Jan. 14, 1969 J. W. HAAGEN-SMIT 3,421,989

MERCURY POOL ELECTRODE

Filed Nov. 24, 1964 Sheet 1 of 2

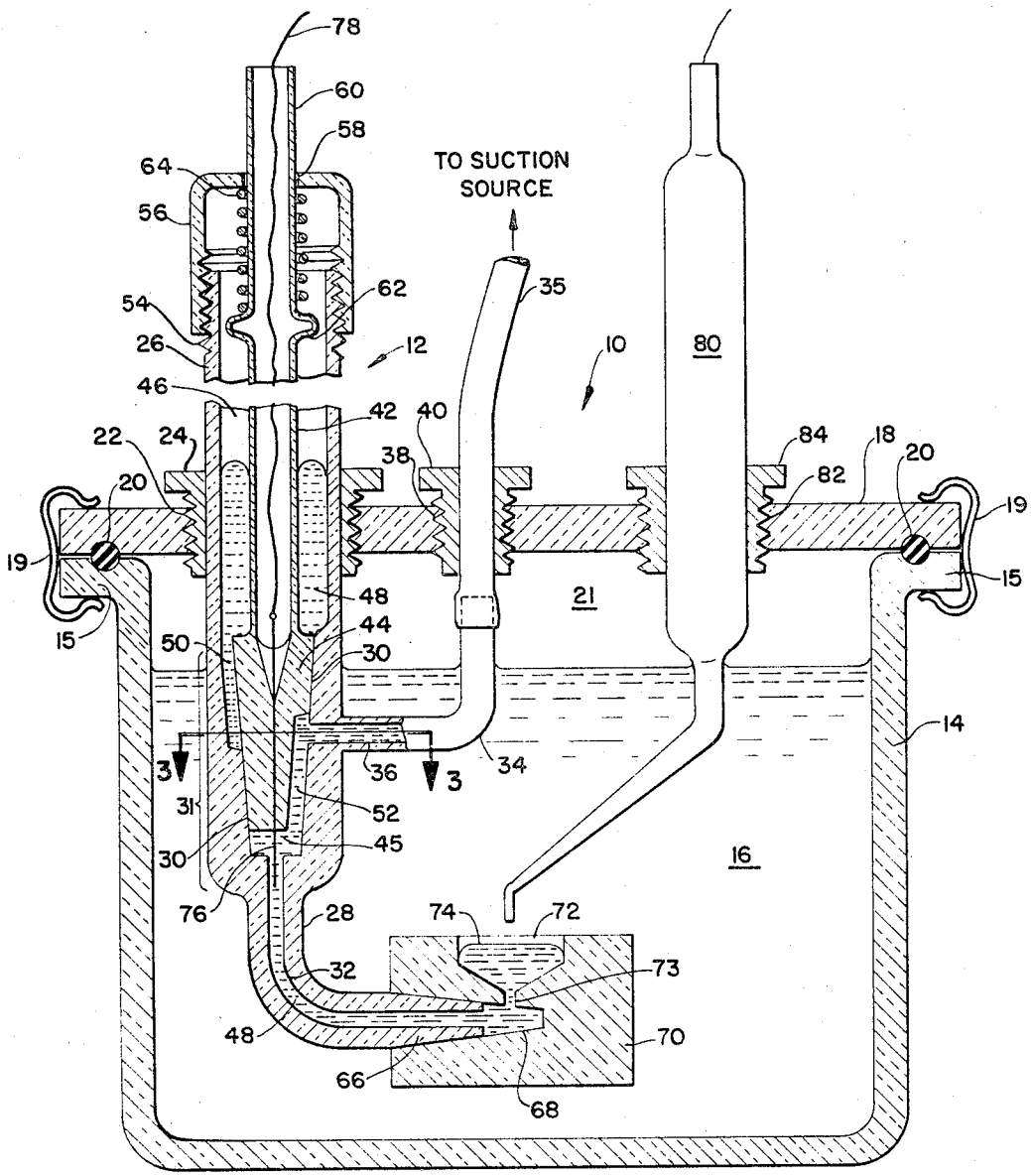


FIG. 1

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MERCURY POOL ELECTRODE

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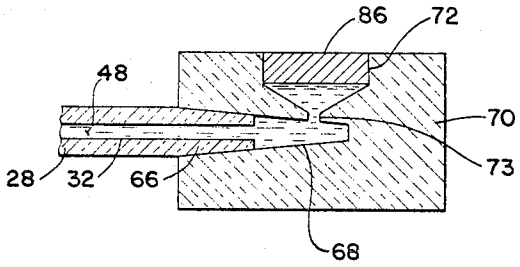


