

June 5, 1956

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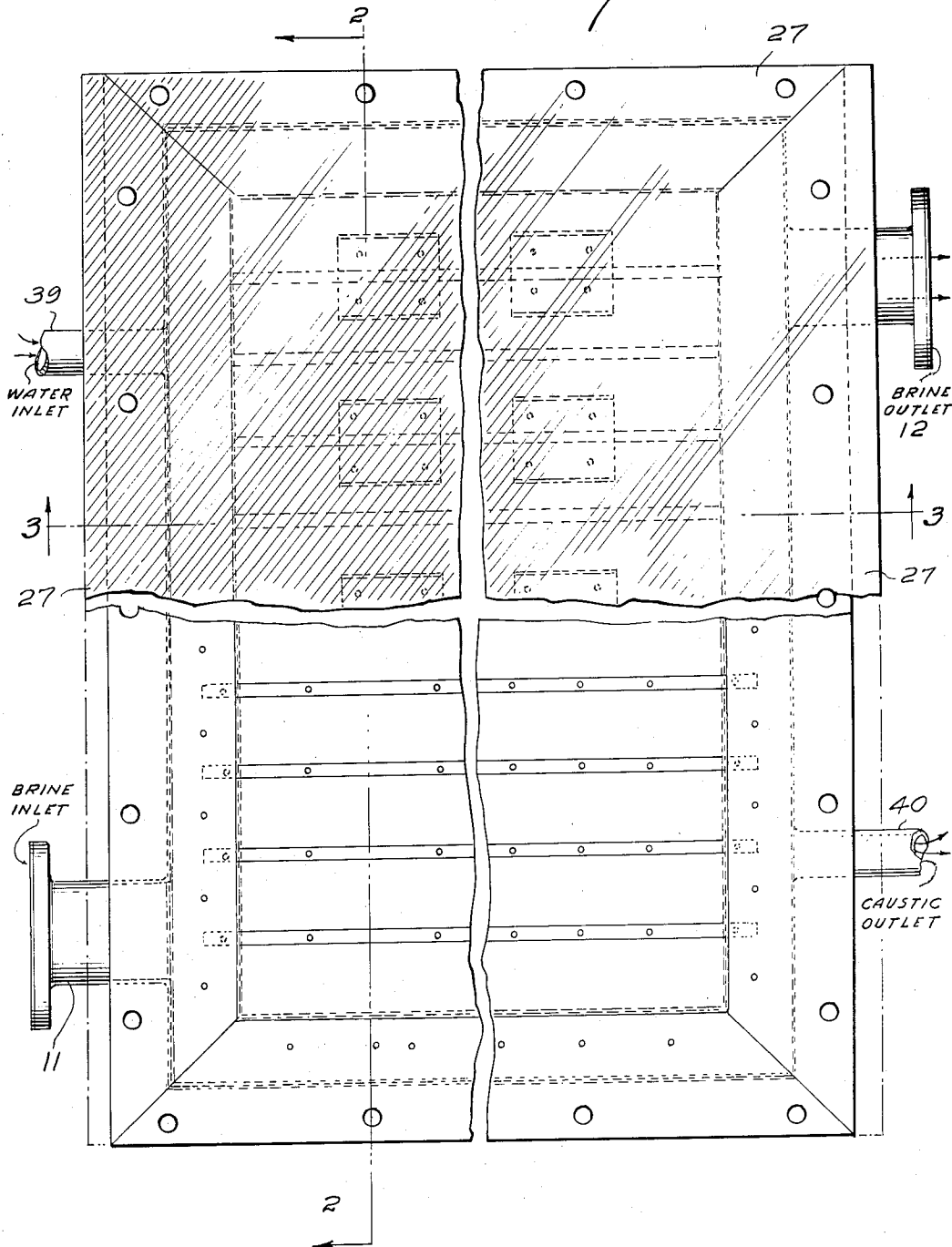
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MERCURY TYPE, CAUSTIC, CHLORINE CELL

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Fig. 1.



