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P. H. DOWLING

2,328,626

MANUFACTURE OF ELECTRICAL RECTIFIERS

Filed Aug. 19, 1939

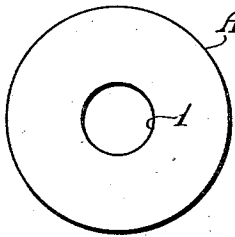


Fig. 1

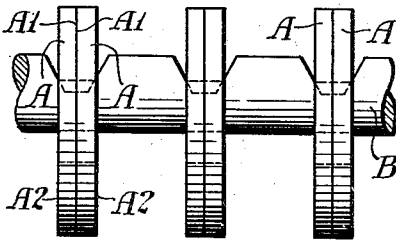


Fig. 2

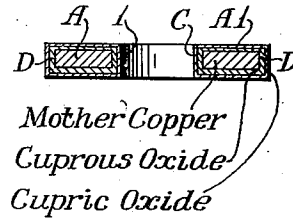


Fig. 3

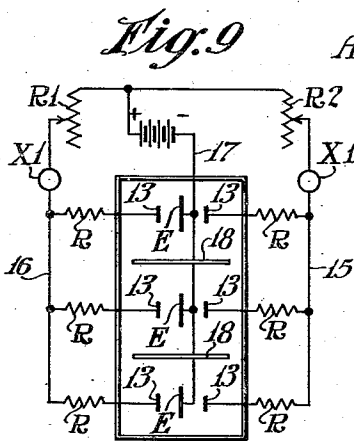


Fig. 9

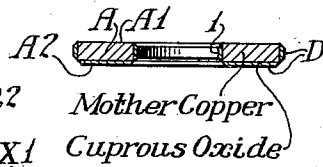


Fig. 4

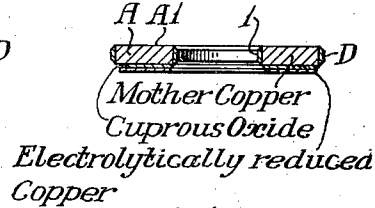


Fig. 7

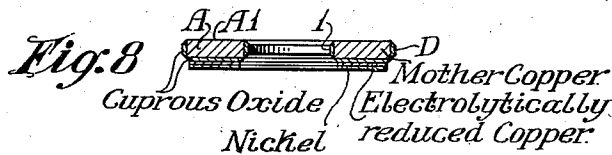


Fig. 8

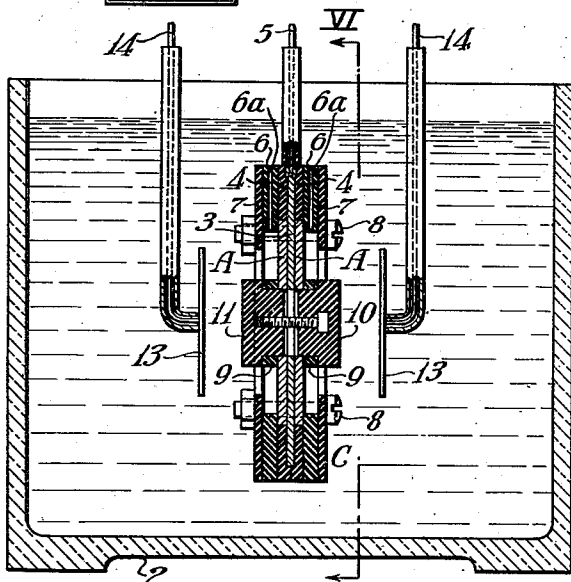


Fig. 5

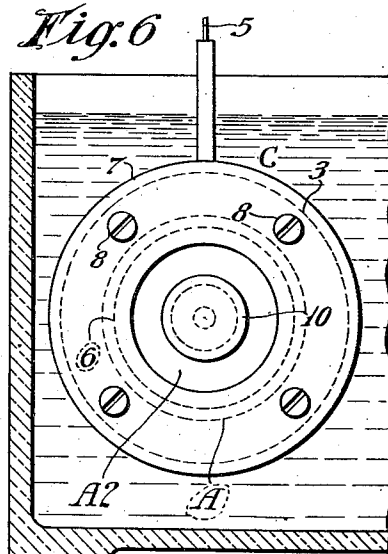


Fig. 6

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2,328,626

MANUFACTURE OF ELECTRICAL
RECTIFIERS

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Application August 19, 1939, Serial No. 291,052

