Aug. 4, 1959 M. P. NEIPERT ET AL 2,898,284

MERCURY CATHODE CHLORINE CELL

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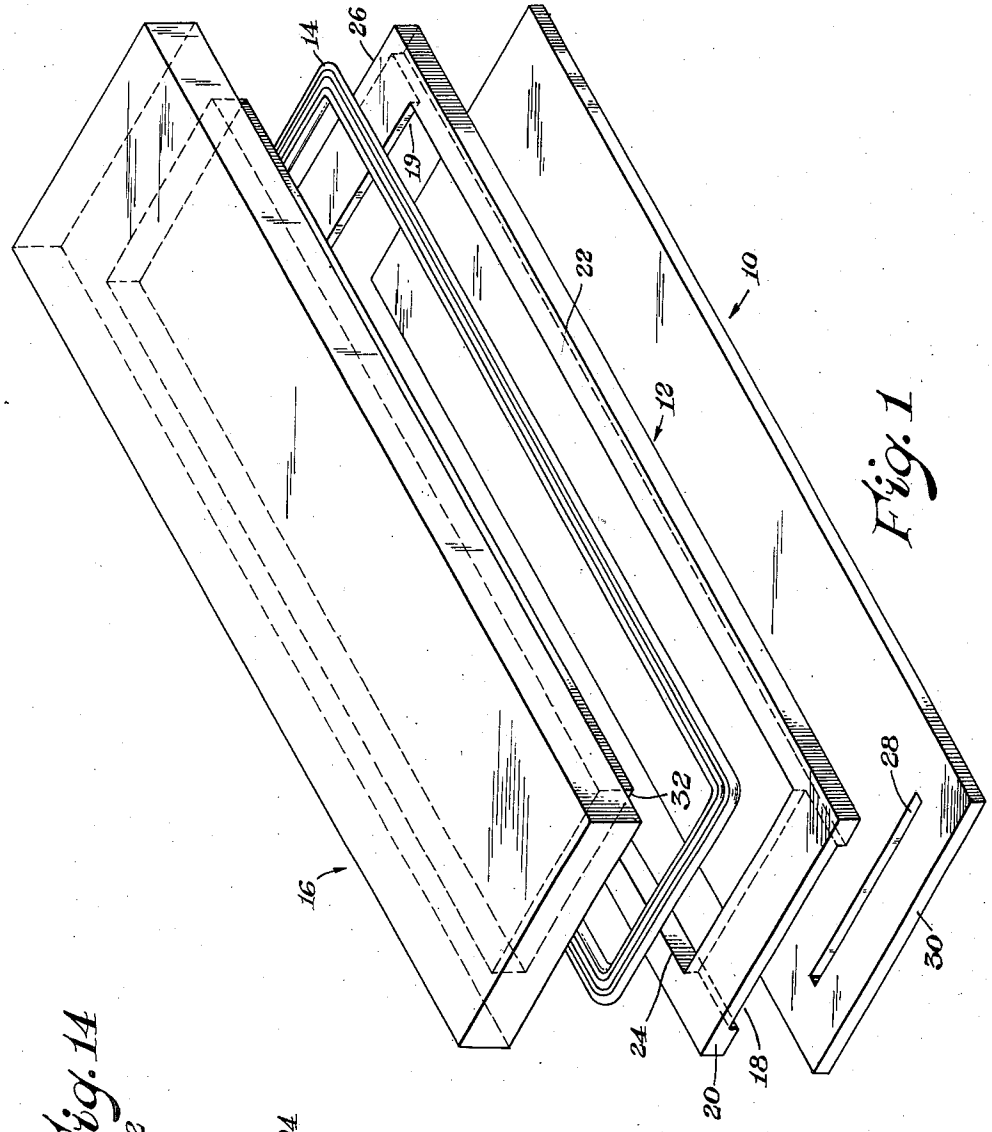

Fig. 1

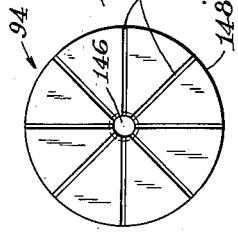

Fig. 14

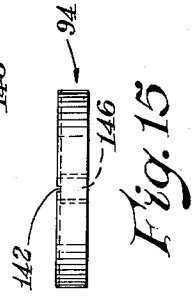

Fig. 15

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Aug. 4, 1959 M. P. NEIPERT ET AL 2,898,284

MERCURY CATHODE CHLORINE CELL

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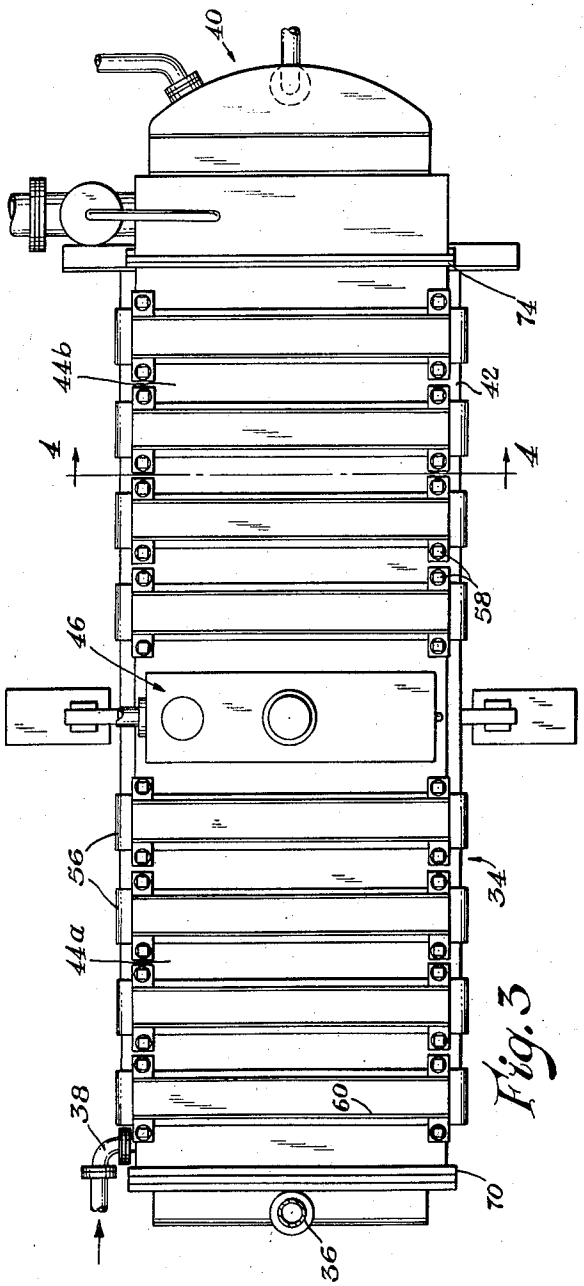

Fig. 3

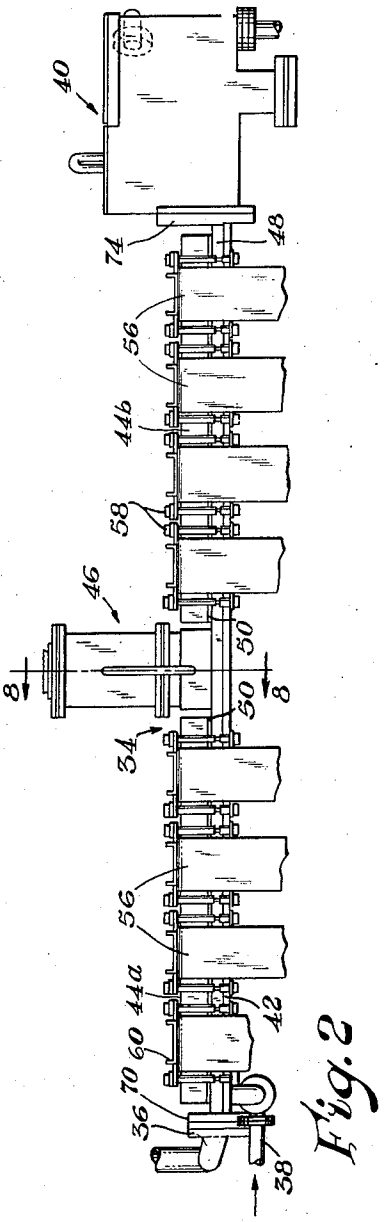

Fig. 2

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MERCURY CATHODE CHLORINE CELL