FIG. 2

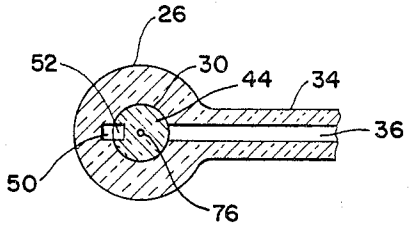


FIG. 3a

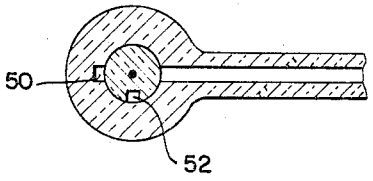


FIG. 3b

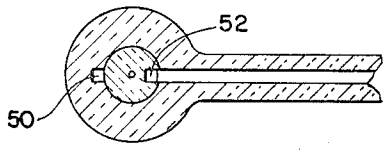


FIG. 3c

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MERCURY POOL ELECTRODE

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U.S. Cl. 204—195 14 Claims
Int. Cl. B01k 3/06

ABSTRACT OF THE DISCLOSURE

The specification discloses a mercury pool-type electrode for use in electrochemical analysis apparatus and is comprised of two tubular bodies, one within the other, forming a mercury reservoir therebetween and also defining a valve, an exchangeable electrode cup connected to the reservoir which allows various mercury surface areas to be in contact with a test solution and a suction source connected to the cup to empty the mercury from the cup. In operation, the mercury pool electrode and a reference electrode are sealably inserted into a sealed electrolysis cell containing the test solution and containing a gas which does not adversely affect the solution.

This invention relates to an improved electrode assembly of the mercury pool-type for use in electrochemical analysis apparatus.

In chronopotentiometry, polarography and similar electroanalytical techniques, mercury pools are often utilized as electrodes. An advantage of this type of electrode is that a smooth surface is exposed to the solution to be analyzed. However, after a mercury pool electrode has been used for one experiment, the mercury is no longer clean and must be replaced.

In certain experiments, the test solution must be sealed off from the ambient atmosphere during the electrolysis process to prevent interaction between the solution and the ambient air from possibly contaminating the solution. For such experiments, a sealed electrolysis cell is employed containing an atmosphere which will not adversely affect the solution.

In sealed electrolysis cells presently available, the mercury pool comprising one of the electrodes is retained in the bottom portion of the vessel, or container, which holds the test solution. Normally, a valved outlet located in the bottom wall of the vessel is provided for removal of the mercury.

Existing sealed electrolysis cells have several disadvantages. First, the utilization of a specially constructed vesel, having mercury removal apparatus mounted in the bottom wall, is required. Second, because the mercury pool is confined by the walls of the vessel, the dimensions of the vessel itself determine the surface area of the mercury pool electrode. Since it may be desirable to use mercury pool electrodes of different surface areas for different experiments, this can only be accomplished by having available an assortment of cells, the cost of which may create an economic burden. In addition, when different cells and accessory equipment are used in successive experiments, variables are introduced which may adversely affect the accuracy of comparative results.

It is an object of the present invention to provide an improved mercury pool electrode for use in sealed electrolysis cells.

It is a further object of the present invention to provide a mercury pool electrode for use in a sealed electrolysis cell, which electrode eliminates the necessity of using specially constructed electrolysis vessels.

It is a still further object of this invention to provide a mercury pool electrode in which mercury pools having various surface areas are made available, yet which may be used with the same electrolysis cell and accessory equipment, for conducting different experiments requiring different electrode surface areas.