7 Claims. (Cl. 204—15)

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

One object of my invention is to provide a novel and improved method for reducing the outer surface of the copper oxide layer of a copper oxide rectifier element to metallic copper to facilitate making electrical contact with such oxide surface.

Another object of my invention is to provide an improved method for producing a good metallic contact with the cuprous oxide layer of a copper oxide rectifier by first electrolytically reducing the outer surface of the copper oxide layer to metallic copper, and then plating nickel onto the metallic copper so formed.

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

The process disclosed herein is an improvement upon that described and claimed in the copending application for Letters Patent of the United States, Serial No. 213,876, filed by myself and John D. McCluer on June 15, 1938, for Electrical rectifiers, now Patent No. 2,197,632, granted April 16, 1940.

The present application is a continuation-in-part of my prior application, Serial No. 225,369, filed August 17, 1938, for Electrical rectifiers, now abandoned.

I shall describe one form of rectifier embodying my invention, and one process for rectifier manufacture also embodying my invention, 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 my 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 exaggerated form, a rectifier element as it appears in another step in the process of manufacture embodying my invention. Fig. 4 is a side view showing a rectifier element as it appears in still another step in the process of manufacture embodying my invention. Fig. 5 is a longitudinal sectional view of an electrolytic bath utilized in the process of manufacture embodying my invention. Fig. 6 is a side view of a masking device illustrated 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 sec-

tional view showing a rectifier element as it appears in a further step in the process of manufacture embodying my invention. Fig. 8 is a vertical sectional view similar to Figs. 3, 4, and 7, showing a completed rectifier element constructed in accordance with my invention. Fig. 9 is a diagrammatic view showing a circuit arrangement which may be used during one step in the process of manufacture embodying my 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 1, although this particular form is not essential to my 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 the 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 blanks, and to remove the cuprous oxide coating from only one face A1 of the blanks. This treatment may take a variety of forms, but will preferably consist in subjecting the blanks to a solution consisting of 2% by volume of sulphuric acid, and .1% 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° C. 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 1 to 3 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 to me on October 5, 1937, for the Manufacture of electrical rectifiers.

The elements are next treated to reduce the outer surface of the cuprous oxide coating of the blanks to metallic copper. This reduction may be accomplished 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.

In accordance with my present invention, I accomplish the desired reduction by immersing the elements in an electrolytic bath comprising a dilute solution of ammonium hydroxide and passing a current through this bath to the elements from an insoluble anode such as platinum or carbon, and in Figs. 5 and 6 I have shown a pair of elements A immersed as the cathode in the electrolytic bath, the bath being contained in a tank 2, and 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 insulated 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 washers 6 are preferably each provided at their upper edges with one or more vents 6a to allow the escape of gases. 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.

An anode is preferably provided for each element, and, as shown in Fig. 5, each of these anodes consists of an insoluble electrode 13 such as platinum to which external connections are made by a conductor 14. To accomplish the desired reduction, current is of course passed from the electrodes 13 to the rectifier elements, and I have found that with an ammoniacal solution consisting of .2% by volume of concentrated NH_4OH in water at room temperature excellent results may be obtained with a current density of about 12 amperes per square foot maintained for a period of from 3 to 8 minutes 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 face of the element.