Filed June 2, 1958 6 Sheets-Sheet 3

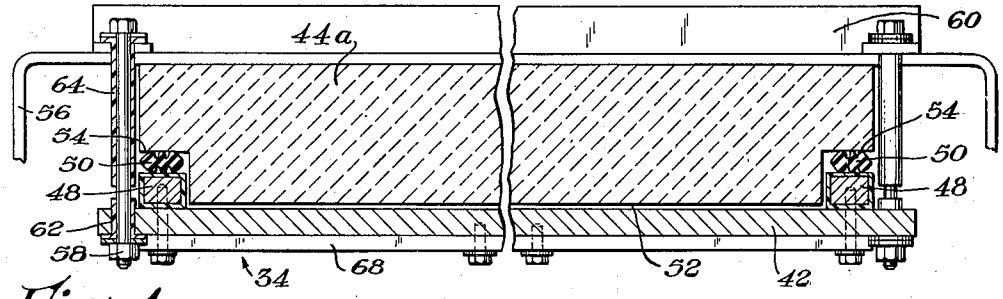

Fig. 4

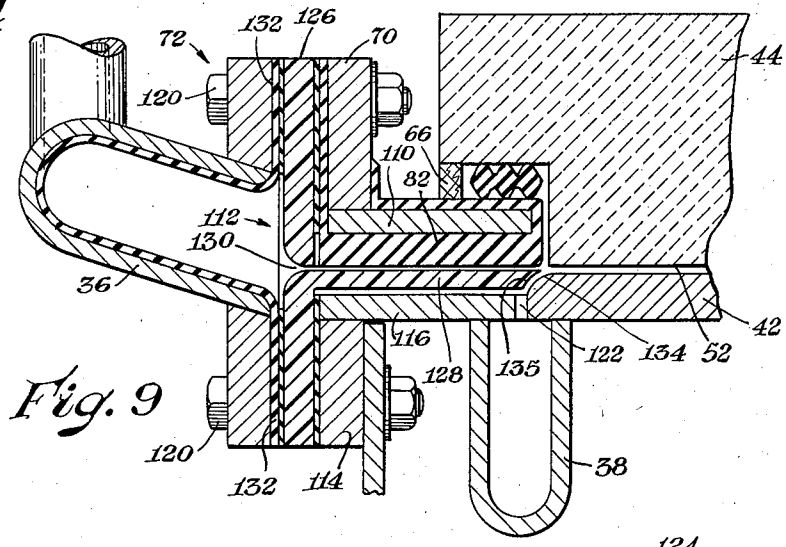

Fig. 9

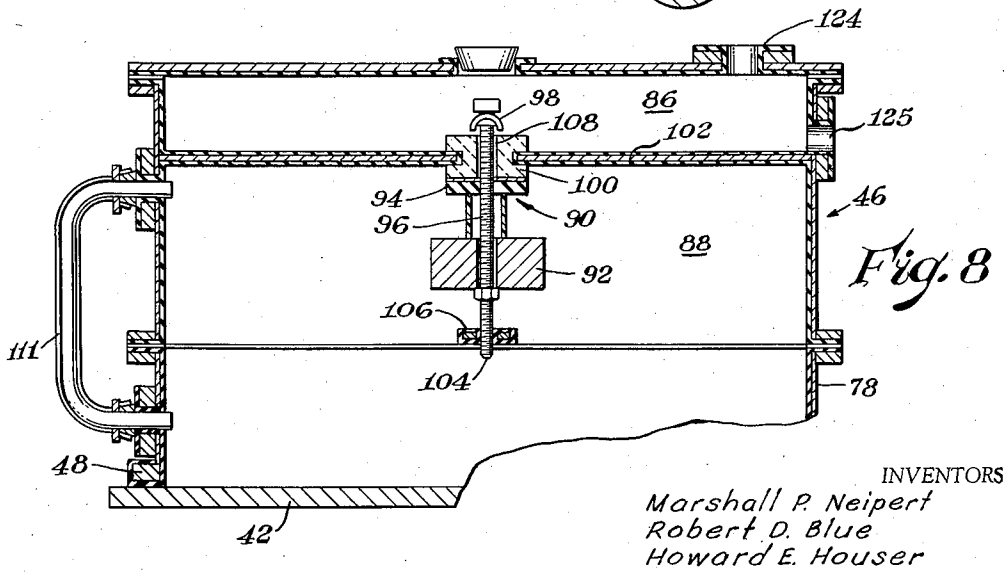

Fig. 8

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MERCURY CATHODE CHLORINE CELL

Filed June 2, 1958 6 Sheets-Sheet 4

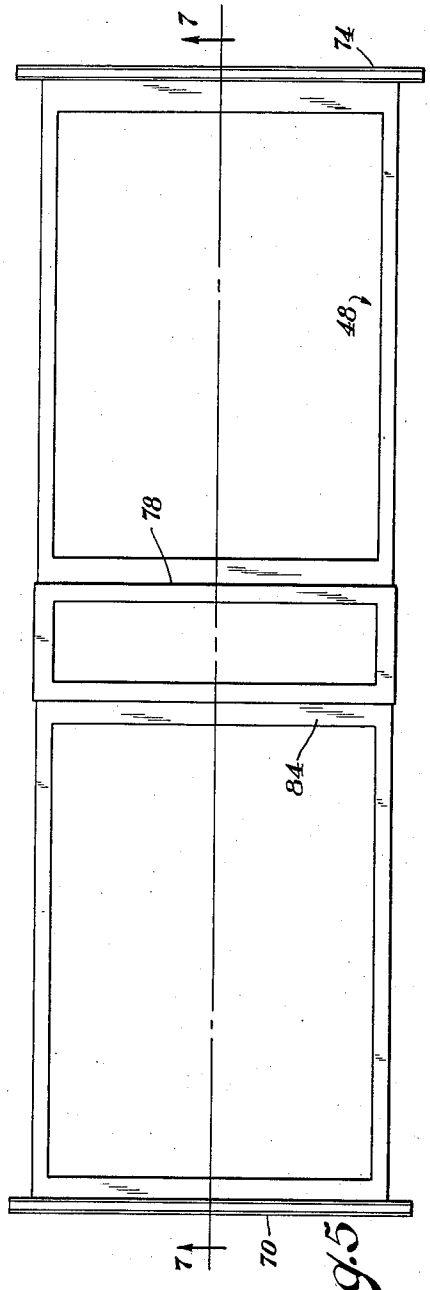

Fig. 5

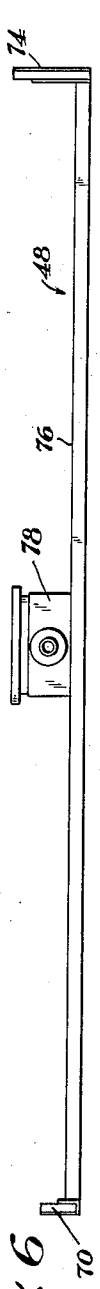

Fig. 6

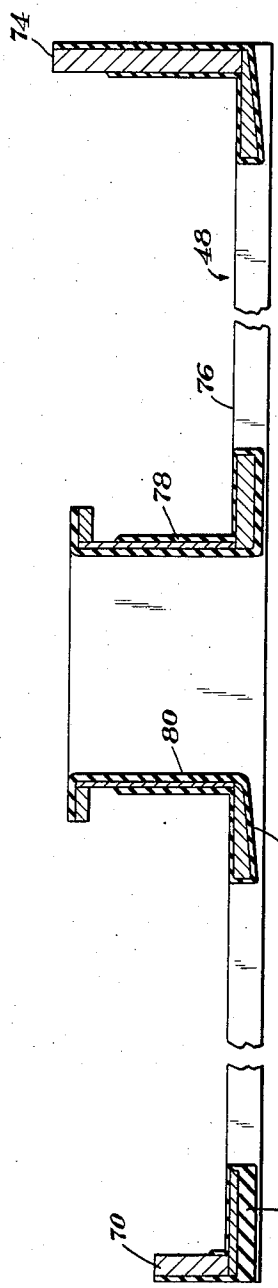

Fig. 7

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MERCURY CATHODE CHLORINE CELL

