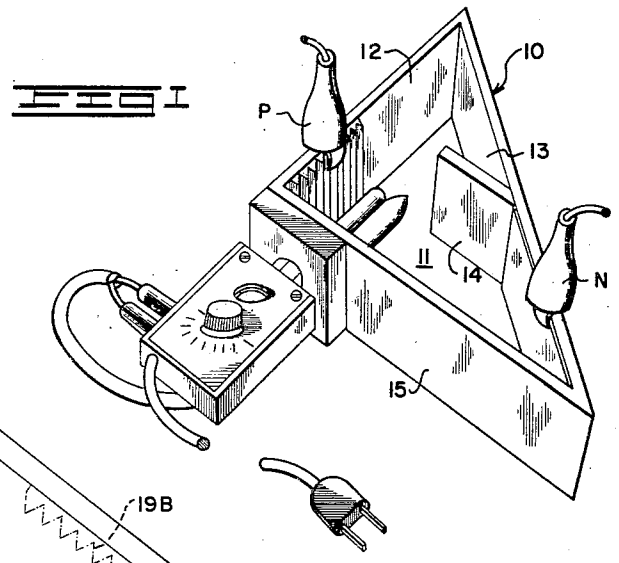
Feb. 11, 1964 R. O. HULL, JR., ETAL 3,121,053

ANALYTICAL ELECTROPLATING APPARATUS

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FIG I



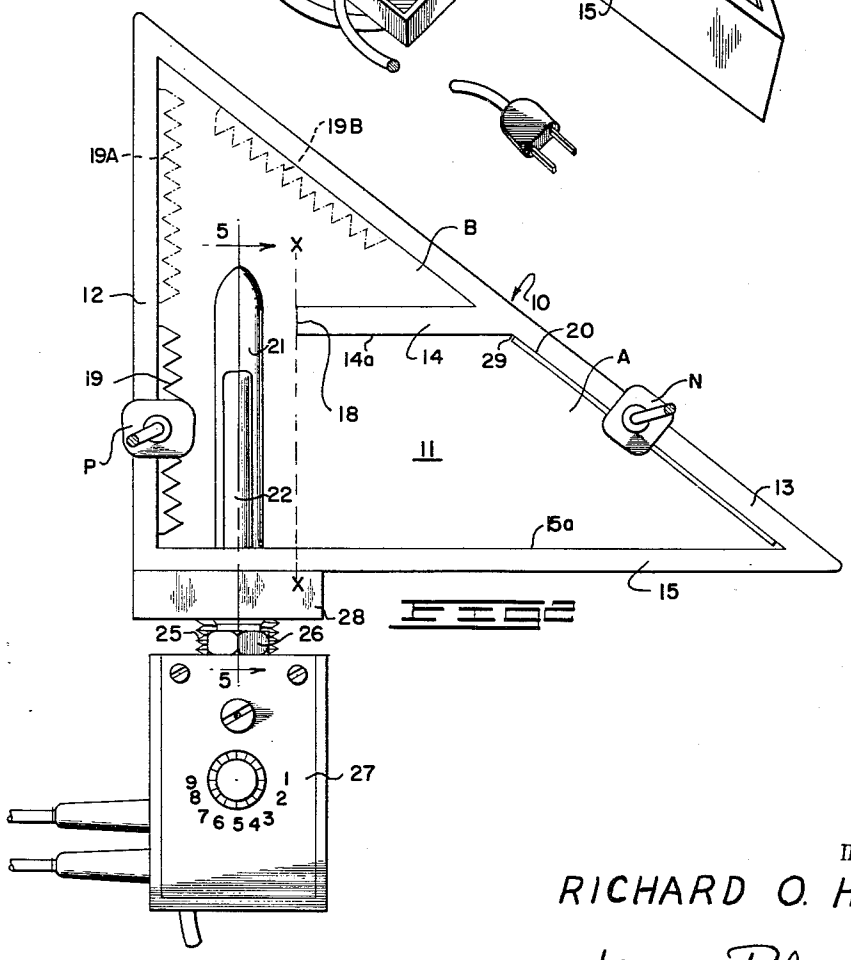


FIG 2

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ANALYTICAL ELECTROPLATING APPARATUS

