable manner as by quenching them in water, and the elements are then treated to remove the cupric oxide layer from the entire surface of the blank, and to remove the cuprous oxide coating from only one face A1 of the blank. This treatment may take a variety of forms, but will preferably consist in subjecting the blanks to a solution consisting of 2 per cent by volume of sulphuric acid and .1 per cent by volume of hydrochloric acid in water. The temperature at which the solution is used is not critical, but the desired action of the solution is materially speeded up if the solution is hot, preferably at a temperature of 80° to 100° centigrade. The elements are preferably immersed in the solution for a time interval which is approximately twice as long as is required to remove the cupric oxide. After the elements are immersed in the solution for the desired period of time, the elements are then removed from the solution, washed in water, and thoroughly dried.

The elements are next preferably immersed for a short period of time (of the order of one to three seconds) in concentrated nitric acid, and are then thoroughly rinsed in water to remove all traces of the acid. To insure that no impurities are left on the elements from the water, the final rinse water should be distilled water unless the available water is known to be free from injurious impurities. The immersion in the nitric acid removes any loose or finely divided copper left on the blanks by the treatment

of the sulphuric and hydrochloric acid solution and insures that the copper oxide surface will be sufficiently clean for the next step which should preferably be performed before the elements have had any chance to accumulate any foreign substances either from the atmosphere or otherwise. The elements following this step will appear as illustrated in Fig. 4 in which D designates the coating of cuprous oxide remaining on the inner and outer edges of the blank and on one face A2 of the blank.

The portion of the process of manufacture of the rectifier elements thus far described is well-known, and for a further description of this portion of the process reference may be had to Letters Patent of the United States No. 2,094,642, granted October 5, 1937, to Philip H. Dowling, for the Manufacture of electrical rectifiers.

In accordance with our present invention, the elements are next treated to reduce the outer surface of the cuprous oxide coating of the blanks to metallic copper. This may be done in a variety of ways, but it is essential that the means employed for reducing the copper should not impair the rectifying properties of the elements, and it is also essential that the resultant copper coating should adhere firmly to the oxide coating and should make good electrical connection with it. It is further essential that the surface of the oxide at the copper-cuprous oxide junctions should not be reduced because if it were reduced the elements would become short circuited and would therefore be rendered useless for their intended purpose.

We have found that the desired reduction can be accomplished electrolytically by immersing the elements as the cathode in a suitable electrolyte through which a current is passed from an insoluble anode such as platinum or carbon, and in Figs. 5 and 6 we have shown a pair of elements A immersed as the cathode in an electrolytic bath 12 contained in a tank 2, the elements being mounted in a device C which serves both as a means for making electrical contact with the mother copper of the elements, and also as a means for masking the outside and inside edges of the elements to prevent the copper oxide from being reduced adjacent the edges where it joins the mother metal. The device C may assume a variety of forms and, as here shown, comprises a metal washer 3, such for example as brass cemented, as by a latex compound, between two rubber washers 4, and connected to a terminal wire 5. The rubber washers 4 have substantially the same thicknesses as the elements A following the previously described acid treatment, and substantially the same inside diameters as the outside diameters of the elements, and the elements are disposed within the openings in these washers with their faces, from which the oxide has been removed, in contact with the metal washer 3. The outside edges of the elements are masked by means of a pair of rubber washers 6 having inside diameters that are slightly smaller than the outside diameters of the elements, and which washers are clamped against the outer edges of the oxidized faces of the elements in concentric relation thereto by means of insulating clamping washers 7 and bolts 8, whereby portions of the washers 6 overlap the oxidized faces of the elements adjacent their outer edges and serve to substantially seal the oxide surfaces against the action of the electrolyte for a small annular area inside of the adjacent copper-cuprous oxide junction. The inside edges of the elements are

masked by means of a pair of rubber washers 9 having outside diameters which are slightly larger than the diameters of the holes in the elements, and which washers are clamped against the inside edges of the elements in concentric relation to the elements by means of a pair of insulating clamping members 10 and 11 in such manner as to substantially seal the copper oxide surfaces of the elements against the action of the electrolyte for a small annular area adjacent the inner copper-cuprous oxide junction.

