

March 7, 1939.

R. O. HULL

2,149,344

APPARATUS AND PROCESS FOR THE STUDY OF PLATING SOLUTIONS

Filed March 22, 1935

2 Sheets-Sheet 1

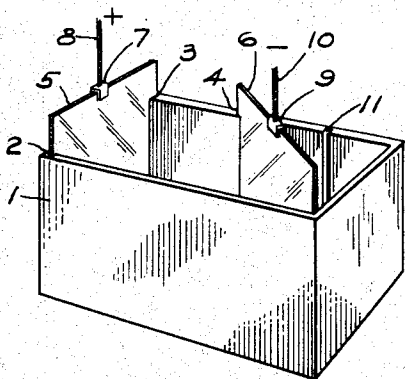


Fig. 1.

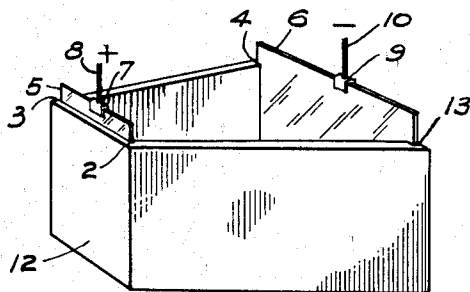


Fig. 2.

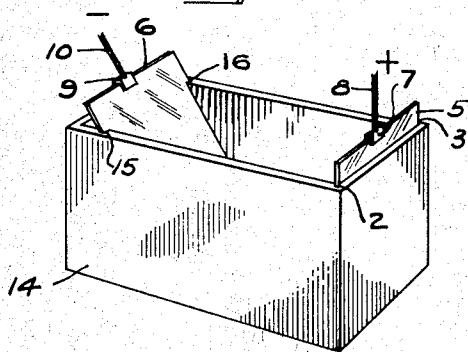


Fig. 3.

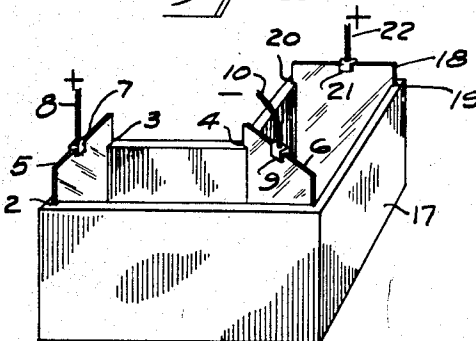


Fig. 4.

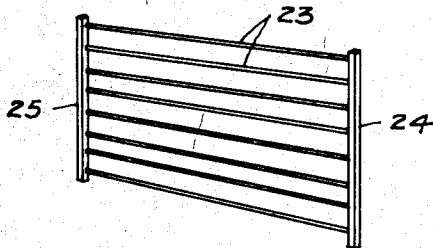


Fig. 5.

INVENTOR.
RICHARD O. HULL.

BY

Albert B. Briggs.
ATTORNEY.

March 7, 1939.

R. O. HULL

2,149,344

APPARATUS AND PROCESS FOR THE STUDY OF PLATING SOLUTIONS

Filed March 22, 1935

2 Sheets-Sheet 2

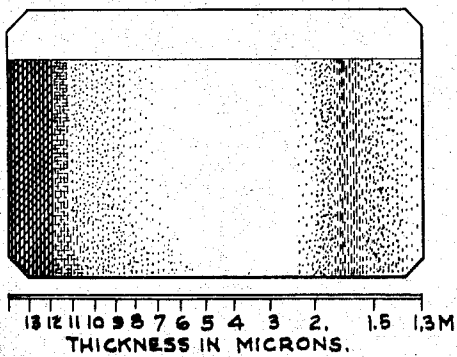


Fig. 6.

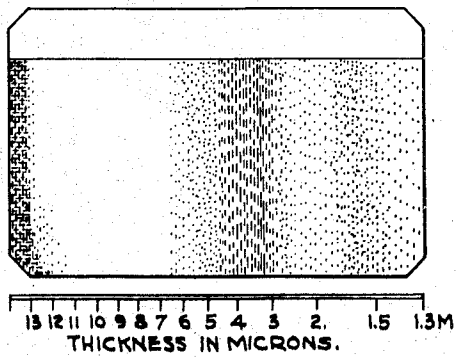


Fig. 7.