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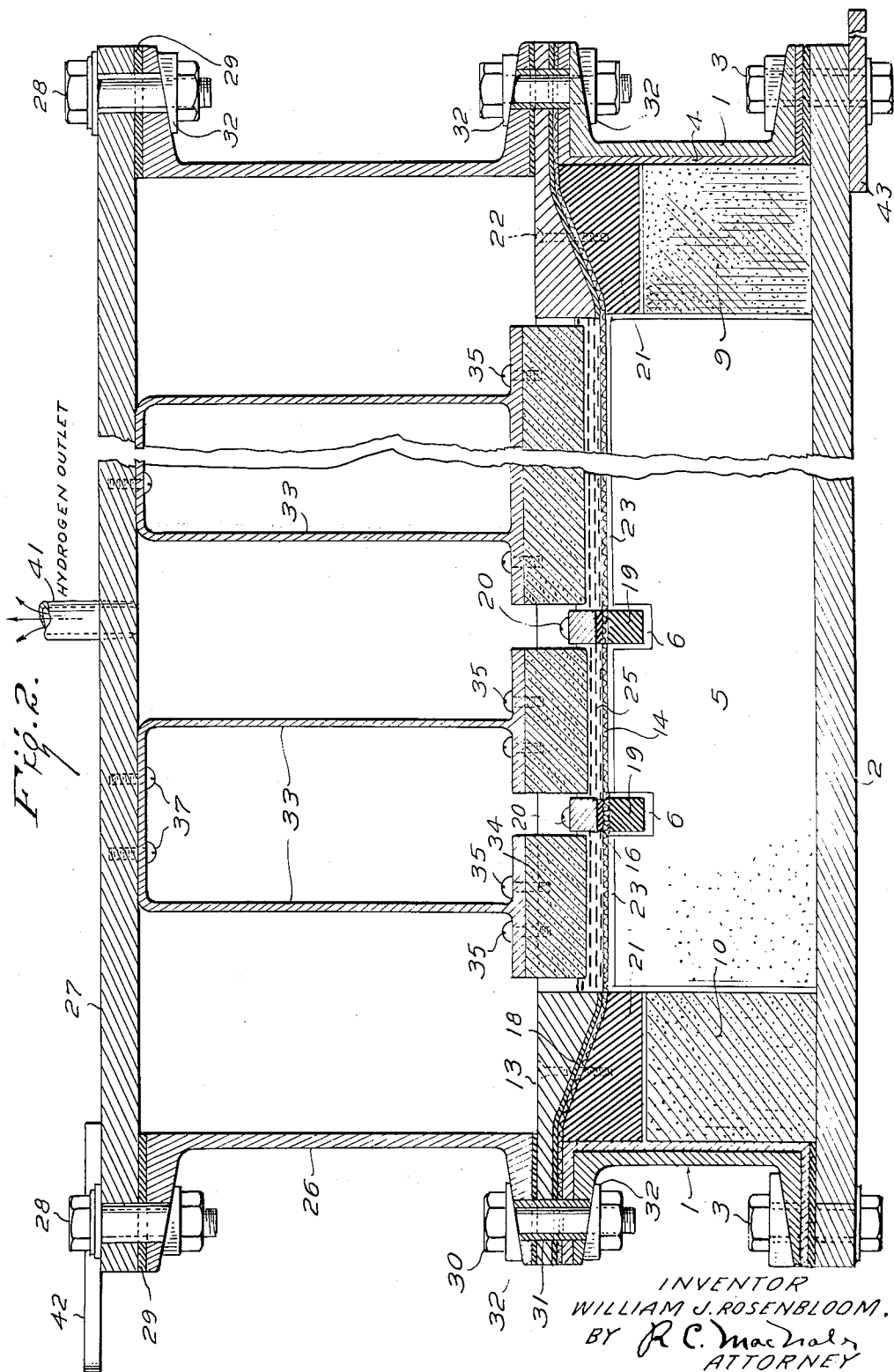
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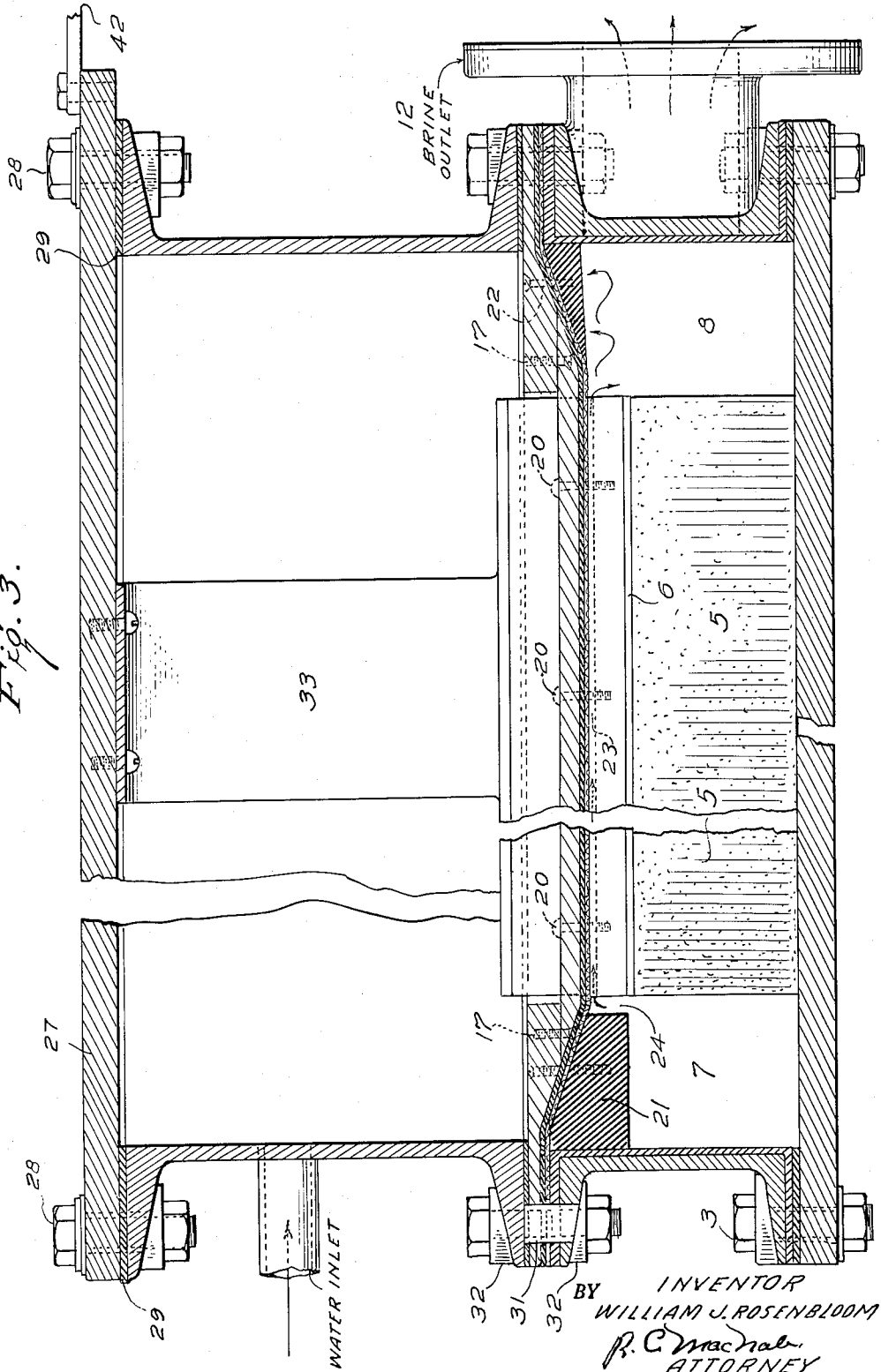
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Fig. 3.



