Oct. 29, 1940.

H. L. STEWART

2,219,342

APPARATUS FOR ELECTROLYSIS

Filed June 26, 1936

2 Sheets-Sheet 1

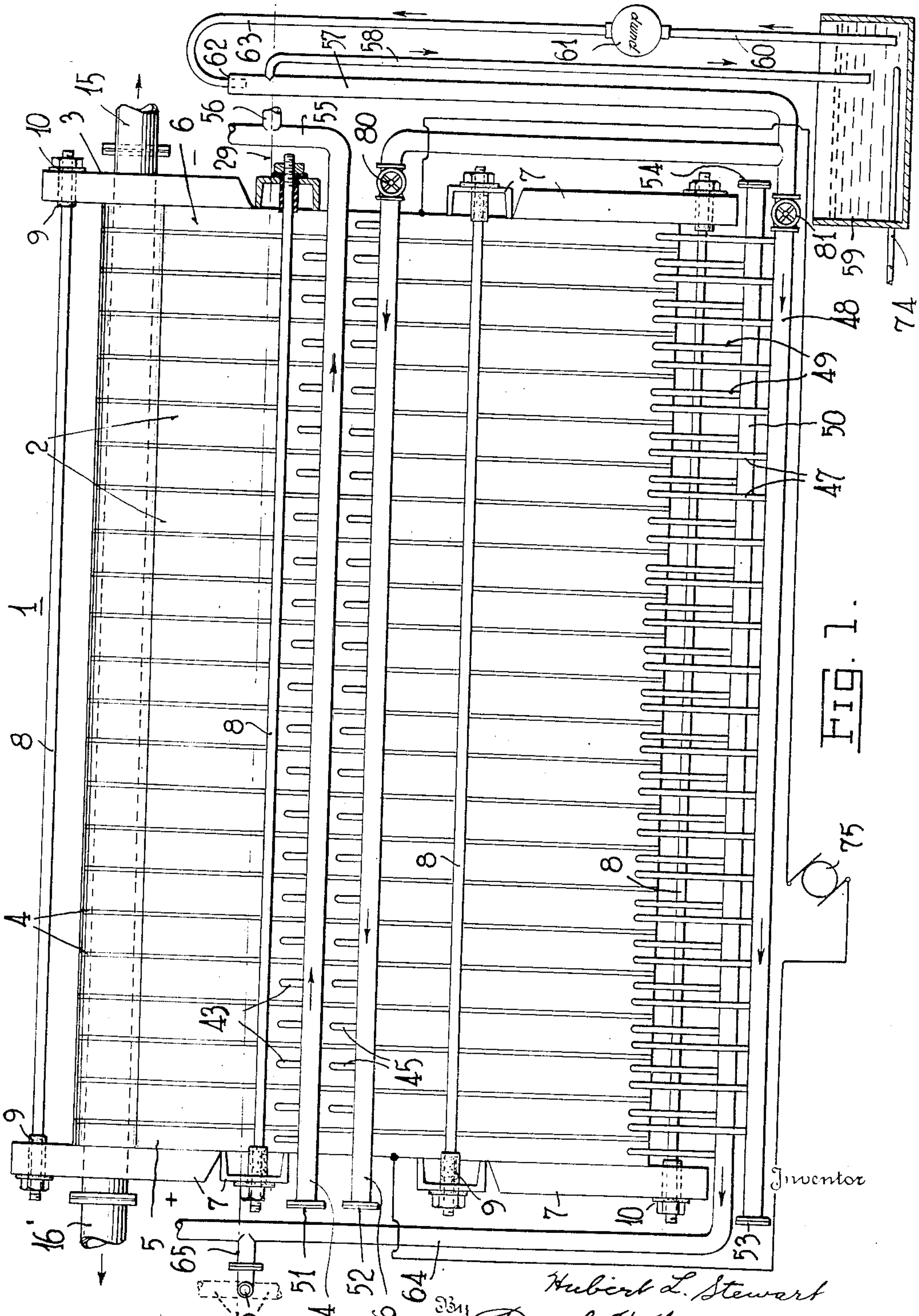

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FIG. 2.