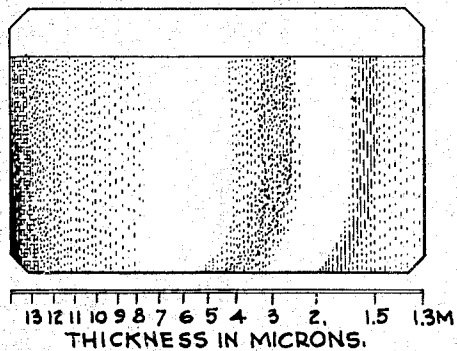


Fig. 8.

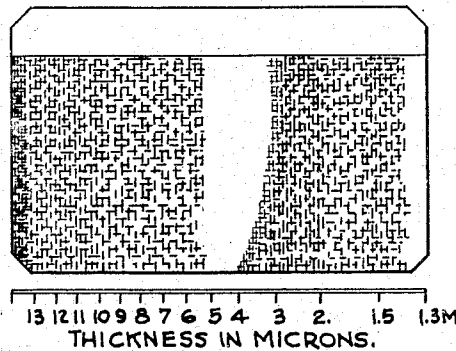


Fig. 9.

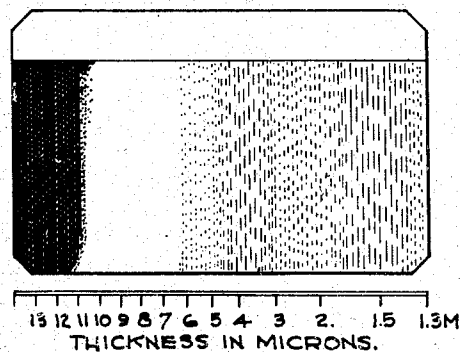


Fig. 10.

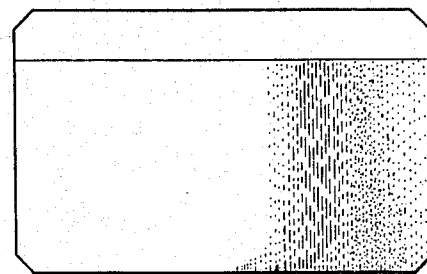


Fig. 11.

INVENTOR.

RICHARD O. HULL.

BY

Albert O. Kriggs

ATTORNEY.

UNITED STATES PATENT OFFICE

2,149,344

APPARATUS AND PROCESS FOR THE STUDY
OF PLATING SOLUTIONS

Richard O. Hull, Lakewood, Ohio, assignor, by
mesne assignments, to E. I. du Pont de Nemours
& Company, Wilmington, Del., a corporation
of Delaware

Application March 22, 1935, Serial No. 12,416

2 Claims. (Cl. 204—1)

This invention relates to improved apparatus and processes for the examination and evaluation of processes of electrodeposition, and is more particularly directed to apparatus and processes involving the use of a cathode so located in an electrolyte that a given area on the cathode receives current through a cross-sectional area of electrolyte of different magnitude than does another, equal area on the cathode, whereby the characteristics of a plating process at a number of current densities are quickly determined.

The character of an electrodeposit obtained with particular electrodes and a particular solution varies widely with variations in the current density employed. A given plating bath may produce an excellent deposit at one current density, while the same bath, under the same conditions, but at a different current density may produce an extremely poor deposit. The effects of varying current densities will be described more fully hereinafter.

Those working in the prior art have realized, to some extent, the great influence of current density upon the character of an electrodeposit, and it has been the practice to plate specimens at first one and then another current density. To determine the effect at a given current density, it is ordinarily the practice to use a small rectangular box which has means for holding a flat anode and a flat cathode in a parallel relation a definite distance apart. A series of such cathodes are plated at various current densities, and, by comparing the cathodes, some idea can be gained as to the characteristics of the plating solution.

In order to obtain an idea as to how a plating solution will act on the irregularly shaped articles frequently plated, it has been the practice to use U-shaped, L-shaped, curved, or recessed cathodes to simulate, to some extent, the conditions encountered in commercial plating. Such cathodes are electroplated with slightly varying current densities at more or less recessed parts, but so many variables are encountered that one cannot interpret the effects attributable to a particular current density. It has usually been preferred, therefore, to use parallel flat cathodes when definite current density limits were to be determined.

In evaluating and comparing baths, and in evaluating addition agents, brightening agents, etc., the prior art methods have been entirely inadequate and the results misleading.