Filed April 13, 1961 2 Sheets-Sheet 2

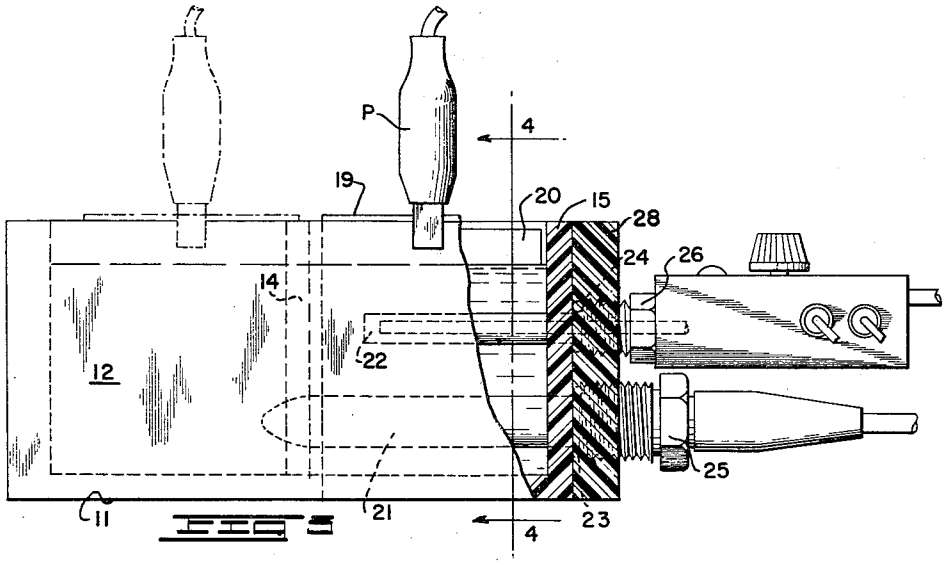


FIG 3

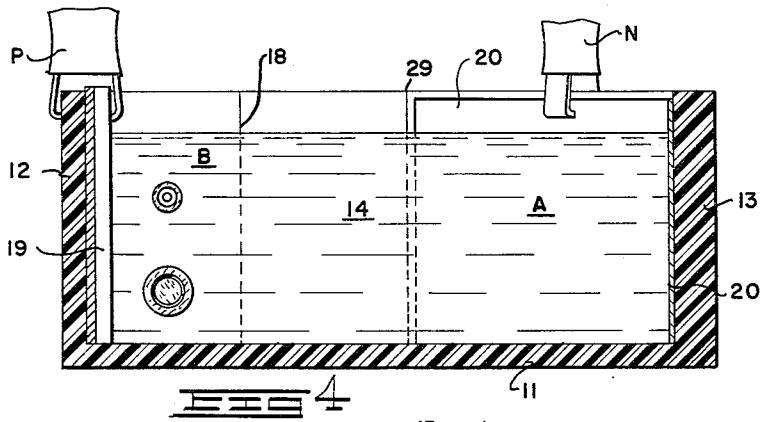


FIG 4

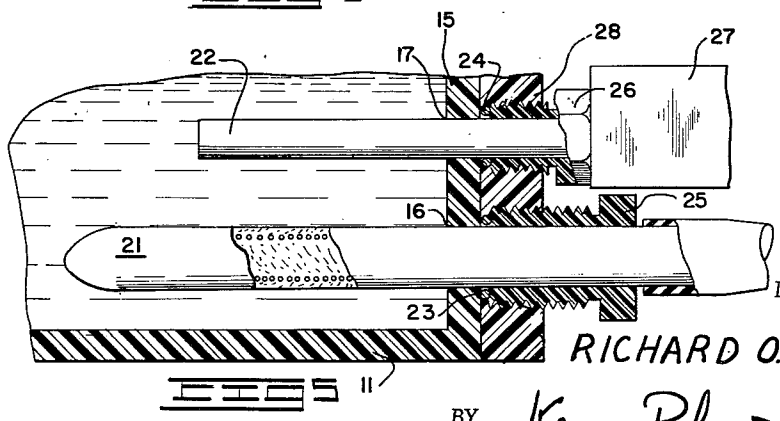


FIG 5

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United States Patent Office 3,121,053 Patented Feb. 11, 1964

