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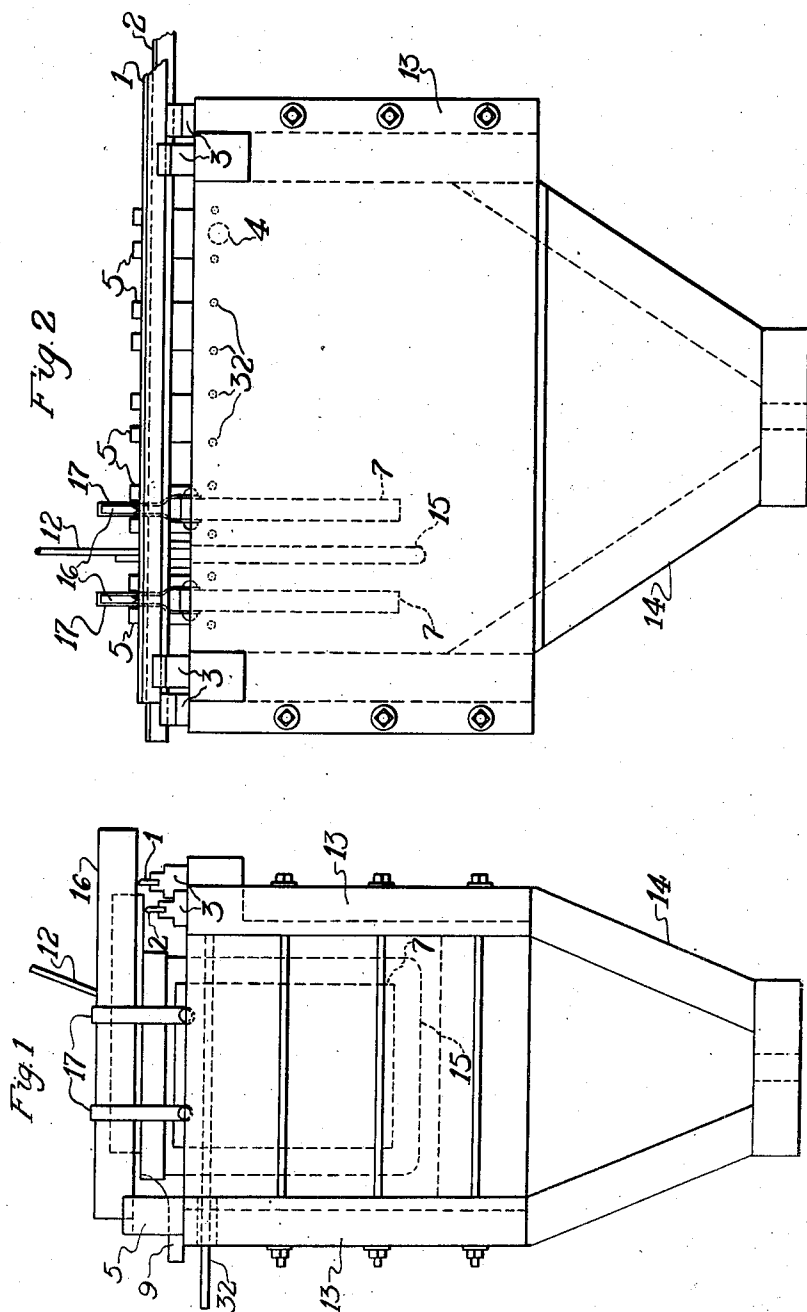
G. E. JOHNSON ET AL