In determining the bright range of a bath, for instance, those in the art have had to use the above crude methods. The determination of the

bright range of a solution has, therefore, involved a large number of hit or miss guesses; the tester trying first one and then another current density until he feels that he has found the approximate bright range. The exact determination of the bright range of a solution was extremely tedious and difficult, if not impossible.

The determination of the bright range was further complicated by the large number of variables. Relatively small changes in temperature, for instance, cause a shifting of the bright current density range. Moreover, the use of the bath changes its character. By reason of these and other variables, a worker had no assurance that the bright range would remain in the same current density range while he made the numerous tests required to locate it.

After a bath has been in use, the bright range shifts, and the whole tedious procedure of locating it by hit or miss must be repeated, again with the danger of not finding it. Platers frequently return solutions to the maker with the complaint that the solutions are exhausted, or faulty, whereas the plater has simply failed to find the bright range.

In studying new solutions, new addition agents, new brighteners, and the like, the prior art methods have been particularly disadvantageous. A bath may have one very narrow bright range which entirely escapes notice. Again, the bath may have a number of bright ranges, and an experimenter finding only the poorest will consider the bath of no commercial value. With such a bath, moreover, there is a great probability that all of the tests will be made at current densities outside of the bright ranges, and the experimenter will feel that he has thoroughly examined the bath and that it has no bright range. Again, the bright range may be in a surprisingly high or low current density range, and an experimenter may entirely miss it.

For these reasons, an experimenter may report an addition agent, a brightener, or a bath of no commercial interest, and a valuable contribution to the art will be lost. This is especially true as later experimenters, relying on the work already reported, are dissuaded from further study of the addition agent, brightener, or bath.

It is an object of my invention to provide means and methods for overcoming the difficulties experienced by the art. It is a further object of my invention to provide means and methods whereby the characteristics of a plating bath at an infinite number of current densities can be quickly and easily determined. A further object

of my invention is to provide means and methods for examining plating solutions to determine the presence or absence of bright ranges, and, if any are present, their extent and number. A still further object of my invention is to provide means and methods for rapidly and accurately studying plating solutions to determine their value, to determine the optimum concentration of constituents such as addition agents, metal salts, etc., and to determine the optimum operating conditions. A still further object of my invention is to provide means and methods for comparing solutions with regard to throwing power. Other objects will appear hereinafter.

My objects are accomplished, briefly, by the use of a cathode so located in an electrolyte that a given area on the cathode receives current thru a cross-sectional area of electrolyte of different magnitude than does another, equal area on the cathode. Or, expressing the invention rather specifically and with more particular reference to the preferred forms of apparatus, I employ a cathode so located in a confined electrolyte that it falls substantially in one confining plane, and makes an angle of less than ninety degrees with at least one adjacent confining plane. The most accurate and most valuable results are obtained when the anode is located outside of the volume of electrolyte which is included between the cathode and the plane which is located at an acute angle.

By following the teachings of my invention, one quickly obtains a record of the effects of a particular bath at an infinite number of current densities. Such an accurate and continuous record could not be obtained by prior art methods by any expenditure of time and effort.

The means and processes of my invention are an extremely simple answer to a complex question, but an answer that has escaped the grasp of the art, and without which the research on electroplating has been reduced to an endless repetition of routine hit or miss guesses, which missed more than they hit. By the use of the processes and apparatus herein described, the research worker can strike out incisively towards the evaluation of a type of baths or group of addition agents, and feel sure that his results are conclusive. The practical plater, moreover, can quickly evaluate his bath and make such changes in constitution or operating conditions as are required.

In order more fully to understand my invention, reference should be had to the accompanying drawings wherein:

Figure 1 illustrates, in perspective, a typical cell for the practice of my invention,

Figure 2 illustrates a modified form of cell,

Figure 3 shows a further modified form of cell,

Figure 4 illustrates a still further modified test cell,

Figure 5 shows a modified form of cathode, and

Figures 6 to 11, inclusive, show cathodes cadmium plated according to the processes of my invention.

Considering the drawings in more detail, it is noted that, in Figures 1, 2, 3, and 4, the anodes are designated by a plus sign, and the cathodes by a minus sign, in the usual way. In Figure 1 a hard-rubber cell 1 is provided with grooves 2, 3, and 4 in its side walls. An anode 5 slides into grooves 2 and 3, and closely fits the bottom of the cell. A rectangular cathode 6 slides into the cell with one edge in groove 4 and with the opposite edge in the corner of the box. The cathode likewise fits the box closely. Clip 7 and lead 8 make

electrical connection with the anode 5, and clip 9 and lead 10 serve the same function for the cathode 6.