3,121,053

ANALYTICAL ELECTROPLATING APPARATUS

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Filed Apr. 13, 1961, Ser. No. 102,818
2 Claims. (Cl. 204—195)

This invention relates to analytical electroplating apparatus. More particularly, it concerns electroplating cells of a new and improved design for use in the examination and evaluation of processes of electrodeposition, electrode materials and electrolyte compositions.

Some years ago, a new form of apparatus for the study of electroplating was developed which subsequently has come into widespread use as an analytical tool. This basic type of apparatus is referred to as a Hull cell, after the original inventor, and is described in U.S. Patent 2,149,-344.

Although the Hull cell in general provides a very useful analytical device for investigating electroplating operations, experience in the use of such cells has revealed certain deficiencies. For example, with the apparatus disclosed in U.S. 2,149,344, there is inadequate provision for the control of solution composition, polarization, electrolyte temperature and other variables which occur during the electrolysis. Obviously, if the results of any particular run in a Hull cell are to be properly interpreted by the investigator, the analytical apparatus should allow the different process variables to be controlled in a known manner.

One example of a difficulty which is encountered in the operation of Hull cells is variation in solution or electrolyte composition. Thus, when repeated tests are performed on a single sample of electrolyte, using the methods and apparatus available heretofore, a variation in metal content takes place due to limitation in the size of the anode area which is available for use. When an anode of insufficient size is used, excessive polarization also results. These factors critically influence the reliability of results and data obtained in the operation of a Hull cell, and it has been found that the ratio of the relative anode to cathode area is of major importance in maintaining the metal content of the bath at a desired level.

Another difficulty encountered in operation of Hull cells available heretofore is the temperature rise which occurs as the electrolyte sample is electrolyzed due to the passage of a relatively large current through a relatively small volume of electrolyte. Since the electroplating cells are made of material which is generally thermally non-conductive, it has not been practical to alleviate this temperature rise problem by surrounding the electroplating cell with a temperature controlled bath.

Another problem has been variation in composition of the electrolyte during electrolysis. This not only results in critical changes in metal content, but also produces changes in pH. Since pH control can be very significant in the type of analytical procedure which is carried out in a Hull cell, for example, in nickel plating, it is important that the pH of the electroplating solution undergo as small a change as possible during the analytical procedure.

Another problem encountered in the use of Hull cells is that of maintaining the electrolyte at controlled elevated temperatures so as to duplicate as closely as possible the conditions which will be found in commercial use of the electrolyte composition and other materials undergoing analysis. One solution to this problem of providing elevated temperatures involves the placement of a heating element within a depression in the base of a Hull cell in such fashion as to reduce any interference in the flow of current from the anode to the cathode by the heating element (see U.S. 2,760,928). However, while this type of

cell construction provides satisfactory results in the heating of the electrolyte, it introduces new problems. Thus, additions of solid chemicals to the plating bath during an analytical operation become entrapped in the depression in the cell. This creates difficulties in the cleaning of the cell and also in maintaining proper control on the electrolyte composition during the electroplating procedure.

A principal object of this invention is the provision of new improvements in analytical electroplating cells of the so-called Hull type.

Further objects include:

(1) The provision of new and improved forms of Hull cells which eliminate or substantially reduce variations in electrolyte composition during use of the test apparatus.

(2) The provision of new improvements in Hull cells which enable the anode area to be varied according to the requirements of the electrolyte being tested, i.e., which eliminate the need for restriction of the anode to a fixed area as in Hull cells known heretofore.

(3) The provision of new improvements in such electroplating cells which minimize pH change during electrolysis.

