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ANALYTICAL ELECTROPLATING CELL

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This invention is that of an electroplating cell for use in analyzing an electroplating solution to determine optimum plating conditions for it. The invention includes also the method of determining the optimum plating conditions for a plating solution, by application of the steps used in operating with the cell of the invention.

Heretofore, the apparently most helpful, available analytical plating cell is the one known as the Hull cell. It consists of a rectangular trapezoidal container with its two parallel sides serving as insulators between its two remaining opposing sides which are the anode and cathode. The anode surface is perpendicular to the two parallel sides, and thus the cathode surface is inclined to them. Because of this inclination of Hull's straight cathode, the current density along its length is variable. This provides some correlation between the appearance of the electrodeposit with the current density, by means of a single simple plating run in the cell.

However, the Hull cell has two main drawbacks, namely: (a) the current distribution along its cathode must be determined by empirical means, and (b) this distribution is such that much of the essential plating information is bunched together over a narrow portion of the cathode. As a result, the assistance the plater can obtain from the Hull cell has been, and is, limited.

The electroplating cell of the invention not only overcomes the various shortcomings of the Hull cell, but also provides means by which the plater can obtain more directly and simply more helpful indications of the plating characteristics of the plating solution tested and of the optimum plating conditions to use with it.

For example, the cell of this invention gives a linear distribution of the current density directly along its cathode. It also enables the current density to be calculated directly from the total current and voltage of the cell at the time of the test. These features of this new cell occur not only with solutions manifesting low polarization, but also even with those showing high polarization.

Moreover, the new cell enables the quantitative measure of polarization to be predicted from the simple measurements on the cell and the electrical conductivity of the solution. This result follows by considering that the polarization at an equipotential surface, such as an electrode, is constant over its entire surface even though the current density may vary. Prior to this discovery, it was expected that any polarization over the surface of such electrode would vary with the current density, and thus disturb any straight line relationship which might exist for the electrode under conditions of no polarization.

Considered generally, the cell of this invention has a closed bottom and rising vertically from it four sides or walls, particularly shaped and positioned relative to one another and joining to provide with the bottom the basin to hold the solutions to be tested. Two immediately adjacent sides are straight and the other two are curved

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hyperbolically in horizontal cross-section. Thus, the four sides as so joined together present in horizontal cross-section a four-sided figure having two straight sides intersecting, one of which corresponds to the analytical equation: y equals zero, and the other of them is represented by the equation: y equals x ; and the two hyperbolically curved intersecting sides correspond respectively to the equations: $x^2 - y^2$ equals L^2 , and xy equals one-half of $r^2 L^2$, wherein L is the length of one of the two straight sides, and r is the ratio between the respective lengths of these two straight sides. Two opposing sides (i.e. one of the two straight sides and the one opposing it, of the two curved sides) of the cell serve respectively to support the two opposed electrodes, and the other two opposing sides then are the insulators between these two opposed electrodes. In addition, the two straight sides intersect at an angle of essentially 45° to one another, and the inwardly facing surfaces of the two curved walls are segments of hyperbolic cylinders orthogonal to each other at their junction, and with each of them separately respectively orthogonal to one of the straight sides and asymptotic to the other.

The electrode that backs up against the straight side is flat, and is generally preferred to serve as the cathode. The other electrode, generally preferred to serve as the anode, is curved and with its surface that faces the flat electrode, being hyperbolically curved. As is explained below in relation to the detailed description of the cell, under certain conditions the two opposing electrodes even can serve as two of the four walls of the cell, which together with the bottom provide the basin to confine or contain the plating solution to be tested.

The foregoing character of the individual walls of this cell and the positional relationship between them is illustrated by, but not restricted to, the specific example illustrated in the accompanying drawings wherein:

Figure 1 is a perspective view of the cell of this invention;

Fig. 2 is a plan view of the cell of Fig. 1;

Fig. 3 is an enlarged fragmentary plan view of the corner formed by the intersection of the two straight sides of the cell of Fig. 1;

Fig. 4 is an enlarged fragmentary plan view of the diagonally opposite corner from that of Fig. 3;

Fig. 5 is a further enlarged fragmentary horizontal section of the corner shown in Fig. 3, but illustrating in addition an electrode in place;

Fig. 6 is a further enlarged, fragmentary vertical section of a corner formed by the bottom and one of the walls serving as a back up for an electrode, and also showing an electrode in place; and

Fig. 7 is a shortened fragmentary vertical section through the upper part of the two side walls acting as back ups for the two electrodes, and showing a cover in place.