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ELECTROLYTIC CELL FOR PRODUCING INSOLUBLE METAL SALTS

Filed Dec. 22, 1937

2 Sheets-Sheet 1



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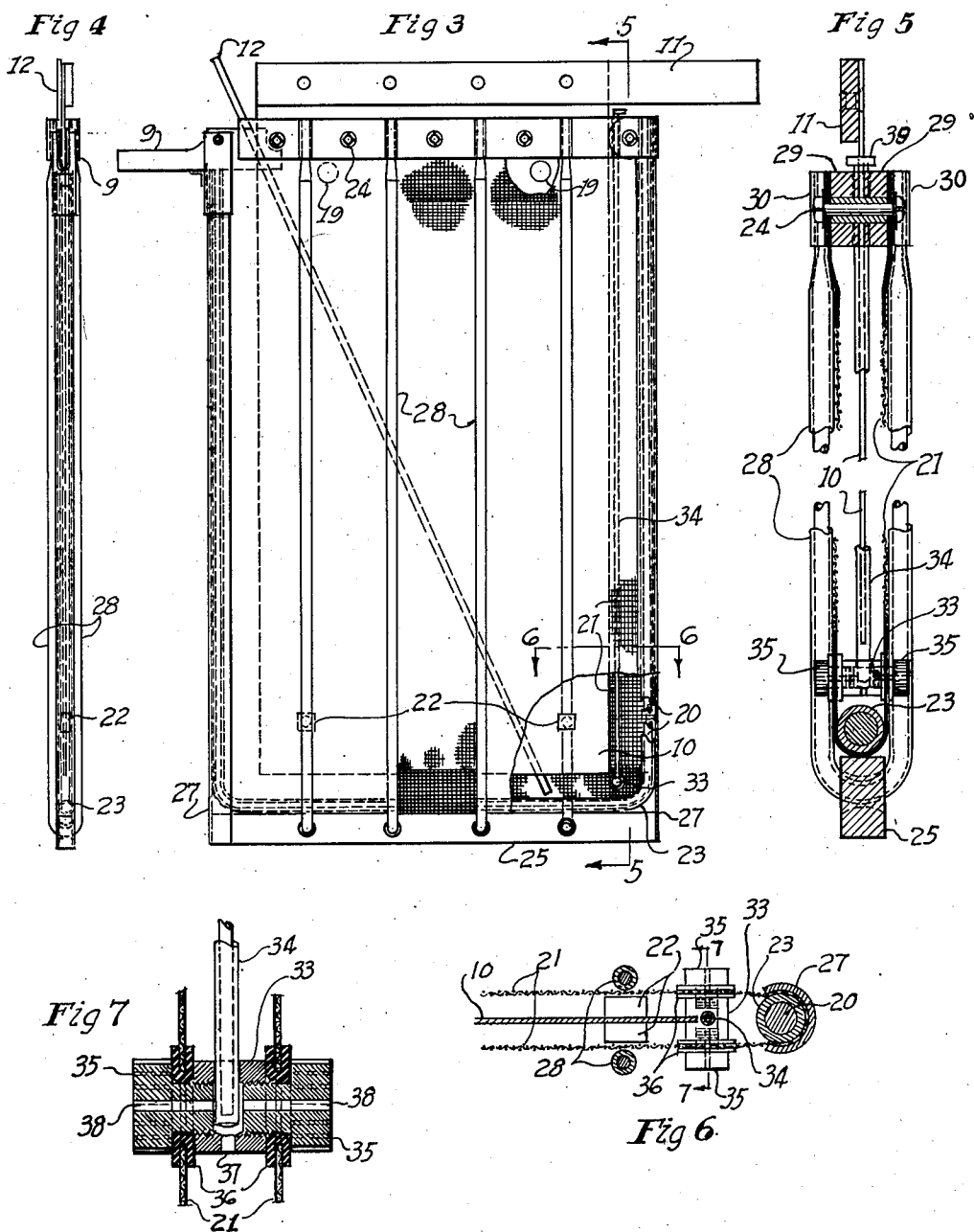
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UNITED STATES PATENT OFFICE

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ELECTROLYTIC CELL FOR PRODUCING
INSOLUBLE METAL SALTS

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Application December 22, 1937, Serial No. 181,153

10 Claims. (Cl. 204—257)

This invention relates to electrolysis and has for an object the provision of certain improvements in electrolytic cell structures. More particularly, the invention contemplates the provision of an improved bifluid type of electrolytic cell. A further object of the invention is to provide an improved cathode assembly for use in bifluid electrolytic cells.

