No. 735,464. PATENTED AUG. 4, 1903.

E. A. BYRNES.

ELECTROLYTIC DIAPHRAGM.

APPLICATION FILED MAY 12, 1903.

NO MODEL.

Fig. 1.

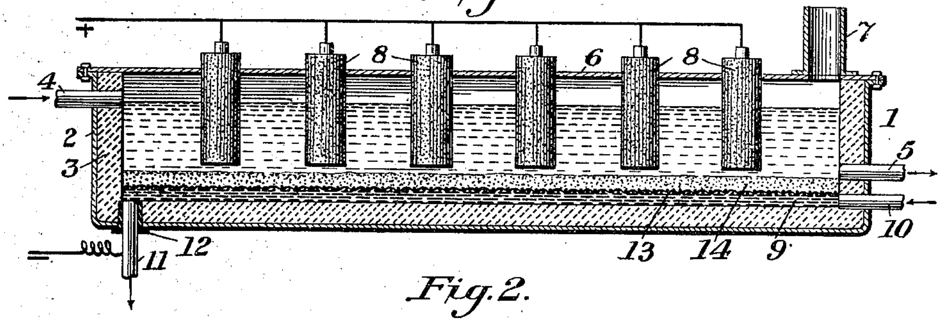


Fig. 2.

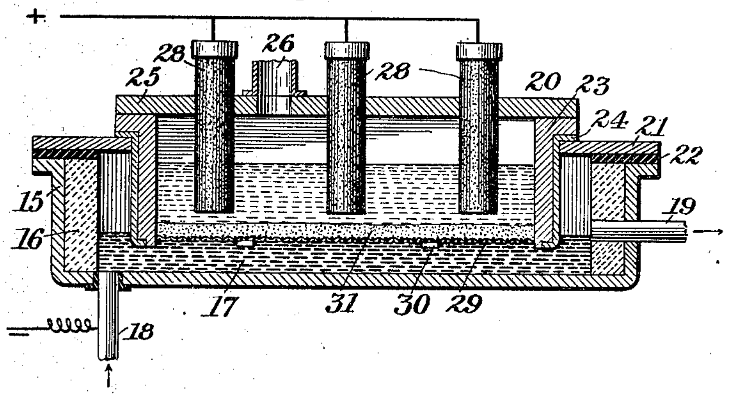


Fig. 3.

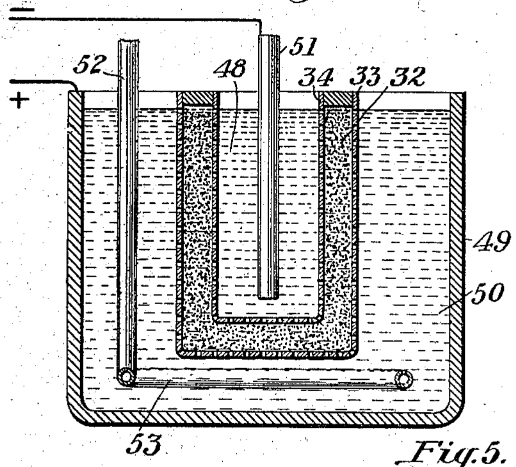


Fig. 4.

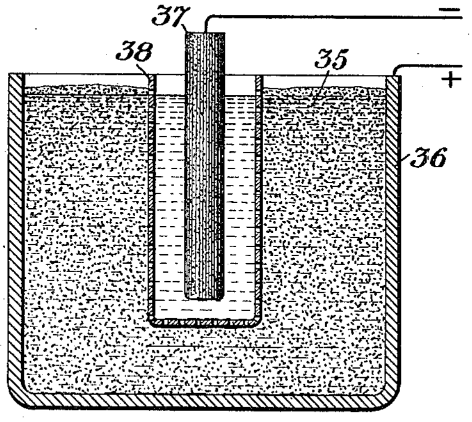
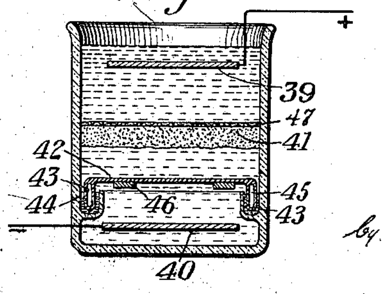


Fig. 5.



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No. 735,464. Patented August 4, 1903.

UNITED STATES PATENT OFFICE.

EUGENE A. BYRNES, OF WASHINGTON, DISTRICT OF COLUMBIA.

ELECTROLYTIC DIAPHRAGM.

SPECIFICATION forming part of Letters Patent No. 735,464, dated August 4, 1903.

Application filed May 12, 1903. Serial No. 156,818. (No model.)