The anode as shown in Fig. 5 consists of a graphite electrode 13, to which external connections are made by a conductor 14. The electrolyte 12 may comprise dilute sulphuric acid, distilled water saturated with carbon dioxide, some tap waters, or any other electrolyte in which electrolytic reduction can be accomplished, and which does not have any injurious chemical effect on the rectifying characteristics of the elements. We prefer, however, to use sulphuric acid in distilled water made up to a concentration of about .35 gram per liter. The concentration should not exceed 17 grams of sulphuric acid per liter and concentrations below .35 gram materially slow up the process. If the concentration becomes too great, the reduced copper does not have good adhering qualities, and the elements tend to have a high resistance in the forward direction. To accomplish the reduction, current is, of course, passed from the anode to the elements, and we have found that excellent results are obtained at a current density of the order of 12 amperes per square foot maintained for about three minutes, preferably with mechanical agitation of the bath, the reduced copper under these conditions being bright, fine grained, extremely adherent, and disposed as a continuous film over the entire exposed oxide faces of the elements. The amount of reduction which can be used before the rectifying properties of the elements become impaired depends on the original thickness of the oxide, and if the reduction is continued for too long a time, there is a tendency for the reduced copper to penetrate the oxide a sufficient amount to reach the mother copper, which condition may result in short circuiting the rectifier elements. As the amount of reduction increases, the forward resistance of the elements decreases. The exact reasons for this decrease are very difficult to determine, but this decrease would appear to be due to one or more of the following: (1) A decrease in the resistance offered by the oxide resulting from the decreased thickness of the oxide. (2) A decrease in the resistance between the oxide and the copper layer formed by the reduction resulting from the fact that as the amount of the reduction is increased the reduced copper penetrates more deeply into the interstices between crystals, thereby providing a contact area between the oxide and the copper layer which may have many times the plane surface area of the oxide layer. (3) A decrease in the resistance per unit area of the contact between the oxide and the copper formed by the reduction.

Upon removing the elements from the electrolytic reduction bath, the elements are thoroughly rinsed in several rinse waters, the last rinse water preferably being distilled water, and the elements are then subjected to a vigorous blast of compressed air. The air blast appears to have the effect of blowing out some of the gas and liquid

which collects in the pores of the reduced copper, and seems to be helpful in preparing the elements for the next step which we shall now describe.

This step consists in depositing electrolytically on the reduced copper layer a layer of nickel. To accomplish this step the elements while still mounted in the support C are made the cathode in a nickel plating solution in the same manner that they are made the cathode in the acid bath during the preceding step. A standard nickel plating solution may be used, which may for example, have the following composition.

	Ounces per gallon	
Nickel sulphate.....	8	
Ammonium chloride.....	1	
Boric acid.....	1	
Sodium chloride.....	½	

The current density during this step depends upon the plating solution used and the pH value of that solution, and with the solution mentioned above mechanically agitated and maintained at a pH value of about 5.8, excellent results are obtained with a current density of about 18 amperes per square foot continued for about two minutes at room temperature. If the washers are plated for too long a period of time, a short circuit may be formed between the nickel and the mother copper which would destroy the rectifying properties of the elements. The maximum permissible current density that can be employed is that at which nickel salts start to become deposited on the elements. The pH value of the nickel plating solution appears to be relatively critical and should preferably be kept below 5.8. The nickel when deposited under the above outlined conditions is bright and very adherent.

We have found that nickel plating is a very helpful step following the reduction of the outer surface of the cuprous oxide to copper. With reduction alone a rectifier is obtained which initially has very good rectifying characteristics, but the rectifier appears to age in the forward direction much more rapidly than when the elements are subsequently plated with nickel in the manner just described. Moreover, nickel plating of the reduced copper surface appears to reduce the tendency of moisture to increase the resistance of the elements in the forward direction.

We have also found that metals other than nickel can be plated onto the reduced copper surface, but that the best results appear to be obtained when nickel is used.

We have further found that if the oxidized blanks are thoroughly clean it is possible to plate the nickel directly onto the cuprous oxide surface without first reducing this surface to copper in the manner previously described. If the cupric oxide has been removed by successively treating the elements with the hydrochloric and sulphuric acid solution and by concentrated nitric acid in the manner previously described, and the elements are immediately transferred to the nickel plating solution, they will be sufficiently clean; but if the excess oxide has been removed by mechanical means for example, then the elements should first be cleaned as by giving them a quick dip (one or two seconds) in concentrated nitric acid followed by a thorough rinse in water which will not leave objectionable impurities on the elements. The nickel plating solution may be the same as that previously described, and if the acidity of the solution is high and the current density is kept relatively low, the solution

will discharge both hydrogen and nickel at the cathode, or in some cases hydrogen alone. The hydrogen will reduce the cuprous oxide to metallic copper, and by properly controlling the acidity of the plating solution and the current density, an underlying layer of copper will be produced next to the cuprous oxide which layer will be covered by an outer layer of nickel.

We have discovered, however, that good coats of nickel, with no visible evidence of copper under them, can be deposited directly onto the cuprous oxide with the hereinbefore described nickel plating solution at current densities of the order of 5 or 6 amperes per square foot in a time of between five and ten minutes when the pH value of the solution is about 5.8.