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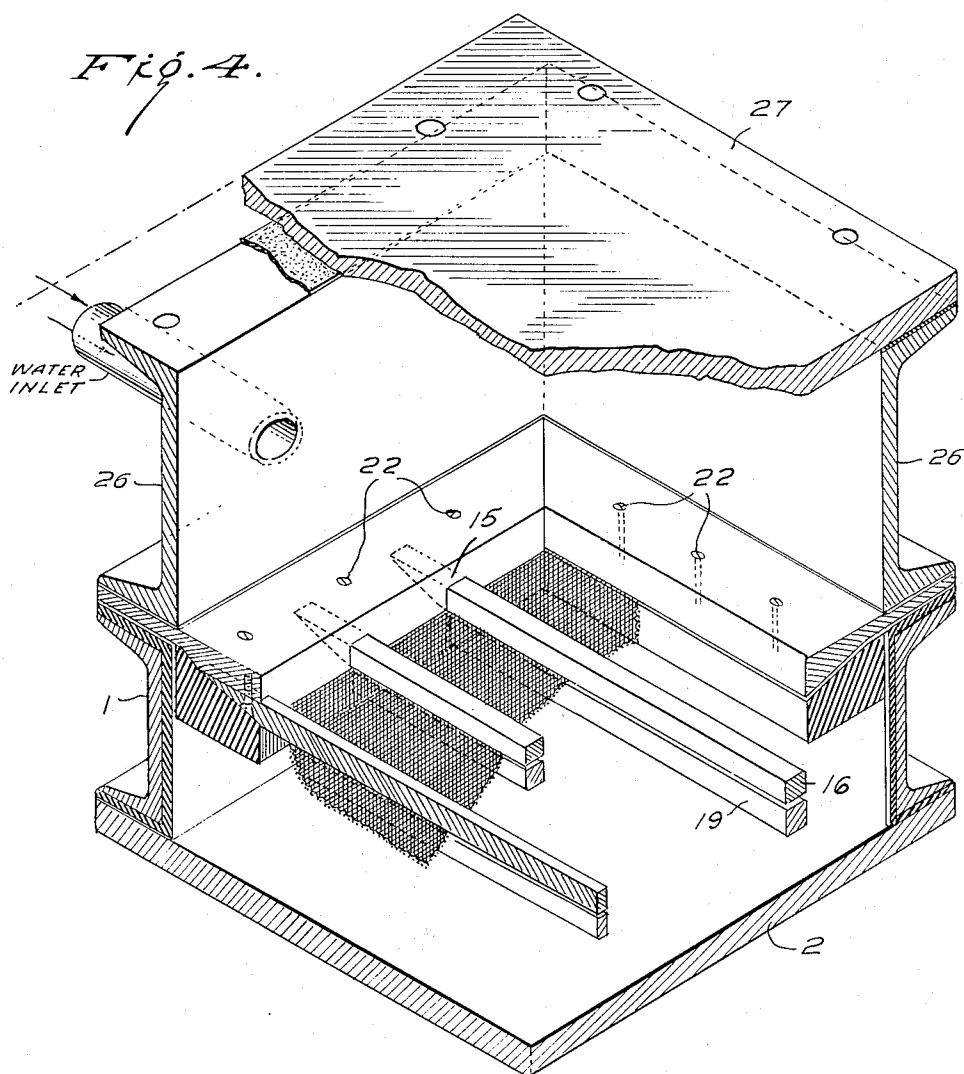
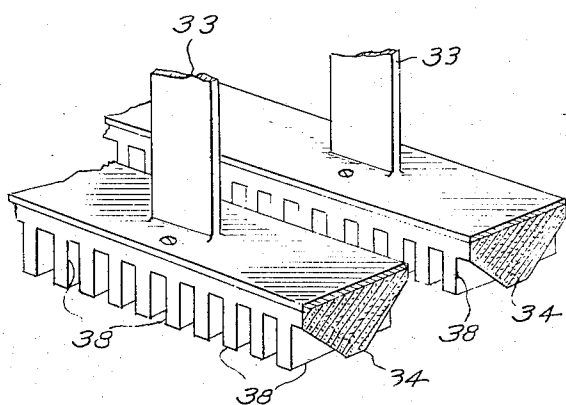
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2,749,301