(4) The provision of improved analytical electroplating apparatus which makes possible close control of the anode to cathode ratio during electrolysis, resulting in satisfactory control over the metal content of the electroplating solution.

(5) The provision of improvements in the design of Hull cells which make it possible to include heating elements and heat control means within the cell without the need to form depressions or other offsets in the cell, so that such cells are easy to clean and maintain and can be manufactured and sold at a minimum cost.

Other objects and further scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description, while indicating preferred embodiments of the invention, is given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

These objects are accomplished according to the present invention by providing in an analytical electroplating cell of the Hull type, a partition which extends outwardly from the side of the cell upon which the cathode is supported, forming a cell portion or chamber extending outwardly from the cathode, and then providing a second cell portion or chamber externally of this first portion and placing in the second portion the anode elements and other auxiliary equipment which is desired for use with the electroplating cell.

The success of the present invention is due to a large extent to the discovery that the total volume of electrolyte contained in the electroplating cell can be varied considerably and can be substantially increased over the volume of electrolyte usable in comparable types of cells known heretofore, so long as the length of the cell portion or chamber formed by the partition which extends outwardly from the side of the cell upon which the cathode is supported is approximately equal to or greater than the width of this portion of the cell. Moreover, it has been discovered that such an arrangement creates a current distribution along the cathode panel, of such nature that reproducibility of test results can be obtained regardless of the anode position in the portion of the cell outside of this cathode containing chamber. In addition, it has been found that heating elements, thermostat control elements and the like can be placed right in the cell proper without materially affecting the reproducibility of test results, provided these added elements are positioned beyond the special sized cell portion or

chamber facing the cathode panel. These discoveries make it possible to produce new forms of Hull cells which alleviate the operational problems referred to above and also at a minimum cost, since the need for milling or special forming of the base or other portions of the cells is eliminated.

A more complete understanding of the construction of the new, improved electroplating cells of this invention can be had by reference to the accompanying drawings in which:

FIG. 1 is a perspective view of an analytical electroplating cell for determining plating characteristics of a plating bath in accordance with the present invention;

FIG. 2 is a plan view of the device shown in FIG. 1;

FIG. 3 is a side elevational view in partial section of the apparatus shown in FIG. 1;

FIG. 4 is a front elevation sectional view taken along the line 4—4 of FIG. 3;

FIG. 5 is a fragmentary sectional view taken along the line 5—5 of FIGURE 2 and enlarged with respect thereto.

Referring in detail to the drawings, the new cells of this invention have a cathode containing portion A and an anode containing portion B, so arranged relative to one another that a cathode member of predetermined cross-sectional area may be vertically mounted within the portion A and angularly disposed to the planes of current flow from the anode as directed by the configuration of the cell portion A.

Referring to FIG. 1 of the drawing, the new electroplating cell 10 comprises a base 11 to which are vertically fixed a back wall 12, a side wall 13, a partition 14 and a front wall 15. The base and walls of the cell 10 may be made from any suitable electrically non-conductive material and may be joined together in any suitable fashion so as to form a fluid-tight junction along the various mating edges of the sides and base to create a fluid-tight triangular cell. Various suitable nonconductive synthetic resins are available from which the base and sides of the cell can be formed. The cells may be produced by molding the plastic material into the desired shape or by cementing together sections of plastic cut out from sheet stock. Polymethacrylate has been found to be a particularly useful plastic from which the new cells may be constructed.

The anode member 19 is vertically mounted against the back wall 12 such as by being clamped thereto with the alligator clamp P which is electrically connected to the positive side of direct current electrical source (not shown). Similarly, the cathode member 20 is vertically mounted against the side wall 13 within the chamber A, such as by being clamped against the wall with the alligator clamp N, which is electrically connected to the negative pole of the direct current source.

A heating element 21 extends through a suitable opening 16 in the front wall 15 and an O-ring 23 is forced by the packing nut 25 around the heating element 21 and against the outside surface of the front wall 15 to form a fluid tight junction between the opening 16 and the heating element 21.