In Figure 1, the cell (designated as a whole by the reference numeral 30) has its bottom or base 10 and rising vertically from it the straight sides or walls 11 and 12 forming with one another an angle of 45° at the corner 13 at which they intersect, and the curved sides 14 and 15 similarly rising vertically from base 10 and each constituting respectively separately a segment of a rectangular hyperbolic cylinder and intersecting with the other orthogonally to form the corner 17. The other end of curved side 14 also orthogonally intersects the lefthand end of wall 12 to form with it the corner 18. Similarly, the other end of wall 15 orthogonally intersects the lefthand end of wall 11, forming with it corner 19. The corners 13, 17, 18 and 19 and also the junctions of the bottom with the four walls are all liquid tight.

On the inner side of wall 12, electrode-holding groove 20 runs vertically down into the bottom 10 and con-

veniently adjacent to and continuous with the inner surface of wall 11. Likewise, at the other end of wall 11 a similar groove 22 runs vertically in that end of wall 15 to the bottom 10. Thus, the vertical grooves 20 and 22 in walls 12 and 15 can serve to hold an electrode (usually the cathode) in place in front, and with its back resting against the inside surface, of wall 11.

A corresponding groove 23 in the inside face of wall 12 at its lefthand end extends vertically down to the base 10 and opposite that groove a corresponding groove 24 at the lefthand end of wall 15. Thereby, the oppositely-facing grooves 23 and 24 can serve to hold in place an electrode (usually the anode) with its back against the inside face of wall 14.

Horizontal groove 25 in the upper surface of base 10 runs transversely along its junction with the inner face of wall 11 and advantageously joins the lower end of each of the vertical grooves 20 and 22 respectively. Thereby, the bottom edge of the electrode can fit into the horizontal groove 25. A similar horizontal groove 27 at the opposite junction of the upper surface of base 10 with the lower end of the inner surface of wall 14 extends transversely along that junction to join the lower ends of vertical grooves 23 and 24 respectively. Thereby, the bottom edge of the electrode (e.g. the anode) can fit into the horizontal groove 27 better to be held against the inner surface of vertical wall 14.

To restrain plating solution from finding its way between the electrodes and the respective inner surface of each of the walls 11 and 14, and for precise work, each vertical end of electrode is enclosed in the fold of a gasket U-shaped in transverse section across its width and inert to the plating solution, such as gasket 28 (Fig. 5). Similarly, the bottom edge of each of the electrodes is enclosed in the fold of a similar gasket extending between each pair of opposed ends of walls 12 and 15, for example, as shown by gasket 29 in Fig. 6. The gasket can be otherwise shaped across its width.

Since these gaskets (U-shaped in section across the width) provide a liquid-tight fit, then an alternative modification of the cell can be a receptacle open at two vertical ends so as to be U-shaped in vertical elevation and consisting of its base 10 and walls 12 and 15 (one straight and the other hyperbolically curved) liquid-tightly joined to the base, and having a continuous U-shaped groove in the inner surface adjacent each of the open ends, such as the joined grooves 20, 25 and 22 and the joined grooves 23, 27 and 24 respectively; whereby the continuous U-shaped groove consisting of joined grooves 20, 25 and 22 can receive in liquid-tight engagement a straight electrode with its two side and bottom edges inserted in a gasket (U-shaped in cross-width section), and the continuous groove consisting of the joined grooves 23, 27 and 24 can receive likewise the other (and hyperbolically curved) electrode with its two side and bottom edges similarly inserted in a gasket (U-shaped in cross-width section). In that way the two electrodes serve as the third and fourth sides that complete the cell.

If it is desired to keep the atmosphere out of contact with the exposed surface of the plating solution and the upper exposed portions of the electrodes, and likewise to prevent general escape into the atmosphere of any gases coming from the plating solution during the plating tests, the top of the cell 30 is closed off by a cover 32 (Fig. 7). When the top edges of the electrodes 33 and 34 extend above the tops of the walls 11 and 14 respectively (which is desirable to keep plating solution from running over the top of an electrode and between it and its respective supporting wall), the under-side of cover 32 has horizontal grooves 35 and 36 so positioned and of such depth and side to side length for them to fit in registry over the exposed top ends 38 and 39 of electrodes 33 and 34 respectively. To avoid building up of undue gas pressure between

the top surface of the plating solution and the under side of the cover, a suitable vent can be provided in the cover.