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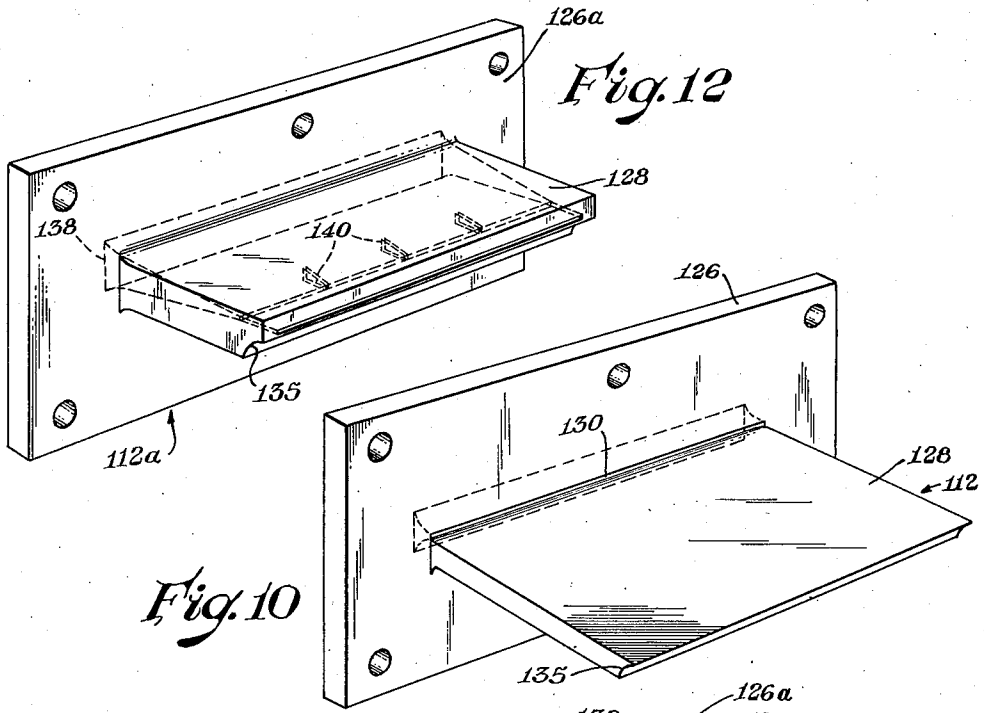

Fig. 12

Fig. 10

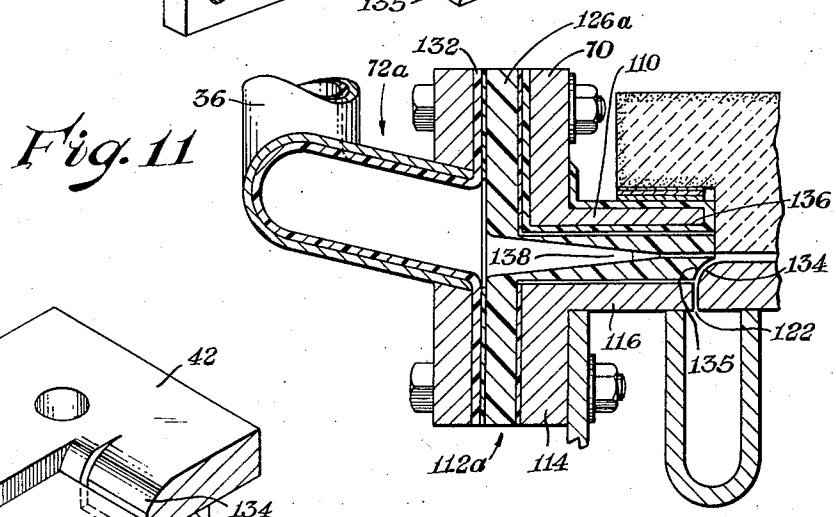

Fig. 11

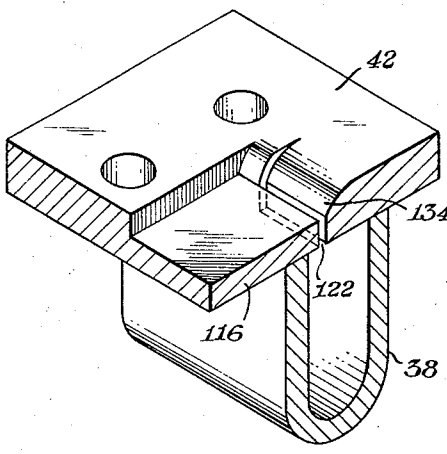

Fig. 13

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MERCURY CATHODE CHLORINE CELL

Filed June 2, 1958 6 Sheets-Sheet 6

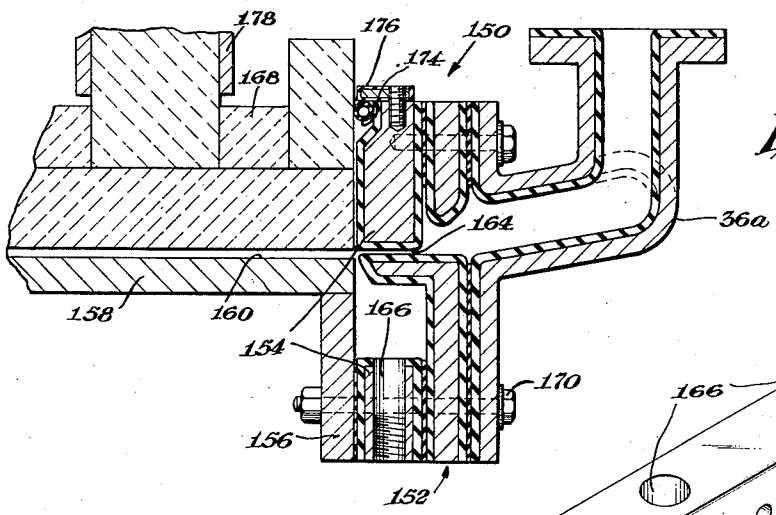

Fig. 16

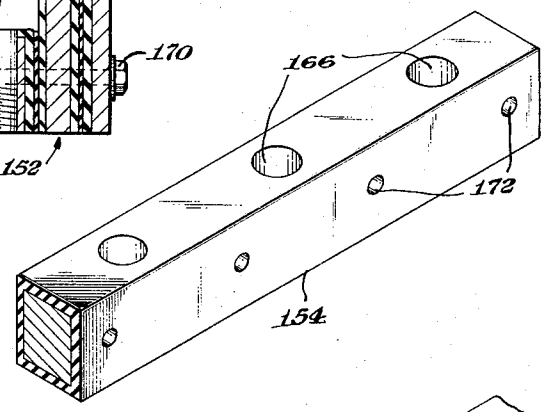

Fig. 18

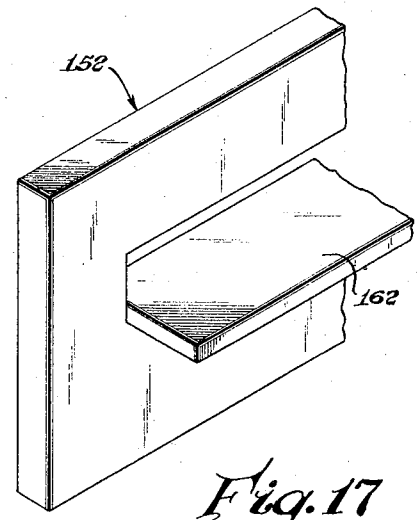

Fig. 17

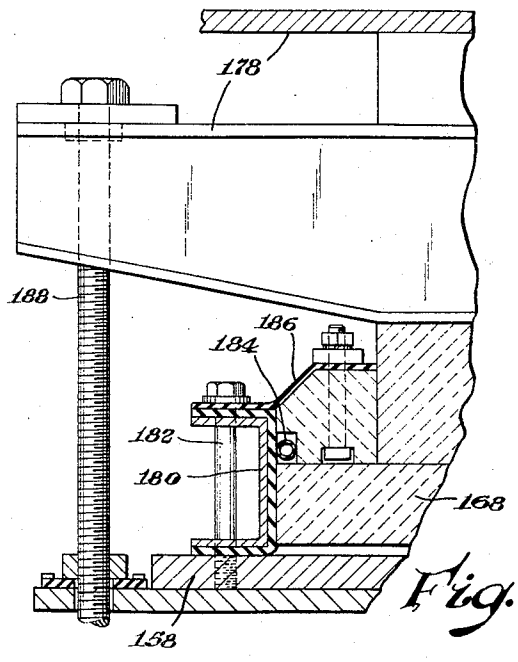

Fig. 19

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United States Patent Office 2,898,284 Patented Aug. 4, 1959

2,898,284

MERCURY CATHODE CHLORINE CELL

Marshall P. Neipert, Robert D. Blue, and Howard E. Houser, Midland, Mich., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

Application June 2, 1958, Serial No. 739,652

12 Claims. (Cl. 204—219)

This invention relates to mercury-cathode electrolytic brine cells, and particularly to slot-type mercury-cathode cells through which the electrolyte is swept at high velocity.