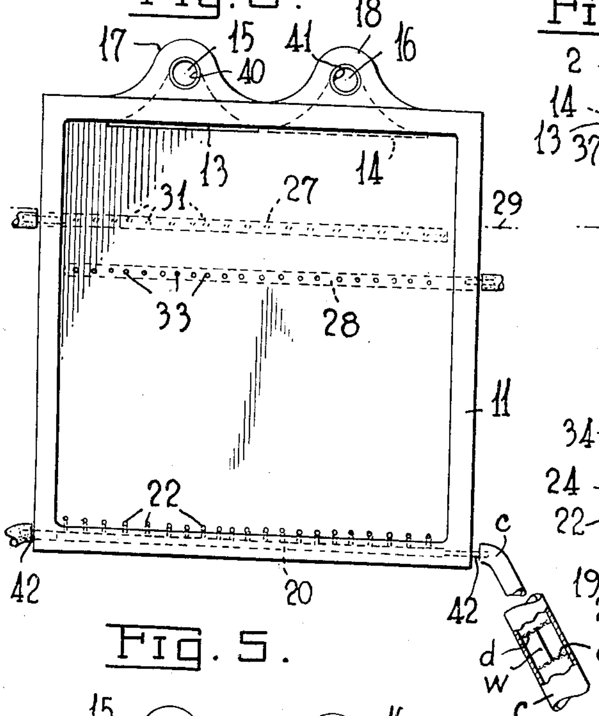


FIG. 3.

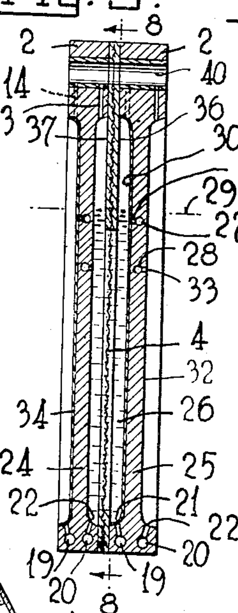


FIG. 4.

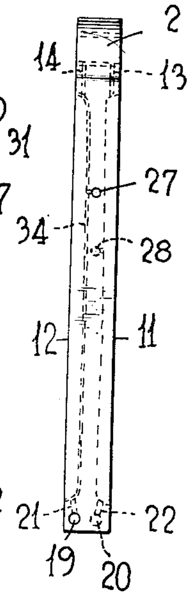


FIG. 5.

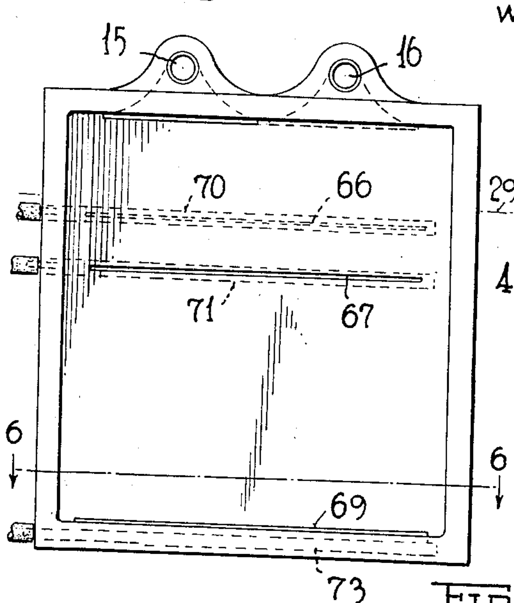


FIG. 8.