A rectifier element manufactured in accordance with the process thus far described ages as well as, or better than, the well-known elements in which contact is made to the copper oxide surface by coating this surface with graphite and then pressing an impressionable electrode such as lead into contact with the graphite coated surface under relatively heavy pressures, and, in addition, has the advantage that it possesses a better lateral conductivity so that a high assembly pressure is not necessary. In fact, an element constructed in the manner just described may be used where contact is made only over limited areas of the reduced surface. Furthermore, by prolonging the reduction for a length of time which is sufficient to materially reduce the thickness of the oxide coating, a lower forward resistance can be obtained than can be obtained by the use of a graphite-lead contact. The exact reasons for this reduction in the forward resistance are very difficult to determine, but this reduction 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. This latter effect seems to be very important because the reduced copper formed on the copper oxide appears to have a waffle-like surface, and the resulting grid need only penetrate into the oxide .001 inch or less in order to produce a contact area several times that of the plane area that would be provided if no penetration took place. For example, if it be assumed that the mesh of the grid formed by the reduced copper is .002 inch square and penetrates the oxide to a depth of .001 inch, then over the plane area of 1 square inch there would be 250,000 of these meshes, each with a perimeter of .008 inch and a peripheral area of .000008 square inch. 250,000 such meshes would then have an "embedded area" of 2 square inches. Adding to this the plane area of 1 square inch would give a total contacting area of 3 square inches instead of the 1 square inch obtained by the older types of contacts. The oxide crystals formed by the reducing process are of the order of .001 to .003 inch across, and it will be evident, therefore, that the reduced copper does not have to penetrate very far between the crystals of the copper oxide before a rather large increase in contact area is achieved. The resistance per unit area between the copper oxide and the reduced copper is sufficiently high so that this increase in contact area will be reflected in a considerable decrease in the overall resistance of the rectifier element as measured in the low resistance direction. In fact, by prolonging the reduction the forward resistance at the usual working voltages can be decreased as much as 50% over the lowest resistance that can be obtained by the older methods of securing contact with the oxide. (3) A decrease in the resistance per unit area of the contact between the oxide and the copper formed by the reduction.

The amount of the reduction which takes place depends to some extent upon the temperature of the reducing solution, the rate of reduction being increased with increased temperatures. If the temperature becomes too high, the reduction may be carried into the oxide too far, and a short-circuited element will result. The ammoniacal solution specified has a relatively high resistance which necessitates a relatively high voltage, and tends to cause heating of the solution by the reducing current. Lower concentrations of the ammonium hydroxide can be used, but the voltage required to effect the desired reduction increases as the concentration decreases. To facilitate temperature control it is desirable that the reducing solution be of a relatively low resistance, and this result may be obtained either by using a higher concentration of NH_4OH , or by adding a small quantity of a soluble neutral salt to the above specified solution. For example, if .05% by volume of a saturated (25° C.) solution of $(\text{NH}_4)_2\text{SO}_4$ is added to the above solution, the voltage required to accomplish the reduction will be decreased 2%. Excellent results can also be obtained by using a very dilute ammoniacal solution of ammonium carbonate. This latter solution can be made by passing gaseous CO_2 through a solution of NH_4OH in distilled water. The concentration of the NH_4OH should be very low, i. e., in the neighborhood of .2% by volume of the usual concentrated NH_4OH (28.5% NH_3 , sp. grav.=.9) or about .05% NH_3 by weight. The concentration of the CO_2 in the solution is not critical, but if

the CO_2 is added until the specific resistance of the solution at 25° C. is in the vicinity of 850 ohm-cm., excellent results are obtained. When this latter solution is used, there is a tendency to produce a streaked copper surface unless the solution is agitated. This may be accomplished by moving slightly the element whose copper surface is being reduced. For a $1\frac{1}{2}$ " element, a motion of $\frac{1}{4}$ " parallel to the face of the element at the rate of one or two cycles per second is sufficient.