MERCURY TYPE, CAUSTIC, CHLORINE CELL

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7 Claims. (Cl. 204—251)

This invention relates to an improved method and apparatus for conducting electrolysis in which a mercury cathode is supported on a porous diaphragm in contact with an electrolyte. More particularly the invention relates to such a method and apparatus for the electrolysis of a concentrated aqueous solution of sodium chloride to produce chlorine and sodium amalgam, and water or other suitable reactant, is floated on top of the mercury to react with the amalgam to produce sodium hydroxide and hydrogen, but it is understood the invention may be employed to advantage in other electrolytic processes using other electrolytes and producing other products, as for instance the production of potassium hydroxide from potassium chloride solutions, the production of metals or hydroxides and sulfuric acid from sulfates and the production of sodium or potassium salts or compounds by the reaction of suitable corresponding reagents with the amalgam in place of water.

In the standard mercury type, caustic, chlorine cell mercury is continuously transferred from an electrolyzer in which electrolysis of the brine takes place to an amalgam decomposer where the mercury is denuded of amalgam by reaction with water. This is accomplished by providing both the electrolyzer and the denuding cells with gently sloping floors and flowing the mercury by gravity serially through the cells on the floor from one end to the other. A suitable mercury trap is provided between the cells to prevent intermixing of the brine in the electrolyzer with the water or sodium hydroxide solution formed in the denuder. The floor of the electrolyzer is made of steel and is electrically connected to the negative terminal of a suitable source of direct current so that the mercury forms the cathode of the cell. The anode is formed of graphite and is suspended in the brine over the mercury. During electrolysis the chlorine ions flow to the graphite anode and chlorine is released as gas. The sodium ions flow to the upper side of the mercury cathode and the sodium released forms sodium amalgam which diffuses through the layer of mercury. The sodium content in the mercury is not generally allowed to exceed about 2%. The mercury containing the amalgam then flows to the decomposer or denuder making contact in its course through the cell with graphite and water to produce hydrogen gas and sodium hydroxide. Denuded mercury is then pumped up to the electrolyzer to complete the cycle.