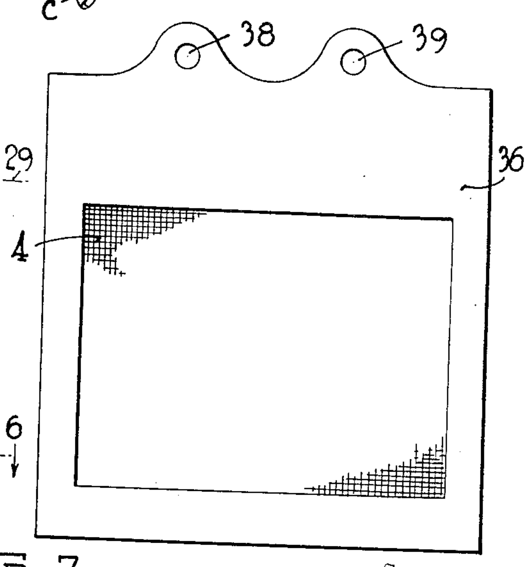


FIG. 6.

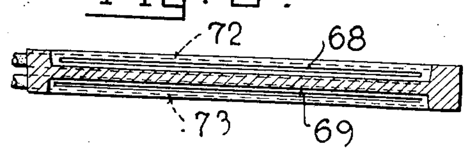
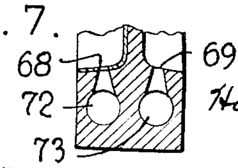


FIG. 7.



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APPARATUS FOR ELECTROLYSIS

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Application June 26, 1936, Serial No. 87,569

6 Claims. (Cl. 204—256)

This invention relates to improvements in apparatus for electrolysis. More particularly, the invention relates to cells employed for the electrolysis of solutions of materials to generate useful products therefrom.

In the accompanying drawings which serve to illustrate the present invention, and in which like reference characters denote like parts in the apparatus.

Figure 1 is a side elevational view of an electrolyzer having a plurality of cells;

Fig. 2 is a view of one side of a plate used as an electrode in an electrolyzer comprising the present invention;

Fig. 3 is a vertical sectional view showing the relative positioning of two plates to form a cell;

Fig. 4 is an elevational view of a vertical edge of a plate;

Fig. 5 is a view of one side of a modified form of plate;

Fig. 6 is a sectional view of a plate on line 6—6 of Fig. 5 in the direction of the arrows;

Fig. 7 is a sectional view of a portion of a plate showing one form of a structural detail thereof; and

Fig. 8 is a view on line 8—8 of Fig. 3 showing the structure of means provided between the plates.

Referring to Fig. 1 of the drawings, the apparatus shown by way of example includes a bipolar electrolyzer of the multi-cell, filter-press type designated generally by the numeral 1, means for introducing liquids into the cells, and means for withdrawing materials therefrom in a particular manner to be described below.

The electrolyzer 1 comprises a series of metallic plates or electrodes 2 clamped together in a heavy frame 3, electrically insulated from one another and separated by diaphragms 4 (described in further detail below) of porous fabric, such as asbestos fabric or canvas. The plates 2 are recessed centrally to form a cell between opposing faces, each cell being divided by the diaphragm material into an anolyte chamber and a catholyte chamber. In the drawings, the electrolyzer is shown with twenty-one intermediate plates each centrally recessed on both sides, and two end plates, the master anode 5 and the master cathode 6, each centrally recessed on the inner side only.

The frame 3 may be of any type suitable for clamping the plates tightly against each other. Channel bolting strips 7 may be welded on the outer side of both the master anode 5 and the master cathode 6. Tie bolts 8 are provided which are properly insulated from the channels at both ends. For instance, a fiber bushing 9 and a fiber washer 10 may be provided to insulate the ends of the tie bolts 8 from the channel strips 7.

Figs. 2 to 8 inclusive illustrate the construction of the plates or electrodes 2. Each plate is provided with passageways in the body thereof for conveniently introducing an electrolyte into the cells and for withdrawing solutions and gases therefrom. The plate, shown in Figs. 2, 3 and 4, is an intermediate plate. It is recessed centrally on both sides, shoulders 11 and 12 being formed at and around the edges. Passages 13 and 14 extend through the shoulders 11 and 12 respectively and communicate with the recess on opposite sides of the plate. The passage 13 leads to a passage 15 and the passage 14 leads to a passage 16. The passages 15 and 16 extend through the thickness of the plate in spaced projections 17 and 18 extending from the upper edge of the said plate. When a plurality of plates are brought together, the passages 15 and 16 coincide with corresponding passages in each plate and form gas offtakes 15' and 16' through which gases from opposite sides of the plates are withdrawn.