A typical mercury-cathode electrolytic cell for making chlorine and alkali comprises a long, narrow trough with a mercury pool cathode at the bottom and graphite anodes suspended from or supported by a rubber-lined cover. The feed brine is flowed through the cell with very low turbulence. The chlorine ions in the brine are attracted to the anode and thus discharged to form chlorine gas, which is usually withdrawn through an outlet line which leads from the rubber lined cover. The cation, usually sodium, forms an amalgam with the mercury, which is removed from the cell and treated with water in a separate denuder to form alkali, the mercury being thus regenerated for re-use.

Caustic soda made with mercury-cathode cells is of higher concentration and purity than caustic soda made with diaphragm type cells, but the cost of producing this caustic has heretofore been higher at most installations as compared to the cost of caustic made with diaphragm cells.

Several factors contribute to the high cost of producing caustic soda by means of mercury-cathode cells. One important factor is the high initial cost of mercury-cathode cells as compared with the cost of diaphragm type electrolytic cells. Another factor is that conventional mercury-cathode cells of the above described type operate at relatively low current densities in order to avoid excessive polarization of electrodes and thus occupy considerable building space per unit of chlorine or caustic producing capacity.

Mercury-cathode cells of conventional design have also proven to be quite sensitive to impurities in the brine, thus necessitating that expensive brine treatment facilities be provided in order to remove bothersome impurities. Also, the amount of mercury required for the cathode has been large, and since some of the mercury is lost during the operation of the cell, the mercury has added to both the initial investment and the cost of operation of such cells.

An attempt to overcome some of these difficulties has resulted in what is known as a slot-type mercury cathode cell. Canadian Patent No. 476,519 to Heller and Saunders illustrates and claims a slot-type cell. In slot-type mercury cathode electrolytic cells the mercury cathode usually comprises a thin layer or film of mercury which is swept through the cell at a high velocity as compared to the rate of flow of the cathode material in a conventional cell as previously described. Also, in many slot-type cells, the chlorine is removed from the cell through the fluid flow channel and does not bubble upward through apertures in the anode. In general, slot-type mercury cathode cells are capable of operation at considerably higher current densities than are conventional mercury cathode cells.

However, though the cell output capabilities are increased over those of conventional cells, the cost of previous slot-type cells has not been lessened appreciably over the cost of conventional mercury cathode cells. Likewise, the adjustment of electrode spacings during the operation of slot-type cells, as well as conventional cells, is not readily and inexpensively done.

Difficulties have also been encountered with the brine input or nozzle systems used in slot-type electrolytic cells. In prior art slot-type mercury cathode electrolytic cells, the brine nozzle has been an integral part of the cell structure. Because of the frictional forces of the brine, the nozzles have a short useful life as compared to the rest of the cell. However, in order to repair the nozzle, it has been necessary to shut down and disassemble the cell. Thus, the repairing of a brine nozzle is costly both in materials and lost production time.

Another difficulty often encountered in prior art type brine nozzles is that the brine stream leaving the nozzle has caused discontinuities in the mercury film which forms the cathode of the cell. Under such conditions, the steel cathode base is exposed to attack by the chlorinated brine which circulates through the cell, shortening the useful life of the cell.

Another limitation of cells in which the brine nozzle is an integral part thereof is that such cells may be efficiently operated over only a limited range of anode-cathode spacings.

It is therefore, a principal object of this invention to provide an improved mercury-cathode electrolytic cell having a high output capacity per unit electrode area.

A further object of this invention is to provide an improved mercury-cathode cell which is more economical to construct and to operate than prior art mercury-cathode cells.

A related object of the invention is to provide an improved mercury-cathode cell which is less sensitive to brine impurities than are prior art cells.

Yet another object of this invention is to provide an improved mercury-cathode cell which may be easily shutdown and restarted.

An ancillary object of this invention is to provide an improved, more efficient, and economical brine nozzle and mercury inlet assembly for a slot-type mercury cathode electrolytic cell.

In accordance with this invention, there is provided a slot-type mercury-cathode electrolytic cell in which the mercury flows in a thin continuous film over a flat sheet-like electrically conductive member which serves as the base of the cell and to which the cathode bus bar is connected. The anode of the cell comprises a block of graphite which also serves as the cover of the cell. The graphite anode, in some embodiments of the invention, is supported upon and spaced from the cathode by an insulating, resilient frame which is sandwiched between the two electrodes around the peripheries thereof. When the anode and cathode are clamped together with the resilient spacer between the two, a gas tight enclosure, except for brine and mercury inlet and outlet openings, is provided. A brine nozzle having readily replaceable brine channel inserts is placed within the brine inlet opening.

The invention, as well as additional objects and advantages thereof will best be understood by reading the following detailed description in connection with the accompanying drawings, in which:

Fig. 1 is a simplified, schematic exploded view of a slot-type mercury-cathode electrolytic cell, illustrating the essential principle of this invention;

Fig. 2 is a side elevational view of an assembled mercury-cathode electrolytic cell, in accordance with this invention; including a center chlorine outlet and an end box;

Fig. 3 is a top plan view of the electrolytic cell shown in Fig. 2;

Fig. 4 is a transverse sectional view taken along the line 4—4 of Fig. 3;

Fig. 5 is a top plan view of the anode-cathode electrode separator frame used in the electrolytic cell of Fig. 2;

Fig. 6 is a side elevational view of the frame of Fig. 5;

Fig. 7 is an enlarged sectional view taken along the line 7—7 of Fig. 5;

Fig. 8 is an enlarged sectional view, taken along the line 8—8 of Fig. 2, of the chlorine vent of the cell shown therein;

Fig. 9 is an enlarged sectional view showing the brine nozzle and mercury input arrangement used in the cell shown in Fig. 2;

Fig. 10 is an isometric view of the brine insert part of the brine nozzle shown in Fig. 9;

Fig. 11 is an enlarged sectional view of an alternative form of brine nozzle which may be used with slot-type electrolytic cells;

Fig. 12 is an isometric view of the insert part of the brine nozzle shown in Fig. 11;

Fig. 13 is a fragmentary isometric view of the brine and mercury input end of the cathode base of a slot-type electrolytic cell;

Fig. 14 is a top view, on an enlarged scale, of the valve **94** of the chlorine vent shown in Fig. 8;

Fig. 15 is a side elevational view of the valve **94** shown in Fig. 14;

Fig. 16 is a side elevational view, in section, of an alternative brine nozzle made in accordance with this invention,

Fig. 17 is an isometric view of the brine inlet lip member of the nozzle shown in Fig. 16,

Fig. 18 is an isometric view of the mercury feed-through block in the nozzle shown in Fig. 16, and

Fig. 19 is a fragmentary view, partly in section, showing an alternative manner of supporting the anode of the cell above the cathode base plate.

Fig. 1 illustrates, in simplified form, the essentials of a mercury-cathode electrolytic cell in accordance with this invention. The cell comprises a flat cathode base plate **10** which is made, for example, of slag-free mild steel. Resting on this is an insulating, for example, a rubber covered metal, electrode separator frame **12**. This latter is surmounted by a deformable gasket type seal **14**, on which seats a monolithic graphite anode **16** which also serves as the cover of the cell. The anode **16** has peripheral projections which fit over the frame **12** and gasket seal **14**, with the bottom surface of the anode resting close to but separated from the cathode base plate **10**. To form an electrolytic cell, the above-mentioned members are clamped together. In operation, a positive bus bar is connected to the anode **16** and a negative bus bar is connected to the cathode member **10**, and brine and mercury are swept through the cell.