It is an object of the present invention to provide an electrolytic cell which shall be relatively simple in design and construction and efficient and inexpensive in operation.

A further object of the invention is the provision of such a cell which shall be capable of operation at high current density with a low voltage drop and which shall require only a minimum of mercury and floor space.

A still further object of the invention is the provision of an improved diaphragm and diaphragm support that permits close positioning of the anode with respect to the mercury cathode, whereby a rapid flow of electrolyte

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is obtained that results in more complete removal of evolved chlorine gas and prevents its accumulation in pockets or on the surfaces of the electrodes.

The above objects and others which will become apparent from the detailed description of the invention which follows, are accomplished by the provision of a three unit cell, the top and bottom units of which comprise compartments for reception of the cathode and anode respectively. The third unit consists of a diaphragm and diaphragm support which is positioned between the upper and lower units. Provision is made for locating the anode close to the cathode, thus lowering the electrical resistance of the cell. This is accomplished by using a relatively thin, porous diaphragm of electrically non-conductive, corrosion-resistant, material in combination with a specially constructed diaphragm support and cathode and anode arrangement. For this purpose the diaphragm support is provided with a plurality of cross bars extending from one side of the support to the other, which divides the mercury cathode into a series of narrow, parallel electrodes extending across the cell. The diaphragm which supports the mercury is attached to the underside of the diaphragm support. This is advantageously accomplished by means of a plurality of non-conducting, corrosion resistant, clamping strips juxtapositioned with respect to the cross bars but located on the opposite side of the diaphragm, in the anode compartment. The anode is provided with a plurality of channels or grooves for receiving the clamping strips. Thus, the strips on the support and the anode with its grooves, cooperate to enable the top surface of the anode to project to within a short distance of the diaphragm and provide a plurality of shallow, narrow passage-ways for the brine electrolyte directly beneath the series of parallel mercury cathodes.

In addition, the invention comprises certain further novel features of construction and operation, as shown in the accompanying drawings and pointed out in the following description.

In the drawings:

Figure 1 is a top plan view of an electrolytic cell constructed in accordance with the present invention with the central part and part of the cover broken away.

Figure 2 is a vertical sectional view taken along line 2—2 of Figure 1 with the anode shown in elevation.

Figure 3 is a vertical sectional view taken along line 3—3 of Figure 1 with the mercury eliminated.

Figure 4 is a view in perspective of one corner of the cell with parts broken away, and,

Figure 5 is a fragmentary detail view in perspective of the electrodes that dip into the mercury.

Referring to the drawings, wherein for purposes of illustration there is shown one form of a preferred embodiment of the invention, the cell consists of a lower unit or anode chamber of generally rectangular shape having side walls 1 and a bottom 2 secured thereto by bolts 3. The side walls may advantageously be formed of channel iron welded together at the corners, and lined on the inside and top and bottom flanges with rubber 4, for preventing corrosion by the electrolyte. Resting on the bottom and in electrical contact therewith is the anode 5 of carbon or graphite. Preferably the anode is of monolithic construction provided with spaced parallel grooves or channels 6 in its top face which extends from one side to the other, although it may be formed of blocks of graphite suitably cemented together in electrical contact. The anode is centrally positioned on the bottom plate and spaced from side walls to provide inlet and outlet fluid headers 7 and 8 respectively (Figure 3) along two opposite sides, and accommodate filler or spacing blocks 9 and 10 (Figure 2) which extend along the other two opposite sides. The spacing blocks

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may be formed of acid resistant brick or the like and serve, in addition to filler members, to position the anode with respect to the diaphragm support about to be described, so as to align the grooves in the anode for reception of the clamping bars on the diaphragm support. The inlet header 7 is provided with a flanged inlet port 11 (Figure 1) for receiving a concentrated aqueous solution of sodium chloride from a suitable source not shown, and the outlet header 8 is provided with a flanged outlet port 12 for discharge of chlorine gas and spent brine solution.