An important feature of the present invention is the provision of passages in the plates for the introduction and withdrawal of liquids. As illustrated by way of example, passages 19 and 20 extend into the body of a plate preferably in the portions of the shoulders 11 and 12 on the lower edge of the plate and substantially parallel with said edge. The passages 19 and 20 may extend from either of the normally vertical edges of a plate (Fig. 2), but preferably from the same edge (Fig. 6) to the opposite edge at which the passages may be dead-ended or they may extend part of the way through as shown. Ports 21 connect the central recessed portion on one side of a plate 2 to the passage 19, and ports 22 connect the central recessed portion on the other side of the plate to the passage 20.

In Fig. 3, two plates 24 and 25 similarly constructed are shown assembled to form a cell 26 of an electrolyzer. Passages 27 and 28 near the level 29 of the electrolyte extend into each of the plates 24 and 25 from either one of the outer edges. In Fig. 2, the passage 27 is shown extending into the electrode from one edge, and the passage 28 is shown extending into the electrode from the opposite edge of a plate.

The passage 27 is connected to the surface of one face 30 of a plate by ports 31. The passage 28 is connected to the surface of the opposite face 32 of the plate by ports 33. The face 30 of a plate is preferably provided with a nickel plating **34** that serves as the anode. The iron surface of face **32** serves as the cathode of a cell.

The diaphragm **4**, referred to above, is clamped between the plates. On either side of the diaphragm, gaskets **36** and **37** are fitted to provide for the proper insulation of the plates from one another and to prevent leakage of the electrolyte solution. A preferred form of gasket is shown in Fig. 8. This gasket made of rubber, for example, frames a central portion of the diaphragm **4** which is left exposed to the electrolyte. The gasket extends inwardly from the outer edge of a plate and beyond the inner edges of the shoulders **11** and **12**. The upper horizontal portion of a gasket extends downwardly from the top of a cell to slightly below the liquid level (see Fig. 3) to prevent, by highly effective means, the mixing of gases, that is, to keep gas generated at the anode separate from the gas generated at the cathode. The lower horizontal portion and the vertical side portions of the gasket prevent current from passing through the diaphragm between the edges of adjacent electrodes. Openings **38** and **39** in the gasket, register with the passages **15** and **16** respectively in a plate. Insulating tubular sections **40** and **41** are provided as linings for the passages **15** and **16** respectively to prevent any escape of current in case entrained electrolyte collects in the gas offtakes **15'** and **16'** (Fig. 1).

Nipples **42** are provided at the outlets of each of the passages **19**, **20**, **27** and **28**, to which nipples, flexible tubular means are removably connected. The tubular means are preferably made of insulating material such as rubber. In Fig. 1, the tubular means **43** are shown connecting the passages **27** of each plate **2** to a manifold **44**. Tubular means **45** connect the passages **28** of each plate **2** to a manifold **46**. Tubular means **47** connect the passages **19** of each plate **2** to a manifold **48**. Tubular means **49** connect the passages **20** of each plate **2** to a manifold **50**. The manifolds **44**, **46**, **48**, and **50** are each dead-ended at **51**, **52**, **53**, and **54** respectively.

The manifold pipe **44** is provided with a vertical extension **55** and a branch pipe **56**. The manifold pipes **46** and **48** are both connected to a vertical pipe **57** provided with a branch pipe **58** extending downwardly into a tank **59**. A pipe **60** leads from the tank **59** to a pump **61**. The pump **61** is connected to the open end **62** of the pipe **57** by means of a pipe **63**.

The manifold pipe **50** is connected to a vertical extension **64** provided with a branch pipe **65**.