A brine entry slot **18** (cut in the end **20** of the frame member **12**) leads into the electrolysis chamber defined by the anode **16**, the rubber covered frame member **12** and the base plate **10**. The brine entry slot is approximately equal in length to the width between the inner surfaces of the sides **22**, **24** of the frame member **12**. A similar slot **19**, shown in dotted lines in Fig. 1, is formed between the base plate **10** and the outlet end **26** of the frame member **12** and serves as the cell outlet slot for brine, chlorine, and the mercury amalgam cathode material. Mercury, which forms the active cathode of the cell, enters the cell through a slot **28** in the cathode base plate **10**. The mercury inlet slot **28** is adjacent to the point of entry of the brine and is substantially coextensive in length with the length of the brine slot **18**.

In practice, the surface of the base plate **10** between the slot **28** and the end **30** thereof is often protected against the brine, as by a hard rubber lining (not shown), since any bare metal of the base plate **10** exposed to the brine would be attacked thereby. The remainder of the base plate surface over which fluid passes is protected from the brine by the thin film of the mercury cathode, which flows over and covers the steel surface of the base plate **10**.

The rubber covered steel rectangular frame **12** of the cell is secured and sealed to the base plate **10** by a series of bolts (not shown) which extend through the base plate **10** and into the steel of the frame member **12**. As thus sealed together, a fluid tight seal is provided between the two member except for the inlet and outlet slots **18**, **19** at the ends of the cell.

The anode **16** is rested on and supported by the sealing gasket **14** when the cell is assembled. The lower peripheral portion **32** of the graphite anode is undercut to provide a rectangular shoulder on the lower part of the anode in order to permit the anode **16** to rest on the gasket **14** yet have its lower surface closely spaced from the mercury cathode film on the base plate **10**. The upper part of the graphite anode **16** is treated with oils or other suitable materials to make the anode substantially impervious to chlorine or other gases. The part of the upper surface of the anode **16** against which the positive bus bar is to be clamped is provided with a conductive coating, copper plated, for example, in order to improve the electrical contact between the anode **16** and the bus bars.

In the operation of the cell shown in Fig. 1, the mercury forms a continuous film over the upper surface of the cathode base plate **10**. The sodium chloride brine enters the cell through the slot **18**, usually at high velocity, and helps to form into a film the mercury which is pumped into the cell through the mercury inlet slot **28**. The fast moving brine sweeps the mercury film along the base plate **10**, as well as sweeps along the chlorine gas which is electrolytically deposited on the anode as current flows between the anode and cathode. The sodium ions, which are deposited at the cathode, amalgamate with the mercury and are removed from the cell as a sodium-mercury amalgam. The brine, chlorine, and amalgam pass from the cell through the slot **19** at the outlet end **26** of the cell into an end box (not shown in Fig. 1) where the brine, chlorine, and amalgam are separated one from another. Because the rapidly moving brine sweeps the under-surface of the graphite anode substantially clean of chlorine bubbles, there is little polarization of the anode and consequently the cell may be run, with a low voltage drop across the cell, at high current densities of the order of 8 amperes or more per square inch of cathode surface.

In the case of long cells, it may be necessary to provide an intermediate port from which the chlorine can be withdrawn. Unless this is done, the chlorine bubbles may, in the extreme case, take up substantially the entire space between the anode and cathode near the end box end of the cell, and materially increase the electrical resistance between the electrodes in that area. As a rule of thumb, it has been found that cells with anode-cathode spacings of ⅛-inch or greater operate with good efficiency without an intermediate port when the velocity of the brine is sufficiently high to correspond to a Reynolds number between 8,000 and 20,000. The exact length of cell which is practical in a particular installation should be determined experimentally, since other parameters than those mentioned may have to be considered.

From the above description of the cell of Fig. 1 and its operation, it is apparent that a cell made in accordance with this invention is economical to manufacture since readily available materials which require but little machining are used in the construction of the cell. The assembling of the cell, and consequently its disassembly for the purpose of making repairs, is simple and uncomplicated. The use of a monolithic graphite block as both the anode and the cover of the cell eliminates the cover

and separate anode problem encountered in conventional mercury-cathode cells in which means must be provided both for removing chlorine through the anode and cover, for adjusting the anode-cathode spacing, and for passing current through the cell cover to the anode or anodes. Likewise, the base or cathode member of cells made in accordance with this invention is considerably less complex and is more economical to manufacture than is the steel beam type of base structure which is typical of conventional mercury-cathode electrolytic cells.

Referring now to the mercury-cathode electrolytic cell assembly shown in Figs. 2 and 3, and to the transverse sectional view of the cell which is shown in Fig. 4, it may be seen that an actual assembled cell is basically the same, both in structure and in operation, as the simplified cell shown in Fig. 1.

A multi-section electrolytic cell **34** has a brine inlet **26** and a mercury inlet **38** adjacent to one end thereof and an end box **40** attached to the other end of the cell. The cell **34** has a single cathode base plate **42**, but has two monolithic graphite anodes **44***a*, **44***b* between whose adjacent ends is disposed a chlorine gas vent **46**. The anodes **44***a*, **44***b* are separated and electrically insulated from the cathode base plate **42** by a rubber covered frame **48**, which functions and is secured to the base plate **42** similarly to the frame **12** shown in Fig. 1. The frame **48**, however, as will be explained in more detail later, particularly in connection with Figs. 5, 6, and 7, also comprises part of the housing for the chlorine vent **46**. Likewise, as in the case of the cell shown in Fig. 1, each of the anodes **44***a*, **44***b* is separated from the frame **48** by a deformable sealing gasket **50**, composed of rubber or plastic which is not attacked by chlorine and brine. The spacing between the lower surface **52** of the graphite anodes **44***a*, **44***b* and the cathode base plate **42** is controlled by limiting the degree of compressibility of the sealing gasket **50**. The degree of compressibility of the gasket **50** is easily controllable, as for example by inserting wooden spacer blocks **66** shown in Fig. 9, for example, of the desired thickness between the mounting flange portion **54** of each anode at the corners thereof and the frame **48**. As the anodes **44***a*, **44***b* become thinner due to erosion of the surface **52** during the operation of the cell **34**, the anode-cathode spacing increases. To change the anode-cathode spacing, blocks **66** of lesser thickness may be substituted at the corners of the anodes **44***a*, **44***b*, letting the eroded surface **52** of the anode approach closer to the cathode plate **42** and maintaining the desired spacing between the electrodes.

The positive bus bars **56** are clamped against the anodes **44***a*, **44***b* and the anode-to-cathode structures are clamped together in spaced relationship between the frame **48** and the gasket **50** by means of the bolts **58** which pass through apertures (not shown) in the base plate **42**. The bolts are insulated from the cathode base plate **42** by the insulating sleeves **62** and **64**. The positive bus bar **56** is clamped tightly against the anode **44**, by means of a strap **60** which extends across the anode and through which pass the bolts **58**. The deformable gasket **50** is thus compressed as the bolts **58** are tightened until the anode **44** rests solidly against the anode-cathode spacing blocks **66**, one of which is shown in Fig. 9. The negative bus bar **68** is bolted or otherwise electrically connected to the under-side of the cathode base plate **42**.

Although the cell **34** shown in Figs. 2 and 3 is a multi-sectional cell, it should be emphasized that the above description of the cell, except for the part thereof which concerns the chlorine vent **46** which is disposed between the two anodes, would also apply to a slot-type mercury-cathode cell having but a single continuous anode.

Referring now to Figs. 5, 6, and 7, the frame member **48** may be seen to have at one end a mounting flange **70** to which is connected the brine inlet nozzle **72** which is shown in Fig. 9, and another flange **74** at the opposite end of the frame **48** by which the end box **40** may be attached to the cell **34**. Between the two flanges **70**, **74** and extending upwardly from the part **76** of the surface of the frame **48** which is at the level on which the gaskets **50** rest, is the base housing **78** of the chlorine vent **46**. As previously mentioned in connection with the frame member **48**, all the surfaces thereof which may come into contact with brine or chlorine are coated with hard rubber (for example, as at **80**) or other material which is substantially immune to attack by brine or chlorine. Also, the frame **48** is secured to the cathode base plate **42** in the same manner (bolts) as is the cell shown in Fig. 1.