In use, the cell 1 is filled with electrolyte to a definite depth and the anode and cathode are put in place. An electric current is then passed thru the electrolyte, anode, and cathode in the usual way. After a predetermined length of time, the plating is discontinued and the cathode removed.

A cathode so plated has a deposit of regularly decreasing thickness from the end which fits in the slot to the end which is held in the corner of the cell. The current and time used should be so selected that the deposit at the end of the cathode which fits in the slot is burned and damaged by excessive current density, and so that the opposite end of the plate has a very slight deposit. In this way one is assured that the cathode records every current density at which a deposit of value might be obtained. The nature and interpretation of the record obtained on the cathode will be considered in greater detail hereinafter in connection with typical plated cathodes.

It is believed that the major factor in the production of a record of the effects of numerous current densities is the location of a cathode in an electrolyte in such a manner that a given area on the cathode receives current thru a cross-sectional area of electrolyte of a different magnitude than does another equal area on the cathode. Considering, for instance, the process of the device of Figure 1, it is seen that a narrow, vertical strip of the cathode 6 receives current through an electrolyte-conductor which has a cross-sectional area equivalent to the area of electrolyte which would be cut by a plane parallel to the anode 5 and passing thru the vertical strip. A contiguous strip of cathode area nearer the near corner of the cell receives current thru an electrolyte-conductor which has a cross-sectional area equivalent to the smaller area of electrolyte which would be cut by a plane parallel to the anode 5 and passing thru the vertical strip. Since the strip nearer slot 4 receives a greater proportion of the electrical current by reason of the greater cross-sectional area of the electrolyte-conductor which supplies it with current, and since the cathode areas are assumed to be equal, it is at once apparent that the vertical strip nearer slot 4 is subject to electrodeposition at a higher current density than the assumed contiguous cathode area.

It is clear, then, that an infinite number of vertical strips of cathode area, each of infinitesimal width, are simultaneously plated at a like infinite number of current densities. It is also clear that in the device of Figure 1 the cross-sectional areas of the electrolyte supplying current to the strips decrease in a regular manner towards the near corner of the cell. It therefore follows, and such is the fact, that the cathode is plated at an infinite number of current densities which are highest at the end of the plate nearest slot 4, and which decrease in a regular manner until a lowest current density is reached at the end of the plate in the near corner of the cell.

Considering the device of Figure 1, the variation of the cross-sectional area of electrolyte may be better visualized by considering the variation of distances between the cathode and the near wall. As the electrolyte is of uniform depth, the cross-sectional areas of electrolyte, above referred to, are functions of the distances between the cathode and the front wall of the cell. That is, the current received by a vertical strip of cathode area is a function of the length of a line intersecting

the area and normal to the near wall; which is to say, parallel to the anode. It is at once apparent that such normals decrease in length as the cathode areas are assumed nearer the near corner of the cell, and it is again clear that the current densities on vertical strips of cathode area decrease in a regular manner from the end of the cathode at slot 4 to the near end of the cathode.

If it is desired to increase or decrease the range of current densities obtained, the cathode should be arranged so that it makes a smaller or larger angle with the front wall of the cell. To make the angle larger, for instance, the cell is provided with a slot 11 which may hold a smaller cathode. When a cathode is held between slot 11 and the corner of the cell, the current density variation is less from one end of the cathode to the other than it is with a cathode positioned as in Figure 1. A cathode held by slot 11, then, records a narrow range of current densities, but the record shows the range in what amounts to a magnified manner.

There are a number of minor factors which cause slight variations from the theoretical order of decrease of current densities. The cathode edge nearest slot 4 may receive current from a great many directions and, in accordance with the well known effect at points and edges, it receives an abnormally large amount of current.

Another factor which one might expect to cause some variation in the theoretical order of decrease of current densities is the variation in distances between the anode and cathode. Numerous experiments have led me to the conclusion, however, that the relation of anode to cathode is of little importance, so long, of course, as the anode does not extend into the portion of electrolyte which serves as a conductor of varying cross-sectional area.