The invention relates further to improvements in the cathode diaphragm frame construction used in bifluid electrolytic cells and particularly electrolytic cells used in processes in which two electrolytes, separated by a porous diaphragm are employed, wherein the electrolytes are circulated independently through the cathode diaphragm compartment and the cell. These processes are designed primarily to produce insoluble metallic salts.

The invention contemplates the provision of apparatus so designed as to (1) prevent the precipitation or reduction of metallic constituents of the anolyte of the bifluid cell on the diaphragm or on the cathode frame parts that support the diaphragm; (2) prevent electrical contact between the diaphragm and cathode frame parts and the electrodes and cell walls; and (3) permit addition of catholyte to anolyte at any desired rate. A cathode diaphragm frame and the diaphragm construction that will permit efficient operation of the electrolytic cell and accomplish these objectives should include the following features:

1. The frame should permit placing the electrodes directly opposite each other and as close together as reasonably possible in order to shorten the path of the electric current.

2. The frame should permit surrounding the cathode electrode with a fabric bag of low electrical resistance which will provide a separate compartment for the solution that surrounds the cathode and, also, will act as a diaphragm separating the two solutions of the electrolytic cell. Diaphragm and frame should be tight, permitting no uncontrolled leakage or interchange of solutions except through the pores of the diaphragm.

3. The frame construction should permit complete electrical insulation of the diaphragm from the cathode and prevent the diaphragm from coming in contact with the anode or the walls of the cell.

4. The frame construction should permit free circulation of the electrolytes within the cathode compartment of the cell and permit elimination of gases formed in the cathode compartment. It

should not present surfaces upon which solids can accumulate that will short-circuit the electrodes and the diaphragm. Space for the collection of such material should be provided.

5. The diaphragm construction should permit the transfer of anions of the catholyte into the anolyte at a controlled rate by electrical migration, by seepage of catholyte through the diaphragm due to maintaining it at a selected higher level than the cell anolyte, or by various types of valve-regulated openings in the diaphragm and frame.

The objectives described and suggested above are accomplished by the invention through the provision of the following operating and structural features:

All contacts between the cathode sheet and the diaphragm frame are eliminated below the solution level.

The cathode sheets preferably are slightly larger in area than the anode, so that the edges of the anode will not project beyond the edges of the cathode, which aids in preventing precipitation or reduction of metallic constituents of the anolyte.

The diaphragm is prevented from coming into contact with the cathode sheet, which it surrounds, by maintaining a hydrostatic head within the diaphragm sufficient to bulge it outward against retaining stay rods. Also by providing spacing blocks of rubber or other suitable insulating material projecting outwardly from both faces of the cathode and non-conducting stay rods adjacent the outer surfaces of the diaphragm, which combine to prevent the diaphragm from coming into contact with either the cathode or the anode.

Bolts or metal fastenings below the solution level of the frame are eliminated. Bolts located below the solution level have been found to act as intermediate electrodes, dissolving on one side and depositing metallic constituents on the other. This action is due to potential differences that may develop between adjacent anodes. The bolt produces a local reduction of resistance in the space between the anodes and a flow of current occurs through the bolt.

Dirt accumulation at the sides and bottom of the cathode sheet and on the surface of the cathode sheet, that may bridge across and make electrical contact with the frame or diaphragm, is prevented by providing a substantial space between the sides and bottom edges of the cathode sheet and the diaphragm and frame parts. The

space below the bottom edge of the cathode sheet provides for the collection of sediment.

All frame parts are constructed of a non-porous, non-conducting material such as hard rubber. This prevents these parts from absorbing the electrolyte and becoming conductors and also maintains their rigidity.