Referring to Fig. 7, it may be seen that the under side **82** of the end of the frame **48** which is adjacent to the brine nozzle mounting flange **70** has an especially heavy coating of hard rubber which is utilized in connection with the brine nozzle **72**. It should also be noted that the spacing increases between the cathode plate **42** and the cross member part **84** of the frame **48** which supports the end of the anode **44***a* which is adjacent to the chlorine vent **46** as the chlorine vent is approached. This rather gradual increase in spacing between the frame **48** and the cathode base plate **42** tends to reduce the turbulence of the brine which is, during operation of the cell **34**, backed up in the housing **78** of the chlorine vent **46**.

Referring now to the chlorine vent **46** and particularly to Fig. 8, a chlorine removal chamber **86** is separated from the brine and chlorine receiving chamber **88** of the chlorine vent **46** by a float operated valve assembly **90** comprising a float **92** and valve **94** which are connected to a bolt **96** and which are free to move axially for limited distances. For example, the stop means **98** limits the downward movement of the valve and the upward movement of the valve is stopped when the valve **94** rests against the seat **100** which is secured to the partition **102** which separates the chlorine removal chamber **86** from the chlorine and brine receiving chamber **88**. As shown in Figs. 14 and 15, the valve **94** has a plurality of grooves **142** in the top surface **144** thereof, the grooves extending outwardly from the centrally disposed aperture **146** to the periphery **148** of the valve **94**. Thus, even though the valve **94** is seated in the closed position, the passageway between the valve **94** and the seat **100** is not completely closed. The lower end **104** of the bolt **96** is maintained in alignment with the aperture **108** in the valve seat **100** by the guide **106** which is secured to the housing **78**, of the chlorine vent **46**. An indicator glass **111**, inserted into the wall of the chlorine vent housing **78**, shows the fluid level within the housing. Chlorine is withdrawn through the port **124** and any brine which, due to fluctuation in brine pressures, passes by the valve **90**, is withdrawn through the port **125**.

Referring to Figs. 9 and 10, there is shown the brine nozzle **72** by which the brine is fed into the cell **34**. In the nozzle assembly **72**, the lower surface of the end **110** of the frame **48** is utilized as the upper part of the brine passageway and is provided with a heavy rubber coating **82** as previously mentioned. The lower surface of the brine passageway is provided by the T-shaped removable insert **112** which is secured to the mounting flanges **70** and **114**. The insert comprises a slotted mounting plate **126**, which corresponds to the transverse part of the T, and a brine flow plate **128**, the "stem" of the T-shaped insert **112**, which extends perpendicularly from the mounting plate **126**. One surface of the brine flow plate **128** is aligned with the edge of the slot **130** in the mounting plate **126**. The length of the slot **130** approximately equals the width of the brine channel in the cell **34**.

The brine inlet **36**, which has mounting flanges **132** extending therefrom, is attached to the cell **34** by the

same bolts and nuts **120** which secure the insert **112** to the cell **34**.

The mercury inlet **38** is secured to the bottom of the cathode base plate **42**, by welding, for example, and supplies mercury to the cell **34** through the mercury inlet slot **122** which is adjacent to but spaced from the end of the brine nozzle insert **128**. It should be noted that the end part **116** of the cathode base plate **42** is thinned to provide room for the brine nozzle insert **112** to be extended inwardly towards the mercury inlet slot **122**. A rounded surface **134**, better shown in Fig. 13, is provided between the top surface of the cathode base plate **42** which faces the anode and the thinned end part **116** thereof. The end **135** of the brine flow plate **128** of the nozzle insert **112** is curved to provide, with the rounded surface **134**, an extension of the mercury inlet slot **122**. The top surface of the brine flow plate **128** is disposed above the top surface of the cathode base plate **42**. This arrangement prevents mercury being swept off the rounded surface **134** by the high velocity flow of brine and thus exposing the surface **134** to attack by the brine.

The brine nozzle insert **112** is the part of the nozzle assembly **72** which is most subject to wear. With the mounting means shown, the nozzle assembly **72** may be easily repaired and new inserts **112** installed when needed without further dismantling of the cell **34**.

Another form of brine nozzle assembly **72*a*** is shown in Figs. 11 and 12. This nozzle assembly differs from the nozzle assembly **72** in that the nozzle insert **112*a*** provides the entire passageway for the brine which enters the cell **34**. To permit the nozzle assembly **72*a*** to be utilized, the thick rubber coating (**82** on the end **110** of the frame **48**) which served as the upper surface of the brine passageway in the nozzle **72**, is removed. However, the "normal" rubber coating, shown at **136** in Fig. 11, is retained on the end part **110**.

The nozzle insert **112*a*** of the nozzle assembly **72*a*** is of T-shaped cross-sectional configuration, with the transverse part of the T being used as the mounting plate **126*a*** for the insert. The brine passage is a slot **138** which passes through the transverse part of the T and extends through the stem of the T, becoming progressively smaller in cross-section towards the outlet end of the stem. Because the brine passage slot is wide, it is often desirable to provide braces **140** between the upper and lower walls of the brine passage. Care must be exercised to set the braces **140** far enough from the the brine exit end of the insert **112*a*** that the continuity of the brine jet is not disturbed. Unless the brine jet is a continuous stream, the sweeping action of the brine on the mercury cathode will be irregular and may result in bare steel of the cathode base plate **42** being exposed to attack by the brine.

The brine insert of the type shown in Fig. 12 has the advantage that changes in the cross-section of the brine passageway may be made by changing inserts **112*a***. In the insert **112** shown in Fig. 10, the brine passageway is limited because the coating **82** is fixed on the end **110** of the frame **48** and the stem of the T **128** cannot be lowered without danger of exposing the curved surface **134** to the brine as previously explained.

Although only slag free mild steel has been mentioned as a material from which the cathode base plate may be made, that material is mentioned because of the low cost of such steel and the ease with which it may be drilled and machined. Other metals may be used provided they have little or no tendency to amalgamate with the mercury of the cell cathode. Nickel is an example of a suitable material.

Likewise, other coatings and surfaces than hard rubber may be used to coat the metal parts of the cell which are exposed to the brine. Rubber is mentioned as being a typical suitable material which is economical and has long life characteristics with respect to resistance to attack by the brine.

The operation of the electrolytic cell shown in Fig. 2 is basically the same as that of the simplified cell shown in Fig. 1. Brine is pumped into the cell **24** from the brine inlet **36** through the slot **130** formed in the brine nozzle insert **112**. The mercury for the cathode of the cell **34** is pumped into the cell from the mercury inlet **38** through the slot **122** in the cathode base plate **42**. The brine is pumped through the cell **34** at high velocity and at a Reynolds number in excess of 8,000. The brine flows between the bottom surface **52** of the anodes **44*a***, **44*b*** and the cathode base plate **42**, but is separated from the base plate **42** by the thin film of mercury which comprises the cathode of the cell. As previously mentioned, surfaces of parts of the cell other than the anode and cathode are protected from the brine by a coating such as hard rubber. Further, the disposition of the top of the stem of the T-shaped brine nozzle insert **112** above the top surface of the cathode base **42** prevents the brine stream from sweeping the mercury off the curved part **134** of the cathode base above the mercury inlet slot **122**. Thus, the curved part is covered by mercury and is not exposed to attack by the chlorinated brine.

The high velocity brine stream sweeps along and assists in the formation of the desired thin film of mercury which comprises the cathode of the cell. In addition, when power is applied to the cell, the brine stream sweeps along the chlorine which is liberated near the anode **44** of the cell. The sodium ions which are released at the cathode combine with the mercury of the cathode to form a sodium-mercury amalgam. The amalgam, chlorine, and brine pass from the opposite end of the cell **34** into the end box **40** where the brine, chlorine, and amalgam are separated and removed.

An end box which is suitable for use with the cell **34** is disclosed and claimed in applicants' U.S. Patent No. 2,848,408, filed August 19, 1958, which is a continuation-in-part of application Serial No. 451,611, entitled "End Box for a Mercury Cathode Electrolytic Cell," filed August 23, 1954, now abandoned.

The chlorine vent **46** is utilized to remove chlorine which has been liberated as the brine is swept past the anode **44*a***. As mentioned previously, in long cells it is desirable that the chlorine be vented intermediate the ends of the cell in order to prevent the brine from becoming saturated with chlorine bubbles and thus reducing the operating efficiency of the cell.