As has been pointed out hereinbefore, if the reduction is carried on for too great a length of time, there is a danger of short-circuiting the rectifier element due to the copper formed by the reduction penetrating to the mother copper. The allowable amount of the reduction depends upon the original thickness of the oxide which, in turn, depends principally upon the temperature and length of time of the original oxidation. For example, an element oxidized for 13 minutes at 1860° F. can be reduced for about 8 minutes at about 12 amperes per square foot in a bath of about 25° C. without causing any difficulty due to the copper penetrating too deeply into the oxide and thus short-circuiting the elements or causing too low a resistance in the current blocking or high resistance direction. Similarly, an element oxidized for 50 minutes at 1860° F. can be reduced for 25 minutes under the conditions outlined above, and will have about the same electrical characteristics as the element which was oxidized for only 13 minutes and reduced for 8 minutes. In the case of the element which is oxidized for 13 minutes and then reduced for 8 minutes, the temperature of the bath should not exceed 30° C.

When the reduction of the copper oxide surface of the elements is prolonged to decrease the forward resistance of the elements, it is necessary in order to avoid danger of short-circuiting the elements that the reduction should be uniform over the entire portion of the surface which is being reduced. As there is naturally a tendency for the current to concentrate at the edges of the elements, the elements should be shielded, or some device should be employed which will reduce the concentration at the edges. One convenient means for accomplishing the necessary shielding consists in making the washers 7 which clamp the masking washers 6 against the outer edges of the elements with an inside diameter of such size that the inner edges of the washers 7 will project past the inner edges of the washers 6 for some distance in the manner shown in Fig. 5.

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 I shall describe presently.

It should be pointed out that a rectifier element constructed in the manner thus far described is superior to rectifier elements in which the oxide coating is reduced to copper in the manner described in the previously referred to Dowling and McCluer application in that the copper formed by the reduction is brighter and tarnishes less readily, and that the elements age better. It is thought that the improvement in the characteristics of the elements is obtained

because of the volatile nature of the electrolyte which insures that no traces of the electrolyte will remain on the elements to later cause corrosion or otherwise affect the characteristics of the reduced surface.

While rectifier elements constructed in the manner thus far described are satisfactory for many applications without further treatment, when the elements are to be used in applications where moisture is present, the aging characteristics of the elements may be improved by depositing a layer of nickel on the reduced copper layer. To accomplish this step, the elements while still mounted in support C are made the cathode in a nickel plating solution in the same manner that they were made the cathode in the ammonium hydroxide bath during the preceding step.

The proper technique for accomplishing the nickel plating in the nickel plating solution has been found to depend upon the amount that the copper oxide has previously been reduced to metallic copper, and even with the same amount of reduction, upon the particular reducing solution used. The standard nickel plating solution described in the previously referred to Dowling and McCluer application may be used, but I prefer to use a more concentrated solution, which may, for example, have the following composition; $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 27 ounces per gallon; boric acid, 6 ounces per gallon; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 4 ounces per gallon. This latter solution is well known, but appears to be better adapted for the plating of the reduced copper surface than the solution referred to in the previously described Dowling and McCluer application.

When the solution just described is used, I have found that in general there are three stages involved in applying the nickel to the reduced copper surface, as follows:

First stage

During this stage there is but relatively little change in the color of the copper surface with but little visual evidence of the deposition of bulk nickel. The duration of this stage may be a large fraction of the total plating time. It depends upon many factors and can be found for any particular set of conditions, only by trial. Throughout this first stage the forward resistance of the elements remains practically unchanged.

Second stage

As the plating progresses into this stage, the plating surface takes on more and more the appearance of bright pure nickel. The forward resistance of the elements, when measured immediately after plating, steadily increases as the nickel becomes brighter, but if, after plating, the elements are allowed to stand, even at room temperature, their forward resistance will decrease until a minimum value is reached at which the resistance becomes stable. This minimum value will be near the value which existed immediately after the previously described reduction of the oxide surface of the copper oxide to copper was completed. This stabilization can be accelerated by the application of heat. A heat treatment of 1 hour at 80°C . has been found to be satisfactory. Other temperatures and times may, however, be used, the necessary time decreasing as the temperature increases. Temperatures higher than 125°C . should not be employed, and, in general, the minimum time for stabilization should not be greatly exceeded so that the volume resistivity of the oxide will not

be unduly increased. However, it has heretofore been customary to preage the rectifier elements for certain applications by a thermal treatment consisting of approximately a 16 to a 24 hour bake at 100°C ., and when this last mentioned treatment is employed, the stabilizing heat treatment just described may be eliminated.