Thinking that the angular relation of anode and cathode might be a major factor, I tried using an anode in the location of cathode 6 with a cathode in the location of anode 5. The cathode received a deposit of uniform thickness, and the current densities appeared to be substantially equal along the cathode length instead of varying as in the device of Figure 1.

The device of Figure 1 was also tried with the anode 5 in various angular relations to the cathode. The anode was rotated to several positions about its central, vertical axis. No perceptible difference in the character of the cathode deposit resulted from the variation of the angular relation. Even when the anode was parallel to the cathode, the results were the same as those obtained with the angular relation of Figure 1. It may be that the current distribution is affected by the effective anode area presented, but even when the anode was normal to the cathode, no greatly different cathode deposit was obtained. This was true, also, when the anode was positioned against the near wall of the cell of Figure 1 at a right angle to the cathode.

While the anode may be located in substantially any position with respect to the cathode, it is apparent that the anode must not extend into the volume of electrolyte which serves as a conductor of varying cross-sectional area if the best results are to be obtained. In other words, it is preferable that the anode be so located in a device such as the one of Figure 1, that it does not fall within the confines of a figure defined by the cathode, the near side, and a line parallel to the anode and intersecting the end of the cathode at slot 4.

It is readily apparent that if the anode extends into the volume of electrolyte which serves as conductor of varying cross-section, the electric current will not be carried by conductors of the same cross-sectional areas as in the cells above described, and the current densities on the cathode will vary in a different manner over at least a part of its surface. Of course, the record obtained is of some value and this mode of operation, though not as satisfactory as the type of operation illustrated in Figure 1, may frequently be used to advantage. It will be apparent that even if the anode extends at an angle to, and a little beyond, a line intersecting slot 4 and normal to the near wall of the cell of Figure 1, the cathode is still so located in an electrolyte that a given cathode area receives current through a cross-sectional area of electrolyte of different magnitude than does another equal area on the cathode, but the magnitudes may not vary uniformly with successive areas selected in a given direction, and there may also be other equal areas which receive current through the same cross-sectional area of electrolyte. Or, in other words, the current densities may not change in the same sense and in a regular manner from one end of the cathode to the other.

It may sometimes be desired to obtain a cathode on which the current densities vary in a more arithmetical progression than do the current densities on a cathode plated in a cell such as the one shown in Figure 1. To this end, a cell such as that shown in Figure 2 may advantageously be used. In Figure 2, for instance, there is seen a test cell similar to the one shown in Figure 1, but in the device of Figure 2, the anode is parallel to the cathode. Suitable slots 2 and 3 are provided for holding the anode 5, and similar slots 4 and 13 are provided for holding the cathode. Cathodes in a cell such as the one of Figure 2 are plated at current densities which vary in a more or less arithmetical progression.

The cross-sectional area of electrolyte may, of course, be varied in numerous ways, as by placing the cathode so that it makes an angle of less than ninety degrees with the bottom of the cell or with the liquid level. As seen in Figure 3, an anode 5 is held by slots 2 and 3 as in the device of Figure 1. The cathode 6 is held in the cell by angular slots 15 and 16. The record on cathode 6 will, of course, vary vertically of the cathode rather than horizontally. In similar manner, the bottom of the cell may be placed at an angle to a vertical cathode.

In the modifications shown in Figures 1, 2, and 3, the cathodes are shown as held by grooves in the cell walls. This is a preferred mode of locating the cathodes as they may rapidly and conveniently be inserted and removed. Even though the cathode closely fits the cell, there is still a current leakage around the cathode edges. This leakage may be prevented by sealing the cathodes in place with a suitable insulating material such as paraffin. Or, if desired, suitable rubber strips may be employed to prevent current losses at the plate edges. More will be said hereinafter regarding these current losses.

The current losses may be offset, as in Figure 4, by the expedient of plating both sides of a cathode under identical conditions. As seen in Figure 4, anodes 5 and 18 are positioned in grooves 2 and 3, and 19 and 20 in the ends of an L-shaped cell 17. Clips 7 and 21, and leads 8 and 22 supply current from a common source to the anodes 5 and 18 respectively. A cathode 6 is held be-

tween groove 4 and a corner of the cell in the same angular relation to each side of the L. In use, the current leakage from one side of the cathode equals the current leakage from the other side, and the cathode electrodeposition shows no evidence of current leakage.