The chlorinated brine rises in the brine receiving chamber **88** of the chlorine vent **46** to a height determined by the pressure at which the brine is pumped into the cell. Normally, this height is sufficient to raise the float **92** of the valve, which is made of resin impregnated wood, and seat the valve **94** against the valve seat **100**. However, when sufficient chlorine has bubbled through the brine in the brine receiving chamber **88** to build up a pressure which approaches the brine pressure, the brine level is forced downwardly by the chlorine gas and the valve is opened until the chlorine is vented into the chlorine removal chamber **86** where it is removed through the chlorine removal opening **124**. As the gas pressure is reduced due to the valve **94** being opened, the brine again rises, raising the float until the valve **94** is seated against the valve seat **100**.

Although the valve **94** is seated against the valve seat **100**, some chlorine can pass into the chlorine removal chamber **86** from the brine receiving chamber **88** through the grooves or channels **142** in the top surface **144** of the valve **94**. The indentations or grooves **142** permit a small amount of gas to escape constantly from the brine receiving chamber **88**, and in so doing the flow of gas around the valve **94** is sufficient to prevent valve sticking due to the formation of brine crystals around the valve assembly **90**.

Thus, by means of a chlorine vent or vents disposed between anode segments, longer cell assemblies may be utilized than would otherwise be practicable with efficient

operation characteristics. Because the turbulence and velocity of the brine sweeps the surface of the anode clean of gas bubbles, cells made in accordance with the invention may be operated at high current densities per unit area without excessive polarization of the electrodes. Operation of the cells at high current densities results in an economy in building space per unit of cell output. Also, the cell itself is economical to build because of its small size in proportion to its capacity.

It has also been found that cells made in accordance with this invention may be operated with "raw" brine, that is, sodium chloride brine which is pumped into the cell direct from a brine well and which has not undergone the conventional treatment to remove impurities therefrom. The consumption of graphite due to chemical attack of the lower surface **52** of the anode **44** has been found to be considerably less than with graphite anodes of the type used in prior art mercury-cathode cells. The slow rate of consumption of the graphite not only represents a saving in anode cost, but also means that the anode-cathode spacing need be adjusted less frequently than is the case with mercury-cathode cells of more conventional construction.

The use of the monolithic or composite graphite anode as both anode and cell cover represents a saving due both to the simplicity of the mechanical construction of the anode and from the fact that the anode bus bars are connected directly to the anode without having to pass through a separate cell cover. Clamping the bus bars directly on the anode results in a saving of up to .1 volt over the prior art means of applying power to the anode. In a 30,000 ampere cell, a saving of .1 volt loss in potential in applying power to the cell represents a substantial saving in power.

While brine and mercury inlet nozzles of the previously described types are very satisfactory in operation, they are rather expensive to manufacture because the large cathode base plate must be machined to form the mercury inlet slot and to accommodate the insertion of the brine nozzle.

Figs. 16, 17, and 18 illustrate an alternative form of composite brine nozzle and mercury inlet slot assembly in accordance with this invention which may be attached to the fluid entry end of a cathode base plate. The composite brine nozzle and mercury inlet slot assembly, indicated generally by the numeral **150**, comprises a brine inlet member **36***a* which is similar to the brine inlet members **36** shown in Figs. 9 and 11, a brine inlet lip member **152** (shown in Fig. 17), mercury feedthrough and brine flow member **154** (fragmentary view shown in Fig. 18), a flange **156** which is secured to and extends downwardly from the cathode base plate **158**. The brine inlet lip member **152** is, basically a rectangularly shaped block having a generally rectangularly shaped cut-out part which, when the lip is in position as shown in Fig. 16, has its length dimensional edges parallel with the flow surface **160** of the cathode base plate **158**. The lower edge of the cutout extends outwardly from the body of the block to form the lip **162** comprising the lower flow surface for brine entering the cell to which the assembly **150** is attached. All the surfaces of the lip member **152** which are to be exposed to brine are covered with a coating of rubber or other suitably resistant material.

The mercury feedthrough and brine flow member **154** is, like the brine inlet lip member, a gradually rectangularly shaped block-like member having a generally rectangularly shaped cut-out part into which the lip **152** extends when the composite assembly **150** is operatively positioned with respect to the inlet end of the cell. The projecting end of the lip **152** extends close to but does not touch the end of the cathode base plate **158**. The brine flow surface of the lip **162** is disposed slightly above the flow surface **160** of the cathode base plate. The brine flow surface **164** of the mercury feed through and brine flow member **154** is generally aligned with the lower surface of the anode **168**.

The lower part of the mercury feed through and brine flow member **154** (the part shown in Fig. 18) contains a plurality of bores **166** which are threaded at their lower end to receive mercury conduits or pipes (not shown). Using a plurality of mercury inlet means to feed the member **54** results in a more uniform flow distribution of the mercury entering the cell than is easily practicable when only a single mercury inlet pipe is used.

The brine nozzle and mercury inlet slot assembly **150** is attached to the inlet end of the cell by means of bolts **170** which extend through bores **172** in the mercury feedthrough and brine flow member **154** and through the flange **156**. An inflatable gasket **174** is disposed between the mercury feedthrough and brine flow member **154** and the anode **168** and is retained in position by a strip element **176** secured to the member **154**. The gasket **174** prevents gas leakage between the assembly **150** and the anode **168**.

As may be seen in Fig. 16, the anode **168** is a composite type anode in which the lower or brine facing part is made of a graphite composition which resists erosion by the brine and the upper part of the anode, to which the current carrying buss bars and supporting structures **178** are attached, for example, are made of an anode composition which is made gas impervious and which has high current carrying capabilities. The various anode segments are secured together by suitable electrically conductive bonding material.

Fig. 19 illustrates an alternate manner of supporting the anode **168** with respect to the cathode base plate **158**. The anode **168** is held in position laterally by channel iron members **180** which are rubber covered, for example, on the anode facing side and which are secured to the cathode base plate **158** by means of bolts **182**. An inflatable gasket **184**, which may, or may not, be a continuation of the gasket **174**, is disposed between the anode **168** and the channel members **180** to prevent gas loss along the junction between the juxtaposed members. A second, sheet-like gasket seal **186** between the top of the channel member **180** and the top of the anode **168** further assures the prevention of gas leakage.

As shown in Fig. 19 the anode is supported spatially with respect to the cathode base **158** by means of the bolts **188** which extend between the buss bar and anode supporting structure **178** and the base plate **158** (illustrated as a two layer structure in Fig. 19). Such an arrangement eliminates the need for providing a shoulder on the anode **168** by which the anode rests on a deformable gasket as described previously.

Thus, the brine nozzle and mercury inlet assembly and anode supporting structures shown in Figs. 16 to 19 eliminated the need for expensive tooling of the cathode base plate which may then comprise only a relatively inexpensive flat steel plate, effecting economies in the cost of constructing such cells.

We claim:

1. In a slot type liquid cathode electrolytic cell having a flat cathode base plate, a monolithic graphite anode having a flat surface facing the upper surface of said base plate, and electrode separator means having a polygonal opening through which said anode extends, means for applying brine and mercury to said cell comprising an elongated mercury inlet slot adjacent to the feed end of said base plate, said inlet slot being disposed substantially perpendicularly with respect to the direction of mercury flow through said cell and extending substantially completely across the opening of said separator frame, said base plate having a recess in the top surface thereof and extending from said slot to the feed end thereof, the mercury inlet slot having a curved surface on the downstream side thereof, and a replaceable brine nozzle having an elongated slot-like orifice which is coextensive in length with the length of

the mercury slot, the upper surface of said orifice being substantially aligned with the flat lower surface of said anode, the lower surface of said orifice being disposed slightly above the surface of that part of said base plate which is disposed downstream from said mercury inlet slot, the lower part of said nozzle extending into the recess in the feed end of said base plate, the inner end of the lower part of said nozzle being curved in the direction of mercury flow through said cell.

2. In a slot type liquid cathode electrolytic cell having a flat cathode base plate, a monolithic graphite anode having a flat surface facing the upper surface of said base plate, and electrode separator means having a polygonal opening through which said anode extends, means for applying brine and mercury to said cell comprising an elongated mercury inlet slot adjacent to the feed end of said base plate, said base plate having a rectangularly shaped recess in the top surface thereof and extending from said slot to the feed end thereof, the mercury inlet slot having a curved surface on the downstream side thereof and a two piece brine nozzle having an elongated slot-like orifice which is coextensive in length with the length of the mercury slot, the upper surface of said orifice being a part of said electrode separator frame and being substantially aligned with the flat lower surface of said anode, the lower surface of said orifice being a part of a replaceable insert of T-shaped cross-sectional configuration, said lower surface being disposed slightly above the surface of said base plate which is disposed downstream from said mercury inlet slot, the insert part of said nozzle extending into the recess in the feed end of said base plate, the inner end of the insert part of said nozzle being curved in the direction of mercury flow through said cell.