Resting on the top flange of the side walls of the anode compartment is a diaphragm support indicated generally by the numeral 13, to which is secured the diaphragm 14. The support is of frame like construction with an internally projecting, overhanging portion extending into the cell as shown. The frame is advantageously made of iron for a purpose later described, and is provided on the under side of the overhang with a plurality of notches 15 shown best in Figure 4 for reception of the ends of iron cross bars 16. The cross bars extend across the frame from the inlet header side of the lower compartment to the outlet header side of the compartment and are securely fastened to the frame by means of screws 17 shown in dotted lines in Figure 3. As illustrated the entire underside of the metal diaphragm support is suitably protected with a film of rubber 18 for protection against corrosion. Diaphragm 14 is clamped to the under side of the metal frame by means of clamping strips 19 which may be formed of hard rubber and which are secured to the cross bars 16 by means of screws 20. The diaphragm is securely clamped about its periphery to the underside of the overhanging portion of the metal frame by means of a mating hard rubber frame 21. The hard rubber frame is secured to the metal frame by means of screws 22.

As perhaps best illustrated in Figure 2, the anode 5 projects upwardly between the diaphragm clamping strips 19 to a position closely adjacent the diaphragm 14 when the diaphragm assembly is in position on the side walls of the lower compartment. The space 23 between them may vary from a sixteenth to one-half of an inch, the object being to provide the least electrical resistance or shortest distance possible, commensurate with the width and length of the passage and the velocity of flow of electrolyte for a given desired operating voltage drop.

In order to prevent entrapment of evolved gas, (chlorine) between the diaphragm and the top of the anode, the brine electrolyte is caused to flow upwardly from the inlet header 7 through space 24 into space 23 and from space 23 directly into outlet header 8. In header 8 the gas will separate from the liquid and rise to the top of the header and both liquid and gas will discharge through outlet 12. Thus, the gas evolved at the anode will be swept by the brine across the cell into the outlet header and is prevented from backing up into inlet header 7 by the upward flow of brine through passage 24. This is accomplished by designing the hard rubber frame 21 so that its bottom terminates below the top surface of the anode along the inlet header side of the cell while along the outlet header side of the cell its bottom slopes outwardly from the level of the lower diaphragm surface to a slightly higher plane, as shown in Figure 3.

The diaphragm 14 is formed of thin, porous corrosion-resistant, electrically non-conducting material. Good results have been obtained using fabrics made from synthetic plastic materials known in the trade as Vinyon-N, and Saran. Chemically, Vinyon-N is a copolymer of vinyl chloride and acrylonitrile, and Saran is a copolymer containing about 90% vinylidene chloride and 10% vinyl chloride. The fabrics are preferably woven from twisted, multi-filament threads as contrasted with mono-filament threads. This gives greater strength and increased resistance to distortion and increases the porosity of the fabric to electrolyte. A woven fabric containing 80 x 80

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threads per square inch of 140 and 116 denier have good results although other types of fabric, such as felted fabrics or even thin perforated sheets from $\frac{1}{100}$ " to $\frac{1}{8}$ " thick may be used. Nor need the diaphragm be made of synthetic plastic material entirely or even partly, since it is within the purview of the invention to use other materials such for instance as asbestos cloth, etc. In general the diaphragm should be of sufficient strength to support $\frac{1}{4}$ inch layer of mercury with its superincumbent layer of water or dilute sodium hydroxide on a 2 inch span without sagging more than around $\frac{1}{16}$ of an inch. It must have very little stretch when in use and be able to withstand the corrosive action of chlorine gas, hypochlorites, chlorates, brine and weak solutions of sodium hydroxide at temperature of 80° C. In addition the diaphragm must be easily wetted by the brine electrolyte at all temperatures up to 80° C. and have such properties that the amalgam formed in the mercury does not adhere to it when it is so wetted.

As indicated, the cathode 25 which consists of a layer of mercury about $\frac{1}{4}$ inch thick is carried by the diaphragm between the bars 16 of the diaphragm support. An advantage of forming the grid like diaphragm support of iron or steel, is that it forms a seal with the amalgam in the mercury and prevents intermixing of the brine electrolyte, beneath the mercury, with the sodium hydroxide formed on top of the mercury.