Third stage

As the plating continues beyond the second stage, the nickel surface becomes very bright, but the forward resistance of the elements will not return to its original value. There is no sharp dividing line, either in appearance or in the electrical characteristics of the elements, between the second and third stages.

The successful nickel plating of any particular reduced copper surface formed by the herein-described reducing process depends upon so controlling the current density, acidity and temperature of the plating solution, and plating time that if the plating is done in one continuous operation, the second stage will be reached but not passed. If, however, by plating in a continuous operation it is impossible to obtain the thickness of nickel which is necessary to give sufficient lateral conductivity for certain applications of rectifiers, without causing the forward resistance of the elements to increase, then the plating can be divided into two operations, as will be made clear presently.

The current density employed during the plating step, and the length of plating time that can be employed, depends upon the original amount of the reduction, the pH value of the plating solution, and the degree of agitation of the solution. With the preferred plating solution mentioned hereinbefore, for an element which has been reduced for 3 minutes at a current density of 12 amperes per square foot, if the pH value of the solution is maintained between 5 and 5.2, excellent plating results are obtained with a current density of about 12 amperes per square foot continued for about 3 minutes at room temperature with no agitation of the bath. As the amount of the original reduction is increased, however, it becomes necessary to increase the ampere minutes of plating in order to carry the elements into the second stage, and there is also a tendency for the allowable current density to increase as the amount of the reduction is increased. For example, an element the copper oxide surface of which has been reduced to copper for 8 minutes under the same conditions as an element which has been reduced for 3 minutes, will be plated into the second stage in the preferred nickel plating solution by using a current density of 24 amperes per square foot for 2 minutes. Other current densities and times may be used, but this combination gives excellent results. This combination will not, however, carry into the second stage an element whose copper oxide surface has been reduced for 25 minutes. Such a disc requires more ampere-minutes, and a higher current density will in many instances prove beneficial.

As the pH value of the plating solution is increased, mechanical agitation of the bath becomes increasingly necessary. In adjusting the pH value of the solution, ammonium hydroxide and sulphuric acid may be used, but nickel carbonate and boric acid are preferred. For small elements or batches of elements, a pH value of 5 to 5.2 is preferable with no agitation except just as the elements are placed in the solution.

For larger elements or batches of elements, a higher pH value, in the neighborhood of 5.8-6.0 with agitation throughout the plating operation appears to be desirable. It is desirable to keep the solution clear and free from suspended matter by filtering when necessary. While the current density and plating times specified are not very critical, too low or too high a current density and too short or too long a plating time tend to produce either two high forward resistances or rectifiers which will not stand unprotected exposure to moisture very well.

When the elements are plated into the second stage in a single operation, it appears that a thorough drying of the elements following their removal from the reducing solution, as described hereinbefore, is beneficial in postponing the onset of the third stage. It has been found, however, that this drying is not essential and that good results can be obtained by merely rinsing the elements in clear water between the reducing and the plating steps. A quick agitation of the elements as they enter the nickel plating solution is desirable when the elements have not been thoroughly dried following their removal from the reducing solution, to insure a quick distribution of substantially undiluted nickel solution over the entire surface which is to be plated.

It is thought that the conditions obtaining at the surface of the element, at the moment that the nickel plating commences, rather critically determines the subsequent course of the plating, and the final quality of the electrical contact to the copper oxide. For example, I have found that if the reduced copper surface is allowed to come into contact with the nickel plating solution for even a few seconds with no voltage applied, the contact is likely to be ruined, and the forward resistance of the elements is likely to be rendered permanently high. It is obvious, therefore, that the plating voltage should be applied to the electrodes before the elements are placed in the nickel plating solution.