Excessive failure of the portion of the diaphragm that projects above the solution level is prevented. This portion is exposed to the air and to alternate wetting and drying. Failure due to these causes is prevented by impregnating the diaphragm at this point with a waterproof non-conducting material such as vulcanized rubber or asphalt.

Excessive failure of the portion of the diaphragm below the bottom edge of the cathode, in which sediment that drops off the cathode is collected, is prevented. This is accomplished by impregnating this section of the diaphragm with a waterproof non-conducting material such as vulcanized rubber or asphalt.

Free circulation and mixing of the solution within the diaphragm is obtained by leaving an open space around the sides, edges and bottom of the cathode sheet and the surrounding diaphragm, and by placing holes in the electrode sheet at the solution level.

Control of the amount of catholyte transferred through the diaphragm to the anolyte is obtained by one or all of the following methods:

1. By selection of a fabric of a predetermined porosity.

2. By maintaining a predetermined and adjustable hydrostatic head of catholyte within the diaphragm.

3. By placing a valve in the bottom of the diaphragm, controlled by a rod that extends to the top of the diaphragm frame.

The cathode frame and diaphragm of the invention consists essentially of an insoluble sheet metal electrode held in a non-conducting frame that supports a vegetable fabric or parchment diaphragm. The design permits bifluid cell construction and provides a method of complete insulation of the diaphragm and its supporting frame from the cathode sheet. The construction of the cell and cathode frame of the invention are illustrated in the accompanying drawings, in which

Fig. 1 shows, in elevation, an end view of one form of cell which may be used;

Fig. 2 is a side elevation of the cell shown in Fig. 1;

Fig. 3 is a detailed side elevation, partly in cross section, of the cathode assembly shown in Fig. 1;

Fig. 4 is an end elevation of the cathode assembly shown in Fig. 3;

Fig. 5 is a section taken substantially along line 5—5 of Fig. 3;

Fig. 6 is a fragmentary section taken along lines 6—6 of Fig. 3; and

Fig. 7 is a detailed section of the valve assembly taken substantially along the line 7—7 of Fig. 6.

The cell shown in Figs. 1 and 2 comprises a rectangular tank 13, with hopper bottom 14 made of non-conducting material such as concrete, pottery or wood impregnated with asphalt. 1 and 2 represent anode and cathode bus bars, respectively, which are placed parallel and above the cell and supported by hard rubber support blocks 3. A positive bus bar may be placed on one side of the cell and a negative bus bar on the other, or there may be both positive and negative bus

bars on each side of the cell. Suspended in the cell are anodes 7 and the cathode assemblies 15 enclosing the cathodes 10. The anodes are cast, flat sheets of metal such, for example, as metal to be corroded, having an area preferably slightly less than the area of the cathode sheets. The anodes are suspended from copper bars 16 by copper straps 17 or they may be supported upon positive bus bars by lugs extending out from the upper corners of the anode sheets. One end of the bar 16 rests on anode bus bar 1, while the other end rests on the hard rubber support block 5. Any number of anodes may be placed in a cell, depending upon their thickness and the length of the cell. An overflow opening 4 is provided in the cell wall to take care of any excess anolyte. The construction of the cathode assembly comprising a cathode and a diaphragm supporting frame is illustrated in Figs. 3 to 7.

The cathodes are made of any metal insoluble under the conditions existing in the cells. Iron and copper are two metals which meet the usual requirements. The cathodes are generally in the form of thin sheets held in a non-conducting frame that supports a water-tight bag of a vegetable fabric or parchment. The bag acts as a diaphragm which permits bifluid cell construction. Anodes are placed between the cathodes in the cell. The cathodes are of slightly greater area than the anodes so that below the solution line of the cell their edges will project beyond the edges of the anode. The cathode frames either rest on supports in the cell, or are suspended from a copper bar that is riveted to the sheet and rests on the cathode bus bar on either side of the cell. In the former case, electrical contact between the sheet and the bus bar is obtained by a flexible cable between the sheet and bus bar.