In accordance with the present invention, a mercury electrode cup placed inside a sealed electrolysis cell, a mercury reservoir and a suction source are interconnected by a multi-position valve. By actuation of the valve to appropriate positions, the electrode cup may be filled with mercury from the reservoir, or emptied by means of the suction source. An intermediate, or "off", position isolates the mercury in the cup from both the reservoir and the suction source. Experiments are conducted with the valve in the latter position.

According to a specific exemplary embodiment of the invention, there is provided an electrode, adapted to be inserted into a sealed electrolysis cell, which comprises an outer, vertically-supported tubular body inside of which is coaxially mounted a small diameter tube. The upper end of the inner tube extends a short distance beyond the upper end of the outer tubular body. The lower end of the inner tube terminates in and is supported by the movable member of a three-position valve housed in the lower portion of the outer tubular body. The annular space between the inner and outer tubes serves as a reservoir for the storage of the electrode mercury.

A tubular side arm is attached at one of its ends to the side of the outer tubular body at the portion thereof housing the three-position valve, the other end being connected to a suction source. A lower tubular arm, attached to the bottom of the outer tubular body, interconnects the three-position valve with a removable cup which holds the mercury pool. A fine platinum wire extends through the valve into the interior of the lower tubular arm to provide connection between the mercury contained in the cup and an external circuit.

In use, the electrode is sealingly mounted in the lid of an "air-tight" electrolysis cell with its upper end extending upwardly from the lid. An ordinary, flat-bottomed beaker or other vessel may be used to hold the test solution in which the lower end of the electrode is immersed.

The valve position is controlled by manipulation of the upper end portion of the inner tube which protrudes above the upper end of the outer tubular body. In a first, or "fill," position, the annular space between the inner and outer tubes in which the mercury is stored is brought into communication with the lower tubular arms so that the mercury, by gravity feed, fills the cup to the desired level. In a second, or "off," position, the lower tubular arm (and hence, the cup) is isolated from both the annular reservoir space and the tubular side arm. Electrolysis experiments are performed with the valve in this position. In a third, or "remove," position, the suction

source is connected to the cup through the side and lower tubular arms, and the mercury in the cup is thereby removed by being drawn up to the suction source. To refill the cup with clean mercury from the reservoir for the next experiment, the valve is moved back to the first position.

By providing interchangeable cups of various sizes, mercury pool electrodes having various surface areas are made available. In addition, if an ordinary solid electrode is required for a particular experiment, a disc of solid electrode material may be fitted in the cup. In this case, the mercury in the lower tubular arm and in the cup contacts the lower surface of the disc electrode and serves as the electrical conductor connecting the disc with an external circuit.

The invention, together with further objects and advantages thereof, can best be understood by reference to the following description taken in conjunction with the accompanying drawings in which:

FIG. 1 is a side elevation view, in section, of a complete electrolysis cell employing an electrode constructed in accordance with the teachings of the present invention;

FIG. 2 is a side elevation view, in section, of an electrode block with a solid disc electrode in place; and,

FIGS. 3*a*, 3*b* and 3*c* are cross-sectional views taken along line 3—3 in FIG. 1.

Referring now to the drawings, FIG. 1 illustrates a complete electrolysis cell **10** with an electrode **12**, embodying the present invention, in place. The cell **10** comprises an ordinary, flat-bottomed vessel **14** which contains a solution **16** to be analyzed. The electrolysis vessel **14** is typically made of glass and has an outwardly-extending lip or flange **15**. The interior of vessel **14** is sealed "air-tight" by means of a lid **18** which may be fabricated of an acrylic material such as Lucite. Lid **18** may be sealingly secured over the open top of vessel **14** by any of a variety of commonly-used, well-known means. In the particular embodiment illustrated, a number of spring clamps **19**, spaced uniformly about the periphery of the cell, secure lid **18** to flange **15**. A gasket, such as O-ring **20**, squeezed between the opposing surfaces of lid **18** and flange **15**, serves as a sealing means to prevent gas leakage. The space **21** between the surface of the test solution **16** and the lid **18** is filled (by means not shown) with a gas which will not react adversely with the test solution **16**. Inlet and outlet ports may be provided in lid **18** through which the gas may be flowed into and out of space **21** so that a constant purging action is achieved. Additionally, various auxiliary or accessory electrodes along with means to add and remove test solution also may be mounted in lid **18**.