It should be noted that when the nickel is being plated directly onto the cuprous oxide, it is being plated onto a reducible cathode, and the effect of this appears to be to limit the plating range, particularly in plating solutions the pH value of which is in the neighborhood of 5.8 to 6.0. At relatively high current densities where the nickel plating solution would deposit a good coat on certain metals, such for example, as copper, a deposit of nickel salt will be formed on cuprous oxide instead of metallic nickel. For this reason it appears to be desirable to maintain a rather high acidity in the nickel plating solution, particularly if relatively high current densities of the order of 18 amperes are to be used.

It should be pointed out that while for most applications of rectifiers it appears to be desirable to remove the cupric oxide before subjecting the elements to the electrolytic treatment, it is not necessary to do this, and we have found that the cupric oxide can be reduced electrolytically in the same manner that the cuprous oxide is reduced electrolytically. In cases where rectifiers having a low resistance in the conducting direction are desired, the reduction must be carried clear through the cupric oxide so as to contact the underlying cuprous oxide. Otherwise, the highly resistant layer of cupric oxide will be interposed between the low resistant cuprous oxide and the electrolytically reduced contact material.

Although we have herein shown and described only a few forms of rectifiers embodying our invention and a few processes for manufacturing said rectifiers, 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 our invention.

Having thus described our invention, what we claim is:

1. The process of electrolytically reducing the copper oxide surface of a copper oxide rectifier element to metallic copper to facilitate making contact with said surface which process consists in making the element the cathode in an electrolytic bath comprising approximately .35 gram of sulphuric acid per liter in water and passing a current through said bath to said element.

2. The process of electrolytically reducing the copper oxide surface of a copper oxide rectifier element to metallic copper to facilitate making electrical contact with said surface which process consists in masking the edges of said surface and then immersing said element as the cathode in an electrolytic bath comprising .35 gram of sulphuric acid per liter in water and passing a current through said bath to said element.

3. The process of electrolytically reducing the copper oxide surface of a copper oxide rectifier element to metallic copper to facilitate making electrical contact with said surface which process consists in making the element the cathode in an electrolytic bath comprising approximately .35 gram of sulphuric acid per liter in water and passing a current of the order of 12 amperes per square foot through said bath to said element for about three minutes.
4. The process of electrolytically reducing the copper oxide surface of a copper oxide rectifier element to metallic copper to facilitate making electrical contact with said surface which process consists in masking the edges of the oxide surface and making the element the cathode in an electrolytic bath comprising approximately .35 gram of sulphuric acid per liter in water and passing a current of the order of 12 amperes per square foot through said bath to said element for about three minutes.
5. The process of making contact with the cuprous oxide surface of a copper oxide rectifier element which process consists in first making the element the cathode in a bath containing about .35 gram per liter of sulphuric acid in water and passing current through said bath to said element to reduce the oxide surface to metallic copper, and then plating said reduced surface with nickel.
6. The process of making contact with the cuprous oxide surface of a copper oxide rectifier element which process consists in first masking the edges of the oxide surface, then making the element the cathode in a bath containing about .35 gram per liter of sulphuric acid in water and passing a current of about 12 amperes per square foot through said bath to said electrode for about three minutes to reduce the oxide surface to metallic copper, and finally plating said reduced surface with nickel.
7. The process of making contact with the cuprous oxide surface of a copper oxide rectifier element which process consists in first masking the edges of the oxide surface, then making the element the cathode in a bath containing about .35 gram per liter of sulphuric acid in water and passing a current of about 12 amperes per square foot through said bath to said electrode for about three minutes to reduce the oxide surface to metallic copper, and finally making the element the cathode in a nickel plating solution and passing a current of about 18 amperes per square foot through said plating solution to said element for about two minutes.
8. The process of making contact with the cuprous oxide surface of a copper oxide rectifier element which process consists in first masking the edges of the oxide surface, then making the element the cathode in a bath containing about .35 gram per liter of sulphuric acid in water and passing a current of about 12 amperes per square foot through said bath to said electrode for about three minutes to reduce the oxide surface to metallic copper, and finally making the element the cathode in a nickel plating solution consisting of 8 oz. nickel sulphate per gal., 1 oz. of ammonium chloride per gal., 1 oz. of boric acid per gal. and $\frac{1}{2}$ oz. sodium chloride per gal. and passing a current of about 18 amperes per square foot through said plating solution to said element for about two minutes.
9. The process of making contact with the oxide surface of a copper oxide rectifier which consists in making the element the cathode in a nickel plating solution consisting of 8 oz. nickel sulphate per gal., 1 oz. of ammonium chloride per gal., 1 oz. of boric acid per gal. and $\frac{1}{2}$ oz. of sodium chloride per gal. and passing a current of the order of 5 or 6 amperes per square foot through said solution for from five to ten minutes, said solution having a pH value of about 5.8.

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