While I have shown flat plate cathodes in the above described modification, I may of course use various type of cathodes. In Figure 5, for instance, there is shown a cathode consisting of a plurality of metal rods 23 secured at their ends to metal strips 24 and 25. When used in place of the cathode of Figure 1, the cathode of Figure 5 serves to produce a record similar to that obtained with the plate cathode. However, cathodes such as the one of Figure 5 have proven none too satisfactory because the variation in the nature of the deposit is not so easily seen as with a plate cathode, and the current may reach the rods by so many paths that the current density variation picture is more extended and is quite different from that obtained with plate cathodes. It will be readily apparent that a single rod could be used as a cathode by locating it, as in Figure 1, with one end in slot 4 and with the other end in the near corner of the cell. Numerous other types of cathodes which can be used to accomplish the desiderata of my invention will readily occur to those skilled in the art.

It will also be apparent that the cell may be constructed of any suitable insulating material. I have found hard-rubber, wood, and glass quite satisfactory, and paraffined cardboard served very well in the construction of a small cell which was given only a little use.

Various other modifications which may be made in the use and construction of test cells according to my invention will be discussed hereinafter.

Considering, now, the test plates illustrated in Figures 6 thru 11, it is first noted that considerable difficulty was encountered in making a suitable graphical representation of the plates. The areas are not all clear to the eye, and to distinguish them a cathode must be viewed from various angles. It was found that a photostat of the test plates shows the areas with remarkable clarity, and the figures are drawn from negative photostats with reference to the plates as seen by the eye. Similar areas are indicated by similar types of shading in the several views.

In Figure 6 there is shown a cathode plated in a box similar to the one of Figure 1. The cathode was sealed in the cell with paraffin to eliminate current leakage at the cathode edges. The cathode was plated for three minutes at a temperature of 20° C. in a cadmium plating solution of the following composition:

	Grams per liter
Cadmium oxide (CdO)-----	43
Sodium sulfate (Na ₂ SO ₄)-----	60
Sodium cyanide (NaCN)-----	120
Nickel sulfate (NiSO ₄ ·7H ₂ O)-----	1
Sulfite cellulose waste-----	10

The thickness of the cadmium deposit was determined, and the approximate thickness, in microns, is indicated below the cathode. Considering the time of deposition and the thickness of the cathode at a given point, it is, of course, possible to arrive at an approximation of the current density by electro-chemical calculation. Of course, the cathode efficiency must be considered, but, for most purposes, it is sufficient to assume a one-hundred per cent efficiency. If a more accurate approximation of the current density is

desired, the cathode efficiencies may be more closely approximated by determining the cathode efficiency at a few widely separated current densities.

At the right end of the cathode, there is a very thin, slightly foggy cadmium deposit. Moving to the left, the white fog becomes slightly denser until, at a thickness of about 1.6 microns, the character of the electrodeposit changes rather abruptly, being more heavily fogged and very slightly yellowish. This first zone, from a thickness of 1.3 to 1.6 microns, was deposited at calculated current densities of from about 10 to 14 amperes per square foot.

Moving more to the left, the heavily fogged area becomes lighter, and fades from a light fog into the bright range at a thickness of about 2.5 microns. A thickness of 2.5 microns corresponds, roughly, to a current density of 21 amperes per square foot. The bright range extends to the left to a deposit thickness of about 7.2 microns. It is noted that the bright range is slightly wider at the top of the plate than at the bottom. The bright current density range extends from about 21 to 57 amperes per square foot.

To the left of the bright range, the deposit becomes successively more hazy until a deposit thickness of about 11.2 microns is reached. This point corresponds to a current density of about 85 amperes per square foot. Moving still more to the left, a narrow, white, crystalline deposit is noted which extends to the thickness of 11.9 microns, or to the current density of 93 amperes per square foot. To the left of the white area is a grey, crystalline deposit which extends to the left end of the cathode. The extreme left end of the cathode was plated at a current density in excess of about 112 amperes per square foot.

On a single cathode, then, one sees the character of deposit which could be obtained at an infinite number of current densities. The current densities range from about 10 to 112 amperes per square foot, which is well in excess of any practical range of current densities. The cathode is burned at the high current density end, so no higher current density could be used. Practically no metal was deposited at the low current density end, and lower current densities could not be used to advantage. Following the teachings of my invention, one obtains, in a single test, an accurate idea of the behavior of a given plating process at every practical current density.