Electrode **12** is inserted through a threaded hole **22** in the "air-tight" lid **18**. A standard, threaded fitting **24** (the details of which have been omitted) is provided both as a support for electrode **12** and as a sealing member to prevent gas leakage around the electrode.

Electrode **12** comprises an outer tubular body **26**, the lower portion of which is positioned inside vessel **14**. The lower end of the outer tubular body **26** converges into an L-shaped, tubular arm **28**. The interior wall surface in the lower portion of the tubular body **26** is formed into a tapered section **30** generally coaxial with the longitudinal or vertical axis of the body **26**. Tapered section **30** forms the stationary part of a three-position valve designated generally by reference numeral **31**. The bore **32** of the lower tubular arm **28** communicates with the interior of the tapered section **30** at the latter's lower extremity. A tubular side arm **34** is secured to the outside wall of tubular body **26** at a point about midway between the upper and lower extremities of the tapered section **30**, the side tubular arm **34** including a bore **36** communicating with the interior of the tapered section **30**. A tube **35**, made of rubber or other flexible material, is attached to the end of the arm **34** and serves to connect the bore **36** of the arm **34** with a suction source (not shown) located exteriorly of the cell. A threaded fitting **40**, similar to fitting **24**, may be provided to seal the space around the tube **35** where it passes through lid **18**.

Positioned inside the outer tubular body **26**, and generally coaxial therewith, is an inner tube **42** which may be fabricated from small diameter glass tubing. Inner tube **42** terminates at its lower end in a tapered plug **44** made of glass or Teflon or the like. Inner tube **42** may be comolded with the tapered plug **44** or affixed to the plug **44** by any well-known method such as fusion if the plug **44** is glass, or with cement if the plug is made of Teflon or a similar material. The taper of plug **44** corresponds to that of the tapered section **30** of the outer tubular body **26** so that when the tapered plug **44** is nested or seated in the section **30**, the entire longitudinal surface of the plug **44** is uniformly in contact with the corresponding surface of the section **30**. In the nested or seated position of the tapered plug **44**, a small chamber **45** remains in the lower part of the tapered section **30**. An annular space **46** generally above the tapered section **30** is formed when the inner tube **42** is in position inside outer tubular body **26** and serves as a reservoir for the storage of mercury **48**.

A longitudinal channel or groove **50** is cut in the tapered section **30** extending from the upper extremity of section **30** down to a point a little more than half the distance between the upper and lower extremities of tapered section **30**. A similar channel or groove **52** is cut in tapered plug **44**. It extends longitudinally from the lower extremity of tapered plug **44** up to a point slightly above the lowest point of groove **50**.

The outer surface of the tubular body **26** near its upper end is provided with threads **54** adapted to receive a threaded cap **56**. The upper portion **60** of the inner tube **42** protrudes through a centrally located hole **58** in the threaded cap **56**. Sufficient clearance exists between the inner tube **42** and the hole **58** for the combined purpose of venting the annular reservoir space **46** to atmospheric pressure (for reasons explained below) and allowing unconstrained movement of inner tube **42**.

A bulge **62** formed on inner tube **42** serves as the lower seat for a light compression spring **64**. The upper end of the spring **64** bears against the inner top surface of the threaded cap **56**. The purpose of the spring **64** is to provide a downward biasing force, thus tending to prevent the operator from accidentally pulling the plug **44** from the seated position.

The L-shaped, lower tubular arm **28** terminates in a horizontal tapered section **66** which is adapted to be received in a tapered hole **68** bored in an electrode block **70**. The taper of the hole **68** corresponds to that of the tapered section **66** so that a sealing fit may be achieved when the electrode block **70** is mounted on the arm **28**. The electrode block **70** is preferably made of a fluorocarbon or an acrylic material such as Teflon or Lucite. A horizontally-disposed electrode cup **72**, formed in electrode block **70**, is connected by means of a passageway **73** to the tapered hole **68**.

Electrode block **70**, which is detachably mounted on the lower tubular arm **28**, may be replaced by other electrode blocks having different size electrode cups. The interchangeability of electrode size is found to be of great value in that a variety of experiments can be performed using the same electrolysis vessel, auxiliary electrodes, and other accessory equipment, thereby eliminating many of the variable which frequently affect experimental results.