The top unit of the cell, or cathode compartment, is also rectangular in shape and formed with side wall 26 of channel iron and a top of heavy gage sheet iron or steel 27 secured thereto by bolts 28. For the purpose of sealing the top with the side walls a gasket 29 of suitable material is used at the joint. As shown the top unit is adapted for bolting to the bottom unit with the diaphragm assembly sandwiched therebetween. This is accomplished by means of bolts 30. To insulate the top unit from the bottom unit bolts 30 pass through heavy fiber or hard rubber bushings 31 and both their heads and nuts may be prevented from metal to metal contact with the side flanges by means of stout upper and lower fiber washers 32. As shown a gasket of rubber is used between the bottom flange of the top unit and the top surface of the diaphragm support to prevent leaking at this point and for purposes of insulation. Depending from the top of the cell are a plurality of inverted U shaped iron hangers or conductor straps 33 for supporting activated carbon or graphite electrodes 34 which dip into the pools of mercury forming the cathode. These electrodes or current feeder bars 34 are secured to the hangers by means of screws 35 which pass through iron plates 36 that are in turn welded to the end of the hangers. The hangers may be secured to the top plate by welding or by means of screws 37 arranged to provide an efficient electrical connection between the hangers and the top. As shown in Figure 5 the activated carbon bars 34 are provided with serrations or notches 38 which extend into the bars along the lower edges of the sides and bottom. These notches extend from the bottom of the bar which is submerged in the mercury to a point above the mercury level in the water or sodium hydroxide and are provided for the purpose of increasing the surface area of the bar in contact with the mercury and the water and allow for easy release of hydrogen gas generated adjacent the block by the reaction of the amalgam with the water.

Water is supplied to the upper compartment by means of inlet pipe 39 (Figure 1) and caustic removed from the compartment by way of pipe 40 positioned as shown. A suitable outlet for hydrogen gas from the upper compartment is provided by means of pipe 41 which communicates with the interior of the chamber through the top 27.

Electrical connection is made with the top and bottom of the cell by means of buss bars 42 and 43 welded or bolted to the top and bottom respectively.

In use, the diaphragm assembly is positioned over the anode on the sides of the lower unit and mercury is

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poured into each of the spaces between the cross bars 16 to a depth of about 1/4 inch. The top unit is then lowered on to the diaphragm assembly and the three units tightly joined together by means of bolts 30.

When the cell is to be used for the electrolysis of sodium chloride, water is then admitted into the top compartment through water inlet pipe 39 until it reaches the level of the caustic outlet pipe 40. The depth of the water over the mercury is not particularly important with the exception that it should not be so deep as to substantially increase the weight on the mercury and diaphragm.

A concentrated aqueous solution of sodium chloride is then admitted into the anode compartment through the brine inlet pipe 11 where it first fills the inlet header 7 and then passes upwardly through the narrow space 24 to overflow into space 23 between the anode and the diaphragm. The addition of brine is such, of course, as to maintain space 23 full at all times and the velocity of flow is maintained at a rate sufficient to remove the chlorine gas formed on the anode and sweep it through the cell in suspension in the electrolyte to outlet header 8. From header 8 the spent brine and chlorine are discharged through pipe 12.

An electrical potential is then applied to the anode and cathode by connecting a source of direct current to the buss bars on the top and the bottom of the cell, the top buss bar being of course connected to the negative terminal. The current passes by way of the bottom plate, through the anode, electrolyte, and the mercury to the graphite conductors 34 and leaves the cell by way of the hanger strips 33, top 27 and buss bar 42.

For best results, the concentration of amalgam formed in the mercury should be kept low thus avoiding reaction with the water of the brine adjacent the diaphragm. To speed up the reaction of the amalgam with the water over the mercury, bars 34 are made of activated graphite as stated, and designed to present as great a surface area with the mercury and water as possible.

The cell is operated until the caustic formed reaches a desired concentration of from 25% to 50% or even higher under favorable conditions. Water is then slowly added to the cell through pipe 39 and caustic withdrawn through pipe 40 at a rate sufficient to maintain continuous production of caustic at the desired concentration. Hydrogen liberated in the cathode compartment by reaction of the amalgam with the water is continuously withdrawn.

The cell, provided by the present invention, is simple in construction and capable of trouble free, efficient operation over long periods of time. On the other hand, when replacement of the diaphragm, anode or other parts is necessary the cell may be quickly and easily dismantled and reassembled.