I have also found that when a rectifier element is to be plated on both sides, or when two elements are each adapted to be simultaneously plated on one side by means of an arrangement similar to that shown in Figs. 5 and 6, if there are any differences in the two surfaces which are to be plated, these differences may become increased during the plating operation until the current passing to the one surface is several times that passing to the other surface, and that no amount of change in the position of the elements in the bath relative to the anodes will restore the balance. This difference in current flow may cause one surface to receive most of the nickel, or if the unbalance is not sufficient to have this effect, one surface may be carried into the third stage of plating, with a permanently high forward resistance, while the other surface will only be carried into the second stage and will have a forward resistance which will stabilize at an acceptable value.

Furthermore, when several elements are to be simultaneously plated at different locations in the nickel plating bath, if there are differences in the oxide and rectifying junction resistances of the individual elements and/or in the resistances of the contacts to the copper of the individual elements, unequal current distribution among the various elements will be produced with consequent erratic results in the plating.

In order to avoid these difficulties, I prefer to utilize for the nickel plating bath circuits which

are so arranged that any reduced copper surface is included in a circuit of relatively high impedance. To this end, I insert in every such circuit a series impedance which is sufficiently high so that the voltage drop across it will be at least equal to, and preferably several times, the voltage drop across the bath itself. In many cases this series impedance may be the usual control resistance used in ordinary plating except that it will have a higher ohmic resistance than is usual, which will necessitate that the voltage of the power supply will be higher than usual. By this means the initial plating current can be made practically independent of the initial conditions of the reduced oxide surface, and the distribution of the current among the various surfaces to be plated will be substantially uniform.

Referring to Fig. 9, I have here shown a circuit for accomplishing the proper current distribution to both sides of a number of elements which are all to be plated in the same bath. Each element E is positioned between its individual pair of electrodes 13. All of the anodes on one side of the elements are connected to an anode bar 15, each through its individual fixed resistance R of relatively high impedance. All of the anodes on the opposite sides of these elements are similarly connected to another anode bar 16. The mother copper of each element is connected to a common cathode bar 17, it being pointed out that with this arrangement both sides of each element will have been oxidized and will have had both oxide surfaces subjected to a reducing treatment similar to that described hereinbefore. The total current to the two anode bars 15 and 16 is controlled and is brought to the same value by means of two resistors R1 and R2, suitable ammeters X1 being provided to facilitate the necessary adjustment. In order to minimize the amount of current which can reach any element from a neighboring anode, the separation between adjacent anodes should be large compared to the separation between each anode and its associated element. Preferably insulating shields 18 will be provided between adjacent elements.

As has been pointed out hereinbefore, once a rectifier element has been given a chance to stabilize its forward resistance after being plated into the second stage, the plating may then be continued without carrying it into the third stage. As an example, an element whose copper oxide surface has been reduced to metallic copper for 8 minutes, and has then been plated into the second stage in the manner previously described, can, if it is allowed to stabilize its resistance, be nickel plated for an additional 2 minutes at 24 amperes per square foot with but little effect on the forward resistance, even when measured immediately after the second plating. Stabilization in this case can be completed in about 16 hours at room temperature and ordinary atmospheric conditions. Stabilization which will allow sufficient subsequent plating is not necessarily indicated by the return, after the first plating, of the forward resistance to its original value. The original value of the forward resistance is usually reached before the element is ready for its second plating. There is no visible change accompanying the complete stabilization, and its presence for a given combination of reduction and plating can be ascertained only by trial.

After the nickel plating has been completed, the elements should be thoroughly rinsed in clean water, and then dried, after which they may be removed from the mask.