In the modified electrode plate shown in Figs. 5, 6 and 7, instead of a plurality of ports such as **21**, **22**, **31** and **33** connected to the passages **19**, **20**, **27** and **28** respectively, slots **66**, **67**, **68** and **69** may be provided for ingress or egress of liquids through the passages **70**, **71**, **72** and **73** respectively. The slots may extend part of the way or entirely across the central surfaces of the electrodes and are preferably narrower than the diameter of the passages, thereby forming constricted apertures as shown in Fig. 7.

The electrode plates described above for a filter-press type of electrolyzer make it possible to introduce electrolyte solution or withdraw products of electrolysis or both simultaneously, in a highly efficient manner. If a product of electrolysis formed in a cell, has a specific gravity less than that of the electrolyte, the use of the electrode makes it possible to withdraw the product directly from the upper portion of the surface of the electrode at which the product is formed while introduction of the electrolyte is accomplished at a lower level in the cell. Also, if a product of electrolysis has a specific gravity greater than that of the electrolyte, means are provided in the electrode at which the heavier product is formed, for introducing electrolyte solution at an upper level in a cell at the surface of the electrode while withdrawal of the said heavier electrolysis product is accomplished at a lower level in the cell. The electrode plate employed makes it possible to withdraw products of electrolysis from zones in a cell in which they are most concentrated.

The tubular connections between the cells and the several manifolds may be interchangeable to provide for feeding electrolyte and withdrawing electrolysis products at the desired levels depending upon their relative specific gravities.

The manifolds **44**, **46**, **48** and **50** are preferably spaced some distance from the cell (as much as five feet in some cases) to prevent, as much as possible, any current flow through the liquids in the manifolds. To further prevent any possible loss of current through the insulating tubular connections and the manifolds, suitable means may be provided by which the resistance of the electrolyte in the tubular means is increased. For instance the installation of overvoltage dams may be provided. Such dams may consist of two nickel screen discs placed transversely in the insulating tubular connections spaced apart and connected by a wire of low resistance such as iron or copper. The voltage necessary in such a construction to overcome the resistance of the electrolyte in the said tubular connections is increased in amount equal to the hydrogen and oxygen overvoltages on nickel in view of which the flow of current through the said connections and manifolds will be decreased. A dam comprising two screen discs *d* and *d'* held in spaced relation, and a connecting wire *w* is shown in Fig. 2 in a tubular connection *c*, a portion of which is enlarged for purposes of illustration.

A method of operating the electrolyzer shown in the accompanying drawings may be illustrated in connection with the electrolysis of certain chemicals. Sodium carbonate (Na_2CO_3) solution, for instance, is electrolyzed to produce sodium hydroxide ($NaOH$) and sodium bicarbonate ($NaHCO_3$).

Sodium carbonate in an aqueous solution containing about 1.8 lbs. sodium carbonate per gallon to about 2 lbs. per gallon is pumped from the tank **59** by means of the pump **61** into the pipe **57**. The solution may, if desired, be preheated to about 60° C. to 80° C. by means of a steam coil **74** in the tank **59**. The level **29** of the electrolyte in the cells is maintained constant by means of the overflow pipe **58** which returns surplus electrolyte solution to the tank **59**. The solution entering the pipe **57** flows through the manifold **46**, the flexible tubular means **45**, the passage **28**, ports **33** (or passages **71** and slots **67**) and into the upper zone of the cathode chamber of each cell **26**. The electrolyte also flows through the manifold **48**, the flexible tubular means **47**, the passages **19**, ports **21** (or passages **72** and slots **68**) and into the bottom of the anode chamber of each cell **26**.