What I claim is:

1. A mercury caustic chlorine cell for conducting the electrolysis of a concentrated aqueous solution of sodium chloride which comprises, a body portion provided with side walls, a top and a bottom, a diaphragm dividing the body portion into upper and lower compartments, a grid support for the diaphragm, a brine inlet port in one side of the lower compartment, a combined spent brine and chlorine outlet port in the opposite side of the lower compartment, a plurality of clamping strips for securing the diaphragm to the underside of the grid, said clamping strips extending across the compartment from the inlet port side to the outlet port side, a centrally positioned graphite anode in the lower compartment, a liquid distributing header along the inlet port side of the lower compartment and means for directing liquid therefrom to the top of said anode, a liquid collecting header along the outlet port side of said lower compartment, grooves in the top surface of the anode for receiving the clamping strips, said top surface being disposed closely adjacent the under side of the diaphragm but sufficiently

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spaced therefrom for passage of a thin stream of brine to flow there between, mercury on top of the diaphragm forming the cathode electrode, activated graphite conductors dipping into the mercury, electrically conducting means secured to the top of the body portion for supporting the graphite conductors in suspension in the mercury, a water inlet port in one side of the upper compartment, a caustic outlet port in the opposite side of the upper compartment, means for removing hydrogen from said compartment and means for electrically connecting the anode and cathode to a source of electricity.

2. The subject matter of claim 1 wherein the fabric diaphragm is made of a copolymer of vinyl chloride and acrylonitrile.

3. The subject matter of claim 1, wherein the fabric diaphragm is made of a copolymer of vinylidene chloride and vinyl chloride.

4. An electrolytic cell comprising, side walls and a bottom defining a lower compartment, side walls and a top defining an upper compartment, a porous diaphragm and diaphragm support positioned intermediate the upper and lower compartments in removable sealing engagement with the side walls, a mercury cathode in the upper compartment, an anode in the lower compartment, peripheral, downwardly depending means on the underside of the diaphragm projecting into the periphery of the lower compartment for spacing the anode away from the walls of the lower compartment and aligning it with the cathode in the upper compartment, filler blocks along two opposite sides of the anode, inlet and outlet headers along two other sides of the anode for receiving electrolyte, spaced clamping strips secured to the underside of the diaphragm support and extending from one header to the other, and grooves in the top surface in the anode for receiving the clamping strips, said strips, diaphragm, and anode defining a shallow, narrow, elongated passage extending from header to header for passage of the electrolyte.

5. In an electrolytic cell for conducting the electrolysis of an alkali metal chloride electrolyte, in combination, a horizontal diaphragm assembly comprising a frame having a series of spaced parallel bars extending thereacross, a diaphragm across the lower surfaces of said bars, a layer of mercury on said diaphragm between said bars, a carbon anode substantially coextensive in cross sectional area with the working area of said diaphragm positioned below the lower surface thereof in close juxtaposition thereto and forming therewith a shallow passage, a channel in the upper surface of the anode under each of said bars, a clamping strip attached to each bar below said diaphragm and extending into the corresponding channel in the anode, and means for passing a flow of said electrolyte through said passage across the upper surface of said anode parallel to said channels and clamping strips.

6. In an electrolytic cell for conducting the electrolysis of an alkali metal chloride electrolyte, in combination, a horizontal diaphragm assembly comprising a frame having a series of spaced parallel bars extending thereacross, a diaphragm across the lower surface of said bars, a pool of mercury on said diaphragm between each pair of said bars and between the outermost bars and the sides of said frame, a carbon electrode dipping into each pool of mercury, a carbon anode substantially coextensive in cross sectional area with the working area of said diaphragm positioned below the lower surface thereof in close juxtaposition thereto and forming therewith a shallow passage, channels in the upper surface of said anode, one of said channels being under each of said bars, a clamping strip attached to each bar below said diaphragm and extending into the corresponding channel in the anode, and means for passing a flow of electrolyte through said passage across the upper surface of the anode parallel to said channels and clamping strips.

7. An electrolytic cell comprising side walls and a bottom defining a lower compartment, side walls and a top defining an upper compartment, a porous diaphragm

and a diaphragm support therefor positioned intermediate the upper and lower compartments in removable sealing engagement with the side walls, a mercury cathode in the upper compartment, an anode in the lower compartment, peripheral downwardly depending means on the underside of said diaphragm support projecting into the periphery of the lower compartment for spacing the anode away from the walls of the lower compartment and aligning it with the cathode in the upper compartment, filler blocks along two opposite sides of the anode, inlet and outlet headers along two other sides of the anode for receiving electrolyte, spaced clamping strips secured to the underside of the diaphragm support and extending from one header to the other, and grooves in the top surface of the anode for receiving the clamping strips, said strips, diaphragm, and anode defining a shallow elongated passage extending from header to header for passage of the elec-

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trolyte, said depending means on the underside of the diaphragm support extending below the top surface of the anode in the inlet header so that delivery of electrolyte to said passage is in a vertical direction.

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