A platinum wire **76** is provided in the tapered plug **44** as a means of electrically connecting to external circuitry the mercury pool **74** accumulated in the electrode cup **72** and lower tubular arm **28**. A small hole is formed through the tapered plug **44** generally along its longitudinal axis. This hole receives the platinum wire **76**, the upper and lower ends of which extend from the top and bottom surfaces, respectively, of tapered plug **44**. If the

plug 44 is made of Teflon or a similar material, a suitable cement may be used to hold the wire 76 in place. If the plug 44 is glass, the wire 76 may be fused to the plug with molten glass. The lower end of platinum wire 76 extends into the bore 32 of the lower tubular arm 28 and the upper end of the platinum wire, extending above the upper surface of tapered plug 44, serves as a terminal for lead-in wire 78 which runs inside the inner tube 42 and connects the mercury pool electrode with the external circuitry.

A reference electrode 80, not forming part of this invention, is shown mounted in a threaded hole 82 of the lid 18 by means of a standard threaded fitting 84 similar to the fitting 24. Reference electrode 80 completes the electrical circuit between the mercury pool electrode and the external circuitry.

In a few experiments, because of an adverse reaction between the test solution and the mercury, it may be necessary to use an electrode fabricated of solid material, such as platinum, in place of the mercury pool electrode. In the event such need arises, a solid disc electrode 86 may be press-fit into the cup 72 of the electrode block 70. A typical arrangement is illustrated in FIG. 2. Since the lower surface of the disc electrode 86 is in contact with the mercury, electrical continuity is established through the path provided by the mercury in the cup and in arm 28, platinum wire 76 and lead-in wire 78. Different size disc electrodes may be made to fit the various cup sizes provided by the interchangeable electrode blocks.

With the aid of FIG. 3 of the drawings, the operation of the mercury pool electrode will now be explained. In the position of the valve 31 shown in FIG. 3*a*, groove 50 in tapered section 30 is in registry with groove 52 in tapered plug 44, thus forming a continuous passageway through which mercury stored in the annular space 46 is free to pass, by gravity feed, to chamber 45, then to the lower tubular arm 28 and from there into the electrode cup 72. Since the annular space 46 is vented to the ambient atmosphere, air is free to flow into the annular space 46 as the mercury level therein decreases, thus precluding a hydrostatic pressure unbalance between the surfaces of the mercury in the annular space 46 and in the cup 72 which would tend to restrain the flow of mercury into the cup 72. The filling process may be monitored visually through the transparent wall of vessel 14. When the mercury pool 74 has reached the desired level in electrode cup 72, the tapered plug 44 of the valve 31 is then rotated to the position shown in FIG. 3*b*.

Valve 31 is operated manually by rotating the protruding portion 60 of the inner tube 42, so that the tapered plug 44, which is affixed to tube 42, assumes the desired position. Since all the members of the valve may be transparent, the position of the valve is readily ascertainable. In the position shown in FIG. 3*b*, the electrode cup 72 is isolated from both the suction source and the mercury stored in the annular reservoir space 46. It is in this position that experiments are conducted. At the conclusion of an experiment, valve 31 is further rotated until groove 52 registers with the bore 36 of the tubular side arm 34 as shown in FIG. 3*c* and FIG. 1. By activating the suction source which is attached to the exterior end of the tube 35, the mercury then may be drawn up through lower tubular arm 28 into chamber 45, and from there through groove 52 in the tapered plug and into side arm 34. Normally, no harm results if some of the test solution is also drawn up to the suction source. When the next experiment is ready to begin, valve 31 is brought back to the initial position shown in FIG. 3*a*, thus allowing a new charge of mercury to enter the electrode cup 72 thereby providing a clean electrode surface for the performance of the next experiment.

While particular embodiments of the invention have been illustrated, it will be understood, of course, that many modifications may be made, and it is therefore contemplated to cover by appended claims any such modification which falls within the true spirit and scope of the invention.