In cases where greater lateral conductivity is required than that obtained by the reduced copper-nickel contact described above, as for example might be the case in connection with elements which are to be used in electroplating applications, either the reduced oxide contact alone may be sprayed with a low melting point metal, or this low melting point metal may be sprayed over the nickel plated reduced copper contact. The spraying can be done by well-known processes, such, for example, as the "Shoop" process.

One advantage of a rectifier element constructed in accordance with my invention is that the characteristics of the elements obtained are extremely uniform, which is highly desirable.

Although I have herein shown and described only one form of electrical rectifiers embodying my invention, and one process 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 my invention.

Having thus described my invention, what I claim is:

1. The process of making contact with the cuprous oxide surface of a copper oxide rectifier element which process consists in masking the edges of the oxide surface, making the element the cathode in an electrolytic bath comprising a dilute solution of ammonium hydroxide in water and passing a current through said bath to said element to reduce a portion of the cuprous oxide surface to metallic copper, and then making the element the cathode in a nickel plating solution consisting of 27 ounces per gallon of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 6 ounces per gallon of boric acid, 4 ounces per gallon of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and passing a current of about 12 amperes per square foot through said plating solution to said element for about 3 minutes.

2. The process of making contact with the cuprous oxide surface of a copper oxide rectifier element which process consists in masking the edges of the oxide surface, making the element the cathode in an electrolytic bath comprising a dilute solution of ammonium hydroxide in water and passing a current through said bath to said element to reduce a portion of the cuprous oxide surface to metallic copper, and then making the element the cathode in a nickel plating solution consisting of 27 ounces per gallon of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 6 ounces per gallon of boric acid, 4 ounces per gallon of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and passing a current of about 12 amperes per square foot through said plating solution to said element for about 3 minutes, said solution being maintained at a pH value of 5.0 to 5.2, and finally applying heat to said element to stabilize the forward resistance of the element.

3. The process of making contact with the cuprous oxide surface of a copper oxide rectifier element which process consists in masking the edges of the oxide surface, making the element the cathode in an electrolytic bath comprising a dilute solution of ammonium hydroxide in water and passing a current through said bath to said element to reduce a portion of the cuprous oxide

surface to metallic copper, and then making the element the cathode in a nickel plating solution consisting of 27 ounces per gallon of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 6 ounces per gallon of boric acid, 4 ounces per gallon of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and passing a current of about 12 amperes per square foot through said plating solution to said element for about three minutes, said solution being maintained at a pH value of 5.0 to 5.2, and finally subjecting said element to a temperature of approximately 80° C. for an hour.

4. The process of making contact with the cuprous oxide surface of a copper oxide rectifier element which process consists in masking the edges of the oxide surface, making the element the cathode in an electrolytic bath comprising a dilute solution of ammonium hydroxide in water and passing a current through said bath to said element to reduce a portion of the cuprous oxide surface to metallic copper, and then making the element the cathode in a nickel plating solution consisting of 27 ounces per gallon of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 6 ounces per gallon of boric acid, 4 ounces per gallon of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and passing a current of about 12 amperes per square foot through said plating solution to said element for about 3 minutes, said solution being maintained at a pH value of 5.0 to 5.2, and finally subjecting said element to a temperature of between 80° C. and 125° C. for a period of time to stabilize the forward resistance of the element.

5. The process of electrolytically reducing a portion of 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 .05% NH_3 by weight of concentrated NH_4OH in water combined with a very dilute ammoniacal solution of ammonium carbonate, and passing a current through said bath to said element.

6. The process of electrolytically reducing a portion of 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 .05% NH_3 by weight of concentrated NH_4OH in water combined with a very dilute ammoniacal solution of ammonium carbonate, and passing a current of the order of 12 amperes per square foot through said bath for approximately 8 minutes.

7. The process of electrolytically reducing a portion of 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 .05% NH_3 by weight of concentrated NH_4OH in water combined with a very dilute ammoniacal solution of ammonium carbonate, and passing a current of the order of 12 amperes per square foot through said bath for approximately 8 minutes, the temperature of the bath being maintained at approximately 25° C.

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