Figs. 3 to 7 illustrate in detail the cathode frame or assembly shown in Figs. 1 and 2. This form of cathode frame is so constructed that it may be easily suspended in, or removed from the cell. It comprises a U-shaped main or internal frame, consisting of a brass rod 20, encased in a tube 23 made of insulating material such as hard rubber, around which is stretched diaphragm 21 forming a cathode compartment within which is suspended the iron cathode 10. The top of the frame is closed by means of wood or hard rubber strips 29 and metal top strips 30 provided with grooves or corrugations for the reception of the upper ends of stay rods 28. Bolts passing through these metal strips and insulating strips and through the hard rubber washers inserted in the cathode serve to clamp together these members and top edges of the diaphragm. A copper support bar 11 is riveted along the top edge of the cathode and extends beyond one end of the frame. This extension serves as a means for supporting this end of the frame in the cell. The other end of the frame is supported on the cell walls by means of a spout 9 which is preferably of metal welded to the cathode and which serves as an overflow for catholyte. The diaphragm is spaced from the cathode by means of rubber spacer blocks 22. The holes 19 in the cathode near the top thereof, are gas holes. Catholyte is fed into the frame through the hard rubber catholyte feed tube 12 which is connected to a manifold.

The anolyte is fed into the top of the cell through the feed tubes 32, which are provided with small holes on the under side, and is discharged at the bottom, conveying away the product which forms as it descends past the anode surfaces. From the bottom of the cell the ano-

lyte is conveyed by suitable piping or launders to suitable equipment to remove the product formed in the cell.

The catholyte is fed into the cathode frame at a point below the bottom edge of the cathode sheet by means of a tube 12 made of non-conducting material such as hard rubber, the tube enters the catholyte compartment between the cathode sheet and diaphragm at the top of the cathode frame. In this type of frame, the catholyte circulates upwardly around the cathode sheets and passes out of the frame through the spout 9 which projects over the edge of the cell. In frames of this type the catholyte level in the frames is higher than the level of the anolyte. This type of construction permits continuous circulation of the catholyte through the cathode frame. Regulation of the amount of catholyte constituents that is transferred to the anolyte by seepage through the diaphragm is obtained by controlling the concentration of these constituents dissolved in the catholyte and by adjustment of the catholyte head. Another means of regulation of the transfer is by means of a valve or small opening in the bottom of the cathode frame.

A suitable valve arrangement for controlling the transfer of catholyte to the anolyte is illustrated in Figs. 3, 5, 6 and 7 and shown in some detail in Figs. 5, 6 and 7. (In the interest of clarity, dotted line indications of the valve arrangement have been omitted from Fig. 4.) The valve illustrated in the drawings comprises an internally threaded tubular hard rubber body member 33 having a circular valve stem opening extending through its wall on one side, for the relatively tight or close-fitting reception of a valve stem 34, and having a circular opening or passage 37 for the flow of liquid therethrough extending through its wall directly opposite and in axial alignment with the valve stem opening. The inner wall of the body member 33 adjacent the passage 37 is shaped to provide a smooth, preferably concave, surface for contact with a correspondingly curved, preferably convex, surface formed on the end of the valve stem 34. The concave and convex surfaces co-operate to provide a liquid tight joint when they are in contact.

The body member 33 is disposed between circular openings formed in the diaphragm walls 21 and is held in position by means of hard rubber cap screws 35 which project through the openings in the diaphragm walls and have their threaded ends screwed into the threaded ends of the body member 33. The cap screws 35 are provided with passages 38 extending axially therethrough. The openings in the diaphragm walls are provided with circular or annular soft rubber eyelets 36 having annular grooves in their peripheral surfaces for the reception of the portions of the diaphragm walls adjacent the openings therein.

When the valve is in position in the cathode assembly, the soft rubber eyelets 36 and the portions of the diaphragm walls extending into the peripheral grooves of the eyelets are compressed between the inner faces of the heads of the cap screws 35 and the end faces of the body member 33, and a joint secure against leakage is thus formed.