A thermostat probe 22 extends into the cell through the opening 17 in the front wall 15 and an O-ring 24 is compressed around the element 22 and in contact with front wall 15 to form a liquid tight seal by the threaded packing nut 26, which is carried in front of the thermostat control member 27. A block 28 is fixed to the outside of front wall 15 to provide suitable threaded support for the packing nuts 25 and 26.

The O-rings 23 and 24 used for sealing the opening around the elements 21 and 22 may be made of any suitable material which is impervious to the action of plating solutions to be analyzed in the cell, e.g., polychloroprene or equivalent synthetic rubber-like material.

The vertical partition 14 extends inwardly from the side wall 13 approximately parallel to the front wall 15 and terminates within the cell in a vertical edge 18 short of the back wall 12. The length of the partition 14 measured along the vertical wall 14*a* which faces the front wall 15 from the junction 29 of the partition 14 with the side wall 13, to the vertical edge 18 is at least equal to the perpendicular distance between the opposing faces 14*a* and 15*a* of the partition 14 and the front wall 15. Thus, the cathode chamber A which has been referred to before, is defined by the partition 14, the side wall 13, the front wall 15, the base 11 and a plane X—X which passes through the vertical edge 18 of the partition 14 perpendicular to the front wall 15. The cell portion or chamber B then comprises the remainder of the fluid containing volume of the cell and it is in this latter portion of the cell where the elements 21 and 22 and the anode member 19 are located.

In addition to the anode member 19, anode members 19*a* and 19*b* (as illustrated by dotted lines in drawing FIG. 2) may be employed in the cell or a single anode may be located in any one of these positions within the cell portion B.

Varying quantities of electrolyte may be analyzed or experimented upon by varying the depth of electrolyte introduced into the cell. Also, the size of the anode chamber B can be substantially extended over that illustrated in the drawings so that substantial variation in electrolyte volume can be realized using the cell constructions of this invention. The larger solution volume which can be utilized in accordance with this invention, with the same current density which could be employed in apparatus known heretofore, reduces the solution variation during any test procedure. Furthermore, the unique shape of the new cells allows virtually unrestricted circulation of the electrolyte, thus producing more uniform temperature conditions during electrolysis. Moreover, the ability of the new cells to accommodate larger anode areas provides for improved results in control of anode to cathode ratio and hence metal content of the electrolyzing solution. The increased volumes made possible by the new cell construction also minimize pH change as electrolysis progresses.

The new electroplating apparatus may be used in carrying out all analytical procedures for which Hull cells are known to be useful. The test equipment is particularly useful in obtaining data on electrolytes containing zinc, cadmium, copper, nickel and chromium.

A more complete understanding of the methods of use of the new apparatus may be had by reference to the following example of actual operation in accordance with the invention.

Example I

An analytical electroplating operation is conducted using apparatus as illustrated in the accompanying drawings, having a capacity of 534 ml. When this volume of solution is used, an addition of 4 grams of material to the test cell corresponds to an addition of one ounce per gallon in a larger producing plating operation. This volume of electrolyte also controls the plating area on the cathode so that established current density relationships are applicable. The cathode member is 4 inches in length and 2½ inches in height and is immersed to a depth of 2 inches in the electrolyte, giving an immersion area of 0.055 sq. ft.

A bright nickel electroplating solution having the following composition is employed:

	Ounces per gallon
Nickel sulfate	45
Nickel chloride	7
Boric acid	6

The electroplating operation is carried out at a temperature of 130° F. and a pH of 3.7. The test is conducted at 3 amp. current for five minutes. A nickel anode presenting a surface area of 0.2 sq. ft. is employed which, with the 3 amp. current, results in an anode current density of 15 amp. per sq. ft., which is normal for

the operation of a bright nickel solution. In prior electroplating cells of this general type, limitation in the size of the anode area normally resulted in current densities higher than normal, e.g., up to 60 amp, per sq. ft.

The cell operation is observed to proceed smoothly and periodic tests during the five minutes of operation upon the pH of the solution during electrolysis shows that there is a substantially less increase in pH than is experienced in the use of prior known electroplating cells of this general type. Also, many more tests can be made using the same electrolyte without depleting the solution of important components such as metal concentration, addition agents and brighteners.