3. In a slot type liquid cathode electrolytic cell having a flat cathode base plate, a monolithic graphite anode having a flat surface facing the upper surface of said base plate, and electrode separator means having a polygonal opening through which said anode extends, means for applying brine and mercury to said cell comprising an elongated mercury inlet slot adjacent to the feed end of said base plate, said base plate having a recess in the top surface thereof and extending from said slot to the feed end thereof, the mercury inlet slot having a curved surface on the downstream side thereof, and a replaceable brine nozzle of T-shaped cross-sectional configuration, said nozzle having an elongated slot-like orifice in the stem of the T, the orifice being coextensive in length with the length of the mercury slot, the upper surface of said orifice being substantially aligned with the flat lower surface of said anode, the lower surface of said orifice being disposed slightly above the surface of said base plate which is disposed downstream from said mercury inlet slot, the lower part of said nozzle extending into the recess in the feed end of said base plate, the inner end of the lower part of said nozzle being curved in the direction of mercury flow through said cell.

4. A slot type liquid cathode electrolytic cell comprising a rectangular flat metallic cathode base plate having an input end and an output end, said input end of said base plate having a substantially rectangular recess in the upper surface thereof, said recess communicating with and extending down stream from said input end of said base plate, an electrically insulating rectangular frame, said frame being secured to said base plate with the sides of said frame making a fluid tight seal with the upper surface of said base plate, each of the ends of said frame having an elongated recess in the lower part thereof, a deformable gasket disposed on the upper surface of said frame, a plate-like monolithic graphite anode having a peripheral shoulder portion and having a flat lower surface, said shoulder portion resting on said gasket with the flat lower surface of said anode being spaced from said base plate, means for attaching brine and mercury inlet apparatus to the feed end of said cell, said inlet apparatus including a nozzle which extends into the recess in said base plate, the nozzle including a fluid discharge orifice having substantially parallel upper and lower surfaces, the lower surface being disposed above the non-recessed part of the upper surface of said base plate and below the lower surface of said anode, means for attaching an end box to the discharge end of said cell, and means for applying suitable potentials to said anode and said base plate.

5. A slot type liquid cathode electrolytic cell comprising a rectangular flat cathode base plate of slag free mild steel having an input end and an output end, said input end of said base plate having a substantially rectangular recess in the upper surface thereof, said recess communicating with and extending down stream from said input end of said base plate, a rubber covered steel frame having a rectangular outer periphery, said frame being secured to said base plate with the sides of said frame making a fluid tight seal with the upper surface of said base plate, each of the ends of said frame having an elongated recess in the lower part thereof, a deformable gas impervious gasket disposed on the upper surface of said frame, a plate-like monolithic graphite anode having a peripheral shoulder portion and having a flat lower surface, said shoulder portion resting on said gasket with the flat lower surface of said anode being spaced from said base plate, means for attaching brine and mercury inlet apparatus to the feed end of said cell, said inlet apparatus including a nozzle which extends into the recess in said base plate, the nozzle including a fluid discharge orifice having substantially parallel upper and lower surfaces, the lower surface being disposed above the non-recessed part of the upper surface of said base plate and below the lower surface of said anode, means for attaching an end box to the discharge end of said cell.

6. A slot type mercury cathode electrolytic cell comprising a cathode base plate having a flat upper surface, a rectangularly shaped frame disposed on and against the upper surface of said base plate, opposite sides of said frame member having cutouts which provide slots between said frame and said cathode base plate, the surface of said frame being covered with an electrically insulating material which is substantially immune to attack by chlorinated brine, said frame and said base plate having means adjacent to one of said slots for attaching mercury and brine input means and having means adjacent to the other of said slots for attaching an end box, a monolithic graphite anode supported on said frame and presenting a planar surface towards but spaced from said cathode base plate, said anode being the cover of said cell, and means for applying electrical potentials to said anode and said base plate.

7. A slot type mercury cathode electrolytic cell comprising a cathode base plate having a flat upper surface, a rectangularly shaped frame disposed on and against said flat surface of said base plate, opposite sides of said frame member having cutouts which provide slots between said frame and said cathode base plate, the surface of said frame being made of an electrically insulating material which is substantially immune to attack by chlorinated brine, means adjacent to one of said slots for attaching mercury and brine input means and means adjacent to the other of said slots for attaching an end box, and a monolithic graphite anode supported on said frame and presenting a planar surface towards but spaced from said cathode base plate, said anode being the cover of said cell.

8. A slot type liquid cathode electrolytic cell having an input end and an output end, comprising a metallic cathode base plate having a flat upper surface over substantially the entire active electrode area thereof, a rectangular frame having two side members, an input end member, an output end member, and two cross members disposed intermediate the end members, means for

protecting said frame from attack by chlorinated brine during the operation of the cell, each of the polygons formed by the intersection of the side members with a cross-member and an end member having contiguous coplanar surfaces, the side members being secured to the upper surface of said base plate in a liquid tight manner, each of said end members and said cross members having an elongated recess in the lower surface thereof which faces said base plate, a plurality of monolithic graphite anodes each having a flat lower surface and having a peripheral shoulder, an anode being disposed on at least one of said polygons with said shoulder carried by said contiguous coplanar surfaces and said flat lower surface extending downwardly towards said base plate, means disposed between said anodes and said frame for electrically insulating said anodes from said cathode, means attached to another polygon formed by the intersection of said cross members and said side members for withdrawing gas from said cell while controlling fluid pressure within said cell, means for applying brine and mercury cathode material to the input end of said cell, means for applying suitable potentials to said anodes and said base plate, and an end box attached to the output end of said cell.

9. A slot type liquid cathode electrolytic cell comprising a metal cathode base plate having a flat upper surface over substantially the active electrode area thereof, a rectangular frame secured to said flat upper surface, said frame having side members, an input end member, an output end member, and cross members disposed intermediate the end members, a plurality of polygonal openings being formed by the intersection of the side members with other members in each of said end members and said cross members having an elongated recess in the lower surface thereof which faces said base plate, a plurality of monolithic graphite anodes each having a flat lower surface and having a peripheral shoulder thereon, an anode being disposed over at least one of said polygonal openings with said shoulder carried on said members and said flat lower surface extending downwardly towards said base plate, means covering at least one polygonal opening formed by the intersection of said cross members and said sides for withdrawing gas from said cell while controlling fluid pressure within said cell, means for applying brine and mercury cathode material to the input end of said cell, means for applying suitable potentials to said anodes and an end box attached to the output end of said cell.

10. A slot-type liquid cathode electrolytic cell comprising a cathode base plate having a flat upper surface, a rectangular frame member disposed on the upper surface of said base plate and making a fluid tight seal therewith, a monolithic sheet-like graphite anode supported on said frame member, said anode being electrically insulated from said frame member, and sealed thereto in a fluid tight manner, said anode being the cover of said cell, the surface of said anode which faces said base plate being flat, means including a recess at one side of said frame for introducing brine and liquid cathode material to the space between said base plate and said anode, means at an opposite side of said frame for withdrawing brine, cathode material, and the products of electrolysis, and means for applying suitable electric currents to said anode and said cathode.

11. In a slot type liquid cathode electrolytic cell having a flat cathode base plate, a block-like graphite anode having a flat surface facing the upper surface of said base plate, and means for supporting the anode with respect to the cathode base plate, means for applying brine and mercury to said cell comprising an elongated mercury inlet slot disposed adjacent to the feed end of said base plate, said inlet slot being disposed substantially perpendicularly with respect to the direction of mercury flow through said cell and extending substantially completely across the opening between the base plate and anode, and a replaceable brine nozzle having an elongated slot-like orifice which is coextensive in length with the length of the mercury slot, the upper surface of said orifice being substantially aligned with the flat lower surface of said anode, the lower surface of said orifice being disposed slightly above the surface of that part of said base plate which is disposed downstream from said mercury inlet slot.

12. An electrolytic cell in accordance with claim 11, wherein the means for applying brine and mercury to the cell comprises a composite assembly which is coupled to the feed end of the cell.

No references cited.