The cap screws 35 are of such length that, when extending into the body member in their fully operative positions, a space is left centrally of the body member for the insertion of the valve stem 34 through the valve stem opening and into con-

tact with the concave surface surrounding the passage 37. The valve stem 34 which consists of a rubber covered metal rod (brass, for example) extends upwardly from the valve body member, in close proximity to the edge of the cathode sheet 10, to the top of the frame where it is clamped in adjustment between the cathode strips 29 by the bolts 24.

Provision may be made for permitting the flow of electrolyte between the compartments, through the passages 37 and 38, by maintaining the valve stem in a raised position with its lower end surface out of contact with the surface adjacent the passage 37, and such flow may be prevented by maintaining the lower end surface of the valve stem in contact with the surface surrounding the passage 37. In order to aid in adjusting the position of the valve stem 34, it is provided adjacent its upper end with a head 39. Frictional contact may be depended upon to maintain the valve stem in its upper positions of adjustment or any suitable securing or fastening means may be provided.

Figs. 5 and 6 illustrate a method of insulating the sides and outer surface of the frame from making electrical contact with the sides of the cell and the anode surfaces.

A bottom bar formed of a non-metallic non-conducting material such as impregnated wood or hard rubber 25 is placed below the bottom edge of the diaphragm. The side tubes 27 of the frame, consisting of hard rubber pipe slotted longitudinally on one side to leave about three quarters of the circumference intact, are slipped over the outer edge of the diaphragm. The bottom ends of these tubes 27 fit over the ends of the bottom bar 25 thus locking the bottom corners of the insulating frame. These three members insulate the outer edges of the frame that are submerged in the cell solutions. A grid of U-shaped stay rods 28 whose upper end portions are clamped to the top of the frame by the metal strips 30 and which pass down one face of the diaphragm, through holes in the bottom bar 25 and up the opposite face, prevents the diaphragm from bulging and coming in contact with the surfaces of the anodes. These stay rods consist of a rigid metal rod encased in hard rubber tubing or coated with an insulating material. Their thickness and spacing is such that even when they rest against the anodes the normal bulge of the diaphragm between the rods will not bring it into contact with the anode surface.

The diaphragm is a very important element in a bifluid electrolytic cell. The fabrics used are very slightly permeable to the solutions, acting to keep the anolyte and catholyte separated and so prevent the dissolved salts in the two electrolytes from mixing, and to prevent the cations dissolved at the anode and contained in the anolyte from coming in contact with the cathode and being reduced to a metal. The diaphragm is also important in that it acts as a valve, controlling the rate of addition of catholyte to anolyte. This valve action is obtained by selecting fabric of predetermined porosity and by having a slight hydrostatic head in the cathode frame.

The diaphragm envelope shown in the drawings is formed of a single sheet of material folded along a line extending transversely of its longitudinal center and having its adjacent side edges (when folded) stitched together. The end opposite the fold is open to permit the insertion of the internal frame and the cathode sheet. The sheet

of material, preferably prior to folding and stitching, is impregnated with an insulating material such as asphalt along and adjacent to the fold line and adjacent the end edges for a distance substantially equal to the amount of the material to extend above the solution level.

The migration of the cations to the cathode is prevented by maintaining a slight hydrostatic head within the diaphragm so that the seepage will be out of and not into the cathode compartment formed by the diaphragm. Precipitation of the cations on the diaphragm is prevented by insulating the diaphragm so that it does not come into direct contact with the cathode sheet and by making the anodes of a smaller area than the cathodes so that the current will not have to pass around any of the frame parts.

We claim:

1. In a bifluid cell for producing insoluble metal salts, a cell tank adapted to contain an anolyte solution, a soluble anode mounted in said tank, a cathode assembly mounted in said tank in close proximity to said anode and comprising a rigid U-shaped frame for immersion in the tank and providing side and bottom diaphragm supporting members, a top cathode supporting member rigidly secured to said frame wholly at the upper end thereof, a cathode sheet secured to and wholly supported by said cathode supporting member and extending into the confines of said frame but being spaced at both its side and bottom edges from the side and bottom diaphragm supporting members provided thereby, and a porous diaphragm envelope wholly enclosing the submerged portion of the frame and held in extended position thereby, the diaphragm envelope being secured to said frame at the upper end thereof.