Upon flow of current from a generator **75** (diagrammatically shown in Fig. 1) sodium bicarbonate is generated at the anode of each cell, and sodium hydroxide is generated at the cathode of each cell. The bicarbonate solution generated, having a lower specific gravity than the sodium carbonate solution being electrolyzed, rises in the cells in the anode chambers and is withdrawn near the level of the electrolyte or as close to the liquid-gas interface as is practicable through ports **31**, passages **27** (or slots **66** and passages **70**), flexible tubular means **43**, and manifold pipe **44**; and overflows through the pipe **56**. The generated sodium hydroxide solution, having a higher specific gravity than the sodium carbonate solution being electrolyzed, is withdrawn from the bottom of the cathode chamber of each cell through ports **22**, passages **20**, (slots **69** and passages **73**) flexible tubular means **49**, and manifold pipe **50**; and overflows through the pipe **65**.

As indicated in the drawing, (Fig. 1), the overflow pipe **56** is at a silghtly lower level than the overflow pipe **58**, and the overflow pipe **65** is at a slightly lower level than either pipes **56** or **58**. By means of this arrangement a difference of the static heads of the various solutions is maintained depending upon the specific gravities thereof. The levels at which the electrolysis products are withdrawn will depend upon their relative specific gravities. For this purpose, pipes **55** and **64** may be constructed so as to be extensible. Alternatively, a swivel pipe connection **85** such as that shown connected to the pipe **65** may be provided which may be turned any angle. The pipe **85** is shown in full line in a position at which the liquid is withdrawn at the level of the pipe **65**. Sodium bicarbonate solution preferably has a hydrostatic head greater than that of the caustic soda in order to prevent infiltration of caustic soda from the cathode chamber into the anode chamber. Such infiltration tends to neutralize the effects of electrolysis.

A substantial space between the level of the electrolyte and the tops of the cell chambers is preferred so that no liquid is carried with either the hydrogen or oxygen through the passages **13** or **14** respectively.

As indicated above, the electrode plates are bipolar, nickel plating being provided on the anode side and iron on the cathode side. Stainless steel containing 18% chromium and 8% nickel may be used in the anode, if desired. Copper, cadmium, or Monel metal may be substituted for the iron as the cathode. Iron for the cathode is preferred because of its low overvoltage. One or more leads are attached to the master plates. More than one lead to each of the said plates is used to provide for proper distribution of current.

The cell temperature and current density are maintained fairly constant by regulating the voltage. A cell or electrolyzer may be operated with a current density of about 50 amperes per square foot to about 125 amperes per square foot. The cell temperature ranges preferably from about 60° C. to about 80° C. The temperature should not be so high as to produce too violent an evolution of gases and should not be so low as to raise the resistance of electrolyte too high. The use of the form of plate provided with passages described above is advantageous in that it preheats the electrolyte as the solution flows through the passages.

The rate of introduction of sodium carbonate solution into the cells depends on the concentration of solutions that are to be withdrawn. The feed to the cathode chambers may differ, if desired, from the feed to the anode chambers. In the electrolysis of the sodium carbonate solution, the feed to the cathode chamber may be about 1.0 gallon per hour per kilowatt hour and to the anode chamber about 1.2 gallons per hour per kilowatt hour. For the purpose of thus controlling the feed, valves **80** and **81** may be provided in pipes **46** and **48** respectively. A feed of approximately twenty per cent faster through the anode chamber is found advantageous in preventing the accumulation of solid sodium bicarbonate. The cell feed is preferably at such a rate as to convert from about 40% to about 48% of the sodium present as sodium carbonate into sodium hydroxide, and from about 40% to about 48% of the sodium present as sodium carbonate into sodium bicarbonate leaving sodium carbonate unchanged to the extent of about from 4% to 20%.

Throughout the operation of a cell the cell feed-current density ratio is controlled in such a manner as to give maximum yields of electrolysis products. Periodical analyses of the electrolysis products may be made from time to time to determine the concentrations of sodium hydroxide and sodium bicarbonate.

In the commercial operation of the cell, a current efficiency of between 92 and 98% and an energy efficiency of between 46 and 52% are obtainable. The yields of 0.71 to 0.79 pound of sodium hydroxide per kilowatt hour can be obtained.