It is noted that in evaluating baths, the amount of current and the angle of the cathode should be so selected that the cathode will be burnt at the high current density end, and no more than slightly plated at the low current density end.

The cathode of Figure 7 was plated exactly as was the cathode of Figure 6, but the bath was used at a temperature of 40° C. instead of 20° C. The effect of raising the temperature is instantly apparent. The bright range has shifted to the left, and, as shown, it extends from about 6.7 microns to 13.3 microns of deposit thickness. Or, in terms of current density, the bright range has shifted from the location in Figure 6, 21 to 57 amperes per square foot, to the range 54 to 103 amperes per square foot.

The advantages and simplicity of this means of comparing and studying baths is readily apparent. Only two cathodes were required to show the effect of a change of temperature, and the effects of substantially every current density were revealed.

It is noted that the current density at the extreme left of the cathode of Figure 7 was not great

enough to burn the deposit. The current density, however, was almost great enough, and it was not desirable to change the operating conditions when comparing the results.

5 The cathode shown in Figure 8 was plated under substantially the same conditions as the cathodes of Figure 7. However, the cathode was not sealed in place, but was simply inserted in the cell with one end in the slot 4 and with the opposite end in the near corner. The cathodes of Figures 9, 10, and 11, similarly, were not sealed around the edges.

As has been noted above, cathodes which have not been sealed in the cell display low current density effects by reason of current leakage at the plate edges. The current leakage lowers the current densities at the edges of the plates, with a consequent shifting of the deposit zones. At the bottom edge of the plate, for instance, the lowering of the current densities causes a shift of the deposit ranges to the left. The scale of deposit thicknesses in Figures 8, 9, and 10 refer to the thicknesses found along a line parallel to the scale and midway of the cathode height.

15 The cathode of Figure 8 was plated with a bath of unknown composition. A bath such as the one mentioned in connection with the cathode of Figure 6 was supplied to a customer, and, after a considerable time, the customer complained that the bath no longer gave bright deposits. A sample of the customer's bath was examined according to the processes of this invention with the result shown in Figure 8.

Comparison of the cathode of Figure 8 with Figure 7 shows that the character of the bath changed considerably in use. Instead of one bright range extending from 54 to 103 amperes per square foot, the cathode of Figure 8 has two bright ranges. There is seen a lower range from a deposit thickness of about 1.7 to 2.3 microns, and an upper range from 4.1 to 7.8 microns. These correspond to current density ranges of 14 to 19 amperes per square foot and 33 to 62 amperes per square foot, respectively.

45 The cathode of Figure 9 illustrates the results obtained with a bath of the following composition:

Cadmium oxide (CdO).....	grams per liter...	43
Sodium sulfate (Na ₂ SO ₄).....	do.....	60
Sodium cyanide (NaCN).....	do.....	130
Cobalt sulfate (CoSO ₄ ·7H ₂ O).....	do.....	10
Nicotine.....	drops per liter...	4

A very narrow bright range is seen extending from a deposit thickness of about 3.2 to 5.1 microns. The bright current density range then extends from 26 to 40 amperes per square foot. It is readily apparent that an experimenter testing this bath by prior art methods would probably not find this narrow bright range.

It will be understood that no claim is made herein to the use of nicotine as an addition agent, as such subject matter forms no part of the present invention.

65 The cathode shown in Figure 10 likewise displays a rather narrow bright range. The cathode was plated according to the procedure followed in preparing the cathode of Figure 6, but a bath of the following composition was used:

Cadmium oxide (CdO).....	grams per liter...	43
Sodium sulfate (Na ₂ SO ₄).....	do.....	60
Sodium cyanide (NaCN).....	do.....	120
Nickel sulfate (NiSO ₄ ·7H ₂ O).....	do.....	1
Turkey red oil.....	cc. per liter...	10

The bright range extends from a deposit thickness of 6.2 to 10.8 microns. The computed bright current density range, then, is 49 to 84 amperes per square foot.

The cathode of Figure 11 was plated with the same bath and under the same conditions as was the cathode of Figure 6, except that in this instance there was used a test cell with parallel anode and cathode, as seen in Figure 2. The record on the cathode is, in effect, magnified. It is noted that a cathode plated as was the cathode of Figure 6, except that the anode was rotated until it was parallel to the cathode, was no different in appearance than the cathode shown in Figure 6, and no useful purpose would be served by a separate illustration.