Fig. 2 is drawn to scale and gives the correct shape of the curved walls 14 and 15 for the symmetrical modification of the cell of the invention, i.e. wherein the two straight sides 11 and 12 are equal to one another. In such case, the angle between them at corner 13 is still 45°, and walls 14 and 15 also are equal to one another in length.

The cell of the invention is most effective with the angle between the straight sides being 45°. However, it is recognized that in production, it may not be possible to turn out every cell with that angle being exactly 45° without even the slightest variation. However, with such small variations that thus normally would occur, the cell can give its useful and advantageous results, and is effective, at variations of possibly even approaching about a one degree variation, or so. Accordingly, the angle between the straight sides is referred to as "essentially 45°" to cover such indicated possible variation.

Cell 30 is prepared from any suitable material resistant and inert to the plating solutions under the plating conditions, for example, glass or other suitable ceramic or any acid and/or alkali resistant plastic. Such plastic can be opaque such as hard rubber, "Bakelite," rigid Vinylite or polystyrene, or translucent or transparent as with clear polystyrene or methyl methacrylate polymer, and others. Cover 32 can be of any similar such resistant or inert material. Either the cell or its cover or both can be made of any metal covered with a protecting sheet of any similar inert or resistant material such as rubber or any of the just mentioned polymers or any other of them that is suitable.

Either of the electrodes, and especially the straight one, can have permanent graduations marked along a horizontal edge or elevation to facilitate reading the width and location of any part of the electrodeposit.

In using the cell of this invention, the electrodes are inserted in their respective sets of slots, and its basin (defined by its base and the four walls) is filled to a definite depth with the plating solution to be tested. Then an electric current of suitable amperage is passed through the anode, into the plating solution, and out through the cathode in usual manner. After a predetermined suitable time, the plating is discontinued and the cathode removed, rinsed and dried and examined.

Then, with respect to the electrodeposit made on the cathode in the testing of a plating solution in the cell of this invention, the current density (designated as i) for a particular character of deposit at its location along the length of the cathode is calculated from the following formula:

$$i = \frac{2I}{LA}x$$

wherein

I is the total current,
 L is the length of cathode exposed to the solution,
 A is the area of cathode exposed to the solution, and
 x is the distance measured along the cathode from the intersection of the two straight sides to the location at which the current density is desired;

all expressed in units in the same system.

In addition, the total polarization (designated by V_p) for the cathode and anode and corresponding to the average current density on the cathode is calculated from the formula:

$$V_p = V - \frac{ILr^2}{K_cA}$$

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wherein

V is the total voltage across the cell,

K_c is the electrical conductivity of the solution tested, and

r is the ratio of the length of the straight insulator side to L (i.e. the length of cathode exposed to the solution).

In working with a symmetrical cell (e.g. as the one indicated by the modification illustrated by Fig. 2), r is one.

While the invention has been explained in relation to certain specific embodiments of it, it is understood that various modifications and substitutions can be made in any of them within the scope of the appended claims which are intended also to cover equivalents of these specific embodiments.

What is claimed is:

1. The method of simultaneously determining the comparative appearance of the electrodeposition obtainable from the same plating bath under differing current densities and in a single plating operation, which method comprises passing an electric current from an anode through a confined body of the plating bath to a cathode while the bath is confined at its bottom and confined on two sides by intersecting vertical flat straight boundary planes that form an acute included angle and are positioned relative to one another so that one such side is represented by the analytical equation y equals zero while the other of them corresponds to the equation x equals y ; and then having its confinement completed on two other sides by a curved boundary plane for each of them, such that both of these two curved boundary planes are hyperbolically curved in horizontal cross-section with their inner surfaces corresponding respectively to the equations $x^2 - y^2$ equals L^2 , and xy equals one-half of $r^2 L^2$, wherein L is the length of one of the two straight planes, and r is the ratio between the respective lengths of the two straight sides; and the two curved planes are segments of hyperbolic cylinders and orthogonal to each other at their junction and each of them is orthogonal to its respectively adjacent straight planes and asymptotic to the other; one of the electrodes providing one of the straight planes, and the other electrode providing the curved plane positioned opposite to the first electrode.