Besides electrolyzing sodium carbonate the process may be applied to solutions of potassium carbonate, and of borax. Borax will produce sodium hydroxide and boric acid. Potassium carbonate will be converted into potassium hydroxide and bicarbonate. Disodium phosphate is converted into sodium hydroxide and monosodium phosphate.

It is apparent from the above description that various changes may be made in the form, construction and arrangement of parts without departing from the spirit and scope of the invention or sacrificing all of its material advantages, the forms hereinbefore cited by way of illustration being merely the preferred embodiments thereof.

What I claim is:

1. In apparatus for electrolysis, comprising a generator of the filter-press type having a plurality of electrode plates clamped together face to face and centrally recessed to provide a cell between each pair of plates; manifold means, and connecting means constructed of insulating material between each of the cells and the said manifold means for the passage of solution to or from the cells, and an overvoltage dam in each of the said connecting means, the said dam comprising spaced screens positioned transversely in the said connecting means, and a wire of low resistance connecting the said screens.

2. In apparatus for electrolysis comprising a plurality of cells which cells connect with each other by passage means for conducting liquid to or from the said cells, the said passage means having a wall constructed of insulating material, an overvoltage dam in such passage means, the said dam comprising spaced metallic, foraminate means positioned transversely in the said passage means, and an electrical conductor of low resistance connecting the said spaced foraminate means.

3. Apparatus comprising means for inhibiting the flow of current through a passage having a wall constructed of insulating material and containing an electrolyte, the said means comprising spaced metallic, foraminate means positioned

transversely in the said passage, and an electrical conductor of low resistance connecting the said foraminate means.

4. In apparatus for electrolysis, a solid electrode plate for a bipolar electrolyzer of the multicell, filter press type, having separate anolyte and catholyte chambers and a separate gas offtake for each chamber, a plurality of unconnected passages of relatively small cross section in said plate each extending from an outer edge of the plate into the body thereof to a working face of the plate, one of said passages extending to the surface of the plate at points extending across a working face of the plate adjacent but below the normal level of electrolyte solution in the electrolyzer, and another of said passages extending to the surface of the plate at points extending across a working face of the plate adjacent the lower edge of the working face of the plate, each of the said passages serving alternatively for the introduction of electrolyte solution or for the withdrawal of a solution of a product of electrolysis at the said levels.

5. In apparatus for electroylsis, a solid electrode plate for a bipolar electrolyzer of the multicell, filter press type, having separate anolyte and catholyte chambers and a separate gas offtake for each chamber, a plurality of unconnected passages of relatively small cross section in said plate each extending from an outer edge of the plate into the body thereof to a working face of the plate, one of said passages extending to the surface of the plate at points extending across one working face of the plate adjacent but below the normal level of electrolyte solution in the electrolyzer, another of said passages extending to the surface of the plate at points extending across the said one working face of the plate adjacent the lower edge of the said face, a third of said passages extending to the surface of the plate at points extending across the opposite working face of the plate adjacent the level of the said first-named points, and a fourth of said passages extending to the surface of the plate at points extending across the said opposite working face of the plate adjacent the level of the said second-named points, each of the said passages serving alternatively for the introduction of electrolyte solution or for the withdrawal of a solution of a product of electrolysis at the said levels.

6. In apparatus for electrolysis, a solid electrode plate for a bipolar electrolyzer of the multicell, filter press type having separate anolyte and catholyte chambers and a separate gas offtake for each chamber, a plurality of unconnected passages of relatively small cross section in said plate each extending from an outer edge of the plate into the body thereof, a plurality of elongated slots extending substantially completely across a working face of the plate, one of said passages extending to a slot in the working face of the plate adjacent but below the normal level of electrolyte solution in the electrolyzer, and another of said passages extending to a slot adjacent the lower edge of the working face of the plate, a portion of each of the said passages adjacent the said slots tapering toward the latter and each of the said passages serving altertively for the introduction of electrolyte solution or for the withdrawal of a solution of a product of electrolysis at the said levels.

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