It will be observed that the thickness of deposit is employed as a convenient mode of expressing the location of a bright range or other area. It will be apparent that if the cathodes had been plated a longer or shorter time, the deposit thicknesses would be greater or smaller, but, of course, the areas would not be shifted and the current densities would be unchanged.

While the cathodes are shown with a straight line at the liquid level, it will be understood that there is in fact an uneven, discolored line because of the high current density effect ordinarily noted at the surface of an electrolyte.

By reason of a current leakage at the edges of the unsealed cathodes of Figures 8, 9, 10, and 11, the areas tend, as noted above, to curve to the left near the bottom of the cathodes. This shift to the left indicates, of course, that the deposit was made at a somewhat lower current density near the bottom of the cathodes. This effect is not particularly objectionable in practice, and sealing of the cathodes, or equivalent expedients, are not ordinarily worth the extra time and effort required.

To avoid the effects of eddy currents set up in the electrolyte, it is desirable to agitate the electrolyte during the plating operation. Such agitation also causes the deposition to proceed at higher current densities because the depletion of metal ions, which occurs with quiet solutions, will be avoided. The agitation may be accomplished in any desired manner as by stirring by hand, by stirring with a motor, or by withdrawing a portion of the solution at one point and returning it at another. While agitation is in some instances valuable, for most purposes it is unnecessary.

The applications and advantages of the processes and apparatus of my invention have been partly set forth above. My invention is particularly valuable for the study and evaluation of plating processes with particular reference to the character of deposits obtained at any of an infinite number of current densities. Addition agents, brightening agents, anodes, plating baths generally, and other such plating process materials may quickly be compared and evaluated, as may the influence of such process factors as temperature, condition of work to be plated, and the like. Throwing power and other properties of plating baths may be investigated according to the teachings of my invention. The relative throwing power, or deviation of the metal ratio from the primary current ratio, may be estimated, for instance, by comparing the deposit thickness at any point with that obtained with a solution of zero throwing power, such as an acid copper solution.

One very convenient use of the processes of

my invention is the study of the efficacy of preparations intended to be used in treating electrodeposits, or, conversely, for the study of the effects of such preparations on electrodeposits from new types of baths, etc. A new bright-dip for cadmium, for instance, may be evaluated by dipping one cathode in the new dip and comparing with an identical cathode treated with a standard bright-dip. The effects of the bright-dips on deposits plated at numerous current densities is at once evident. Similarly, a cathode plated in a new type of bath may be held by the long edge and partially immersed in a standard bright-dip. The treated portion can easily be compared with the untreated portion to determine the response of the deposit to the bright-dip.

The above examples have been discussed with particular reference to cadmium, but the processes and apparatus of my invention are obviously applicable to the electrodeposition of any metal or alloy. The electrodeposition of such metals as zinc, tin, nickel, rhenium, copper, and chromium, for instance, has been studied with excellent results. The electrodeposition of numerous alloys, such as zinc-mercury and cadmium-mercury alloys, has also been successfully studied.

It will be readily understood that the cell may be made in various shapes and designs. The boxes of Figures 1 and 3, for instance, could be made to conform to the shape of the effective volume of electrolyte. Numerous other forms which would hold the cathode in a suitable position and would suitably locate the anode will readily occur to those skilled in the art.

While I have disclosed a number of specific processes and apparatus, I do not intend to be limited thereby, the scope of my invention being apparent from the following claims.

I claim:

1. In a process of the character described, the step comprising passing current thru a confined body of a solution of an electrolyte which is confined on two sides by boundary planes which intersect at an angle less than 90° and employing a cathode which constitutes one of said boundary planes the remaining boundary planes being constituted of non-conducting material whereby different areas on the cathode receive current thru different magnitudes of electrolyte solution cross-sectional area taken in planes normal to the direction of current flow and employing an anode located far enough outside of the portion of the body of electrolyte solution which is bounded by said two boundary planes that it does not interfere with the variation of current at the cathode.

2. In an apparatus of the character described, a rectangular box of non-conducting material for holding electrolyte, an anode located at one end of the box, and a flat, vertical, plate cathode located in the opposite end of the box with one vertical edge in a vertical corner of the box and extending diagonally from the corner of the box to the opposite side, the cathode meeting said side at an obtuse angle and meeting the opposite side at an acute angle.

RICHARD O. HULL.