2. In a bifluid cell for producing insoluble metal salts, a cell tank adapted to contain an anolyte solution, a soluble anode mounted in said tank, a cathode assembly mounted in said tank in close proximity to said anode and comprising a rigid U-shaped frame for immersion in the tank and providing side and bottom diaphragm supporting members, a pair of top cathode supporting members rigidly secured to said frame wholly at the upper end thereof, a cathode sheet received and clamped between said cathode supporting members and wholly supported thereby, said cathode sheet extending into the confines of said frame but being spaced at both its side and bottom edges from the side and bottom diaphragm supporting members provided thereby, and a porous diaphragm envelope wholly enclosing the submerged portion of the frame and held in extended position thereby, the diaphragm envelope being secured to said frame at the upper end thereof.

3. In a bifluid cell for producing insoluble metal salts, a cell tank adapted to contain an anolyte solution, a soluble anode mounted in said tank, a cathode assembly mounted in said tank in close proximity to said anode and comprising a rigid frame for immersion in the tank and providing side and bottom diaphragm supporting members, a top cathode supporting member rigidly secured to said frame at the upper end thereof, a cathode sheet secured to said cathode supporting member and extending into the confines of said frame with the side and bottom edges of the cathode spaced from the side and bottom members of the frame, a porous diaphragm envelope wholly enclosing the submerged portion of the frame and held in extended po-

sition thereby in spaced relation with said cathode sheet, the diaphragm envelope being secured to said frame at the upper end thereof, and spacer blocks of non-conducting material positioned between the cathode sheet and the diaphragm envelope in a manner to maintain said envelope spaced from said cathode sheet.

4. In a bifluid cell for producing insoluble metal salts, a cell tank adapted to contain an anolyte solution, a soluble anode mounted in said tank, a cathode assembly mounted in said tank in close proximity to said anode and comprising a rigid frame for immersion in the tank and providing side and bottom diaphragm supporting members, a top cathode supporting member, a cathode sheet secured to said cathode supporting member and extending into the confines of said frame with the side and bottom edges of the cathode spaced from the side and bottom members of the frame, and a porous diaphragm envelope wholly enclosing the submerged portion of the frame and held in extended position thereby, said diaphragm envelope being impregnated adjacent and upwardly a short distance from the bottom diaphragm supporting member of the frame with a substantially waterproof insulating material and being secured to said frame at the upper end thereof.

5. In a bifluid cell for producing insoluble metal salts, a cell tank adapted to contain an anolyte solution, a soluble anode mounted in said tank, a cathode assembly mounted in said tank in close proximity to said anode and comprising a rigid frame for immersion in the tank and providing side and bottom diaphragm supporting members, a top cathode supporting member, a cathode sheet secured to said cathode supporting member and extending into the confines of said frame with the side and bottom edges of the cathode spaced from the side and bottom members of the frame, and a porous diaphragm envelope wholly enclosing the submerged portion of the frame and secured to the cathode supporting member, said cathode assembly being adapted to be immersed in an electrolyte solution to a normal depth such that a portion of the diaphragm extends above the solution, and said diaphragm being impregnated with a substantially waterproof insulating material over the area thereof that normally extends above such solution.