What is claimed is:

1. A mercury pool electrode comprising

a vertical outer tubular element having an upper end open to the atmosphere and a lower portion which is adapted to be sealed in an electrolysis cell, said tubular element having an inner wall;

a lower portion of said inner wall comprising the stationary part of a three-position valve;

a movable valve element, seated in said lower portion of said inner wall, comprising the movable part of said three-position valve;

a tubular side arm, one end of which is mounted on the outer tubular element at the lower portion housing said three-position valve, the other end of which is adapted to be attached to a suction source, the bore of said tubular side arm being extended through the wall of said outer tubular element so as to communicate with the interior of said outer tubular element;

an L-shaped, tubular, lower arm forming a tubular extension of the lower extremity of said outer tubular element, and having an end portion, the bore of said L-shaped, tubular arm communicating with the interior of said outer tubular element;

an electrode cup mounted on the end portion of said L-shaped, tubular arm and positionable inside said sealed electrolysis cell, the interior of said cup communicating with the bore of said L-shaped, tubular arm;

an inner tubular element having uper and lower ends and mounted inside and coaxial with said outer tubular element thereby forming an annular space between said inner and outer tubular elements, the lower end of said inner tubular element being affixed to and suported by said movable valve element, the upper end of said inner tubular element projecting above the upper open end of said outer tubular element;

said annular space comprising a reservoir for the storage of a supply of mercury;

said movable valve element being actuated by manipulation of said projecting upper end of said inner tubular element whereby in a first position of said movable valve element a continuous flow path is formed from said annular reservoir space to said cup while isolating said other end of said tubular side arm from said cup and said annular reservoir space, in a second position of said movable valve element said annular reservoir space, said cup and said other end of said tubular side arm are isolated, one from each of the others, and in a third position a continuous flow path is formed from said cup to said other end of said tubular side arm while isolating said annular reservoir space therefrom; and

a conductor element extending through said movable valve element and terminating in the bore of said L-shaped, tubular arm, adapted to connect the mercury in said L-shaped, tubular arm and electrode cup with an external circuit.

2. The mecrury pool electrode of claim 1 in which said electrode cup is interchangeable with other electrode cups of various sizes whereby mercury pools having various surface areas may be provided.

3. A mercury pool electrode as claimed in claim 1, in combination therewith

a sealable electrolysis cell; and said outer tubular element being sealed in said electrolysis cell.

4. A mercury pool electrode comprising:

a vertically-disposed hollow body, the upper portion of which is adapted to project from a sealed electrolysis cell and comprises a mercury reservoir, and the lower portion of which is adapted to be located

inside said sealed electrolysis cell and comprises a valve assembly housing;
the upper end of said hollow body being open to the atmosphere;
said valve assembly housing having a first port opening into said mercury reservoir, a second port and a third port;
a first tubular arm connected at one end to said housing, the bore of said first tubular arm communicating with said second port;
a second tubular arm connected at one end to said housing, the bore of said second tubular arm communicating with said third port;
said first tubular arm terminating at its other end in a horizontally-disposed cup adapted to be positioned inside said sealed electrolysis cell and further adapted to hold a pool of mercury, the interior of said cup communicating with the bore of said first tubular arm;
said second tubular arm connected at its other end to a suction source adapted to be located exteriorly of said sealed electrolysis cell;
a movable valve element having a passageway, said valve element supported in said valve assembly housing and adapted to be actuated from a point outside said electrolysis cell;
a conductor element, one end of which extends into the bore of said first tubular arm and the other end of which is adapted to be connected to an external circuit;
whereby, upon actuation of said movable valve element to a first position said movable valve element passageway interconnects said first and second ports thereby permitting mercury to flow from said mercury reservoir to said cup, upon actuation of said movable valve element to a second position said first, second and third ports are mutually isolated, each from the other two, and upon actuation of said movable valve element to a third position said movable valve element passageway interconnects said second and third ports whereby the mercury in said cup is removed by said suction source.

5. A mercury pool electrode as claimed in claim **4**, in combination therewith
a sealable electrolysis cell; and said hollow body being mounted in said electrolysis cell with said upper portion of the hollow body projecting from said electrolysis cell and said lower portion of the hollow body located inside said cell.