At the completion of the run with the control solution, further runs are made on the control solution to which additional agents, brighteners or other chemicals have been added in order to determine the effect of these added materials on the electroplating results.

Example II

A chromium plating electrolyte is tested using apparatus as shown in the accompanying drawings and described above. For this test, an electrolyte of the following composition is employed:

	Ounces per gallon
Chromic acid	54
Sulfuric acid	0.54

The electrolyte is heated to a temperature of 130° F. and maintained throughout the test procedure at this temperature by means of the automatic thermostat control. When the electrolyte solution reaches the equilibrium temperature, the current is passed between an insoluble anode, for example, lead, having a surface area of 0.1 sq. ft. and a brass cathode with a surface area of 0.055 sq. ft. The test continues smoothly for ten minutes at 3 amperes current and is then discontinued, the data and test results being recorded and observed as explained in U.S. 2,149,-344, which describes the basic principles and mode of operation of so-called Hull cells. During the ten minute test run, very little increase in temperature is observed in the cell, even though a very high current is employed. A constant temperature is desired because when testing chromium plating electrolytes, a lower temperature might introduce a "burn" on the test cathode which would not be obtained in production. A higher temperature might introduce a haze which would not be present in production. Also, since the covering power of a chromium plating electrolyte increases as the temperature is lowered, a lower test temperature than is used in production will produce misleading results by showing better covering power than is obtained in production and conversely a higher temperature will show less covering power than would be obtained in production. These problems are effectively eliminated by the new test cell structures of this invention.

Having provided a complete description of the invention in such manner as to distinguish it from other inventions and from what is old, and having provided a description of the best mode contemplated of carrying out the invention, the scope of patent protection to be granted the invention is defined by the following claims.

We claim:

1. An analytical electroplating cell comprising:
(*a*) a base,
(*b*) a vertical back wall,

(*c*) a vertical front wall normal to said back wall,
(*d*) a vertical side wall fixed at an acute angle to said back and front walls,
(*e*) said base and walls being formed of electrically non-conductive material and forming a fluid-tight triangular cell adopted to contain plating solution to be tested,
(*f*) a vertical partition extending inwardly from the side wall approximately parallel to said front wall, said partition terminating within said cell in a vertical edge short of said back wall, the length of said partition facing said front wall from the junction of the partition with said side wall to said vertical edge being at least equal to the perpendicular distance between the opposed faces of said partition and said front wall,
(*g*) an anode electrode vertically held against said back wall, and
(*h*) a cathode electrode vertically held against said side wall between said partition and said front wall.

2. An analytical electroplating cell comprising:
(*a*) a base,
(*b*) a vertical back wall,
(*c*) a vertical front wall normal to said back wall,
(*d*) a vertical side wall fixed at an acute angle to said back and front walls,
(*e*) said base and walls being formed of electrically non-conductive material and forming a fluid-tight triangular cell adopted to contain plating solution to be tested,
(*f*) a vertical partition extending inwardly from the side wall approximately parallel to said front wall, said partition terminating within said cell in a vertical edge short of said back wall, the length of said partition facing said front wall from the junction of the partition with said side wall to said vertical edge being at least equal to the perpendicular distance between the opposed faces of said partition and said front wall, said partition dividing said cell into:
(*g*) a first cell portion defined by:
(1) a plane which passes through said vertical edge perpendicular to said front wall,
(2) part of said front wall,
(3) the part of said side wall from the junction thereof with the front wall to the junction with said partition, and
(4) said partition, and
(*h*) a second cell portion which constitutes the remainder of said triangular cell other than said first cell portion,
(*i*) a heating element within said second cell portion,
(*j*) a thermostatic element for control of said heating element within said second cell portion,
(*k*) an anode electrode vertically mounted against said back wall, and
(*l*) a cathode plate vertically held against said side wall within said first cell portion.

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UNITED STATES PATENTS

2,149,344	Hull	Mar. 7, 1939
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