6. In a bifluid cell for producing insoluble metal salts, a cell tank adapted to contain an anolyte solution, a soluble anode mounted in said tank, a cathode assembly mounted in said tank in close proximity to said anode and comprising a rigid U-shaped frame for immersion in the tank and providing side and bottom diaphragm supporting members, a cathode supporting member mounted on the frame at the upper end thereof, a cathode sheet secured to said cathode supporting member and extending into the confines of said frame with the side and bottom edges of the cathode spaced from the side and bottom members of the frame, a porous diaphragm envelope wholly enclosing the submerged portion of the frame and extending around the bottom and side members thereof and held in extended position thereby, the diaphragm envelope being secured to said frame at the upper end thereof and a bottom bar of non-conducting material secured to the lower edge of said assembly below the bottom edge of the diaphragm envelope.

7. In a bifluid cell for producing insoluble metal salts, a cell tank adapted to contain an

anolyte solution, a soluble anode mounted in said tank, a cathode assembly mounted in said tank in close proximity to said anode and comprising a rigid U-shaped frame for immersion in the tank and providing side and bottom diaphragm supporting members, a cathode supporting member mounted on the frame at the upper end thereof, a cathode sheet secured to said cathode supporting member and extending into the confines of said frame with the side and bottom edges of the cathode spaced from the side and bottom members of the frame, a porous diaphragm envelope wholly enclosing the submerged portion of the frame and extending around the bottom and side members thereof and held in extended position thereby, the diaphragm envelope being secured to said frame at the upper end thereof, and side edge protecting members of non-conducting material secured to the side edges of said assembly overlying the side edges of said diaphragm envelope.

8. In a bifluid cell for producing insoluble metal salts, a cell tank adapted to contain an anolyte solution, a soluble anode mounted in said tank, a cathode assembly mounted in said tank in close proximity to said anode and comprising a rigid U-shaped frame for immersion in the tank and providing side and bottom diaphragm supporting members, a cathode supporting member mounted on the frame at the upper end thereof, a cathode sheet secured to said cathode supporting member and extending into the confines of said frame with the side and bottom edges of the cathode spaced from the side and bottom members of the frame, a porous diaphragm envelope wholly enclosing the submerged portion of the frame and extending around the bottom and side members thereof and held in extended position thereby, the diaphragm envelope being secured to said frame at the upper end thereof, a bottom bar of non-conducting material secured to the lower edge of said assembly below the bottom edge of the diaphragm envelope, and side edge protecting

members of non-conducting material secured to the side edges of said assembly overlying the side edges of said diaphragm envelope and engaging end portions of said bottom bar.

9. In a bifluid electrolytic cell for producing insoluble metal salts, a cell tank adapted to contain an anolyte solution, a cathode assembly mounted in said tank and comprising a rigid frame for immersion in the tank, a cathode mounted within the confines of said frame, and a diaphragm stretched over and supported by said frame in spaced relation with said cathode, the diaphragm wholly enclosing the submerged portion of the frame, and a soluble anode mounted in said tank in close proximity to said cathode assembly, the anode being of lesser width and length below the anolyte solution level than the cathode and being mounted in the tank in such manner that the side edges and bottom of the active surface of the cathode project beyond the corresponding side edges and bottom of the active surface of the anode.

10. In a bifluid cell for producing insoluble metal salts comprising an electrolytic cell tank, a diaphragm of porous material mounted in said tank, said diaphragm being of suitable material and so arranged as to separate an anolyte and a catholyte under different hydrostatic heads in said tank while permitting relatively slow migration therethrough of the electrolyte under higher hydrostatic head into the electrolyte under lower hydrostatic head, a soluble anode positioned in the anolyte, a cathode positioned in the catholyte, and an adjustable valve having its opening mounted in said diaphragm and adapted when open to permit passage of the electrolyte under higher hydrostatic head into the electrolyte under lower hydrostatic head at a substantially higher rate than such electrolyte could migrate through the porous diaphragm.

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CERTIFICATE OF CORRECTION.

Patent No. 2,271,341.

January 27, 1942.

GUNNARD E. JOHNSON, ET AL.

It is hereby certified that the address of the assignee in the above numbered patent was erroneously described and specified as "East Chicago, Illinois" whereas said address should have been described and specified as --East Chicago, Indiana--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 17th day of March, A. D. 1942.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.