6. A mercury pool electrode for removable immersion in a test solution vessel comprising:
housing means providing a reservoir for storing a supply of mercury;
an electrode cup for holding a pool of said mercury, said cup being connected to said housing means and separable from the test solution vessel;
means for removing said mercury from said electrode cup;
a valve selectively connecting the reservoir and the cup, and the cup and the removing means, said valve being positionable for filling, isolating and emptying said cup;
means for manually controlling the position of said valve;
a conductor for connecting said pool of mercury with external circuitry;
said housing means comprising an outer tubular element, said valve being located in the lower portion of said outer tubular element;
said valve position control means comprising an inner tubular element positioned inside and generally coaxial with said outer tubular element, an upper portion of said inner tubular element protruding out of the upper extremity of said outer tubular element; and
the annular space between the upper portion of said outer and inner tubular elements defining said mercury reservoir.

7. A mercury pool electrode comprising:
a mercury reservoir;
a suction source;
a horizontally-disposed electrode cup adapted to be mounted inside a sealed electrolysis cell and adapted to hold a pool of mercury;
a valve connected to said reservoir, suction source and cup, said valve being actuatable to assume three operative positions whereby in the first position mercury from said mercury reservoir is permitted to fill said cup to a predetermined level, in the second position said cup is isolated from both said reservoir and said suction source, and in the third position mercury is removed from said cup by said suction source;
a vertically-disposed hollow element providing said reservoir in its upper portion, said valve being housed in the lower portion of said element, the upper end of said element being open to the atmosphere; and
an elongated actuating element adapted to actuate said valve, said elongated element being positioned inside said hollow element and projecting out of the top of said hollow element.

8. The electrode of claim **7** including:
a first tubular element attached at one of its ends to said hollow element at said lower portion housing said valve, the bore of said first tubular element communicating with the interior of said hollow element;
a second tubular element attached at one of its ends to said hollow element at said lower portion housing said valve, the bore of said second tubular element communicating with the interior of said hollow element; and
the other end of said first and second tubular elements being connected, respectively, to said electrode cup and to said suction source.

9. The electrode of claim **8** in which
said valve comprises a fixed part formed in the inner wall of the lower portion of said hollow element and a movable part supported by said fixed part; and
said elongated actuating element is affixed to said movable part.

10. The electrode of claim **9** in which
said fixed part of said valve comprises a vertically-tapered section of said inner wall;
said movable part of said valve comprises a vertically-tapered plug adapted to seat in said fixed part of said valve;
a first vertical groove is provided in said vertically-tapered section of said inner wall extending from the bottom extremity of said mercury reservoir down to a point approximately half the length of said vertically-tapered section; and
a second vertical groove is provided in said vertically-tapered plug extending from the bottom of said plug up to a point a short distance above the lower extremity of said first vertical groove.

11. An apparatus comprising:
a mercury reservoir;
a suction source;
a horizontally-disposed electrode cup adapted to be mounted inside a sealed electrolysis cell and adapted to hold a pool of mercury;
a valve connected to said reservoir, suction source and cup, said valve being actuatable to assume three operative positions whereby in the first position mercury from said mercury reservoir is permitted to fill said cup to a predetermined level, in the second position said cup is isolated from both said reservoir and said suction source, and in the third position

mercury is removed from said cup by said suction source; and

a sealable electrolysis cell, said electrode cup being mounted inside said electrolysis cell.

12. An apparatus comprising:

a sealable vessel adapted to hold a test solution;

means for storing a source of mercury;

means in said vessel other than the walls of said vessel for holding a pool of said mercury in contact with test solution in said vessel;

means for removing said mercury from said holding means;

means operable from outside said vessel for selectively connecting the storing means and the holding means, and the holding means and the removing means for filling, isolating and emptying said holding means; and

means for electrically connecting said pool of mercury with external circuitry.

13. The apparatus of claim **12** in which

said removing means includes a conduit having one end operatively connected to said selectively connecting means and its other end extending outside of said vessel for connection to a source of suction.

14. The apparatus of claim **12** in which

said holding means comprises an electrode cup which is interchangeable with other electrode cups of various sizes whereby mercury pools having various surface areas may be provided.

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U.S. Cl. X.R.

204—219, 225, 250, 279, 286; 251—290