2. The method as claimed in claim 1, wherein the two straight boundary planes are equal in length horizontally.

3. The method as claimed in claim 1, wherein the two straight boundary planes are unequal in length horizontally.

4. An analytical electroplating cell for use in depositing on the cathode in a single electroplating run an electrodeposition showing simultaneously in respectively different portions of it the different results obtainable at various current densities from a plating solution, which cell comprises a bottom and in liquid-tight junction with it and rising vertically from it four side walls liquid-tightly held together so as to form with the bottom an electrically non-conductive basin to receive the plating solution to be tested, two immediately adjacent sides being straight and forming an acute included angle and thereby being positioned relative to one another so that one such side is represented by the analytical equation y equals zero while the other of them corresponds to the equation x equals y ; and the other two sides are hyperbolically curved in horizontal cross-section with their inner surfaces corresponding respectively to the equations $x^2 - y^2$ equals L^2 , and xy equals one-half of $r^2 L^2$, wherein L is the length of one of the two straight sides and r is the ratio between the lengths of the two straight sides; and thereby the two curved sides are segments of hyperbolic cylinders and orthogonal to each other at their junction and each of them is orthogonal

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to its respectively adjacent straight side and asymptotic to the other; and means to hold separately against the opposing surfaces of a pair of opposing walls opposing electrodes, the one against the straight wall being straight and the other conforming to the shape of the curved wall.

5. An electroplating cell as claimed in claim 4, wherein one pair of opposing walls is omitted.

6. An electroplating cell as claimed in claim 4, wherein one pair of opposing walls consists of the electrodes each held separately in liquid-tight junction with the base and the ends of the other pair of opposing walls.

7. An electroplating cell as claimed in claim 4, wherein the two straight sides are of equal length so that r equals one and the cell thereby is symmetrical about the longer diagonal of its horizontal cross-section.

8. An electroplating cell as claimed in claim 4, wherein the two straight sides are of unequal length and whereby the two curved walls are also of unequal length.

9. An analytical electroplating cell comprising an electrically non-conducting receptacle U-shaped in vertical cross-section and open at two opposed vertical ends, and consisting of a four-sided base and in liquid-tight junction with it and rising separately and vertically from each of two opposing sides of it, a side wall, each of which respectively has the same horizontal shape and length as its corresponding side of the base, from which it rises; one of the open ends of the receptacle being adapted to receive, in liquid-tight engagement with its straight wall, base, and curved wall, a flat electrode having one end intersecting the straight wall at an angle of essentially 45° and the other end of the electrode positioned orthogonal to the curved wall; and the other end of the receptacle being adapted to receive, in liquid-tight engagement with its straight wall, base, and curved wall, an electrode hyperbolically curved in horizontal cross-section and with its convex surface facing the straight electrode and positioned with one vertical end orthogonal to the straight wall and the other vertical end orthogonal to the curved wall and asymptotic to the straight electrode; and means for holding each of the thus positioned electrodes in liquid-tight engagement with the receptacle.

10. An analytical electroplating cell comprising an electrically non-conducting receptacle U-shaped in vertical cross-section and open at two opposed vertical ends, and consisting of a four-sided base and in liquid-tight junction with it and rising separately and vertically from each of two opposing sides of it, a side wall, each of which respectively has the same horizontal shape and length as its corresponding side of the base, from which it rises; a straight groove positioned vertically adjacent each end of the surface of each of the two walls facing the opposing wall; a horizontal groove at each end of the upper surface of the base adjacent the open ends of the receptacle and each of them respectively joining the bottom ends of the two opposing vertical grooves at its respective end of the vertical walls, whereby each of the two separate sets of three grooves each (namely, two vertical grooves and one horizontal groove with its ends joining the lower ends of the two vertical grooves) forms a continuous over-all U-shaped groove at its respective end of the two vertical walls; one of the vertical walls being flat over its entire surface facing the other wall, and the latter being hyperbolically curved in horizontal cross-section to appear as a segment of a hyperbolic cylinder with its convex surface facing the entirely flat wall; the groove across one end of the base being straight and intersecting the straight wall at an angle of essentially 45° and at its other end being orthogonal to the curved wall, and the groove across the other end of the base being hyperbolically curved and

being orthogonal to the straight wall where they intersect, and at its end intersecting the curved side being orthogonal to it and asymptotic to the other groove in the base; whereby the U-shaped groove, the bottom of which is straight serves to receive an electrode that is completely flat, and the U-shaped groove at the other end of the receptacle serves to receive an electrode that is hyperbolically curved horizontally and with its convex surface facing the other end of the receptacle.

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