To all whom it may concern:

Be it known that I, EUGENE A. BYRNES, a citizen of the United States, residing at Washington, in the District of Columbia, have invented certain new and useful Improvements in Electrolytic Diaphragms, of which the following is a specification.

This diaphragm was designed for use in the electrolysis of alkali-metal compounds, but is capable of general application.

The invention comprises several novel features, one or more of which may be embodied in a single diaphragm.

Many substances which have a high specific electrical conductivity afford a body of low electrical conductivity when finely divided. Such a poorly-conducting granular body of particles of electrically-conductive material may be advantageously employed as an electrolytic diaphragm. The material used is broken into fragments the size of which is dependent on the requisite porosity and conductivity of the diaphragm. The fragments are aggregated into a body or layer the thickness of which is also dependent on the requisite porosity and conductivity of the diaphragm. Such a layer may be supported as a vertical wall by placing it between sheets of foraminous material or by adding to it such percentage of an inert binder as will convert it into a self-supporting body.

The diaphragm, whether or not of a granular conductive material, may be a horizontal layer floating between the electrodes. If the cell has a cathode of mercury or molten lead, the diaphragm may rest directly upon the liquid metal. When the electrolyte comprises superposed strata of different density, the diaphragm may consist of particles of such specific gravity as to float between the strata. A floating layer of particles which are lighter than any portion of the electrolyte may be retained between the electrodes and prevented from rising by a horizontal sheet of foraminous material fixed above the diaphragm.

The invention will be more readily understood by reference to the accompanying drawings, in which—

Figure 1 is a vertical longitudinal section of a cell for the electrolysis of brine with a mercury cathode. Fig. 2 is a vertical longitudinal section of a cell for the electrolysis of molten sodium chlorid with a molten-lead cathode. Fig. 3 is a vertical central section of a cell having a diaphragm of granular material supported between concentric perforated cups. Fig. 4 is a vertical central section of a cell in which the diaphragm substantially fills the cell; and Fig. 5 is a vertical central section of a cell having two diaphragms, one a floating layer of relatively light particles with a fixed horizontal sheet of wire-gauze above them, the other a floating rigid sheet.

The cell shown in Fig. 1 comprises a vessel 1, which may be of boiler-iron 2 with a lining 3 of Portland cement. The vessel has suitable pipes 4 5 at its opposite ends for the introduction of brine and discharge of the spent electrolyte. The vessel has a cover 6 with outlet-flue 7 for chlorin. Through the cover pass a series of carbon anodes 8. A layer of mercury 9, lying upon the bottom of the cell, serves as the cathode. The mercury is introduced through a pipe 10 in one end of the cell and the sodium amalgam is removed through a pipe 11 at the other end of the cell. The pipe 11 is insulated from the metal casing 2 by a bushing 12 and serves as the cathode-terminal. A sheet of wire-gauze 13, preferably of amalgamated copper or iron, rests upon the mercury cathode, its edges extending nearly into contact with the walls of the cell. Supported upon this sheet of wire-gauze is the floating layer 14, which constitutes the diaphragm. It is desirable that the diaphragm material should be inert toward the electrolyte and its products. One material which has been employed with success and which will resist the action of alkali chlorids and nitrates and their electrolytic products, whether in solution or fusion, is magnetite or ferroferric oxid. Ilmenite or chromite are also available. Broken glass or porcelain are suitable for use in aqueous electrolytes. The size of the fragments and the thickness of the layer are conditioned by the requisite porosity and conductivity of the diaphragm, as stated. For illustration, these fragments may be of such size as to pass through a sieve having a mesh of fifty to the inch, and the floating layer may be from one to several inches in thickness. In using the cell of Fig. 1 the brine is continuously introduced through pipe 4 and the spent solution removed through pipe 5. The mercury is continuously introduced through pipe 10 and the amalgam escapes through pipe 11, the sodium being recovered or converted into its hydroxid and the mercury returned to the cell. The position of the diaphragm adjusts itself to the slightly-varying level of the mercury cathode.

The cell shown in Fig. 2 is a rectangular vessel 15, preferably of cast-iron, the sides of which have a lining 16 of magnesia brick. The cathode is a layer of molten lead 17, resting on the bottom of the vessel. The pipe 18 serves for the introduction of molten lead at one end of the cell and the sodium alloy overflows through a pipe 19 at the other end of the cell. The cell has a cover 21, which is insulated from the body of the cell by a refractory layer 12. A rectangular anode-chamber 20 is supported in an opening in the cell-cover 21. This chamber consists of a casing 23 of material which will resist the action of fused sodium chlorid and chlorin, such as magnesia brick, supported in an iron shell 24. The anode-chamber has a cover 25, with an outlet 26 for the escape of chlorin. The anodes consist of a number of carbon rods 28, which pass through openings in the cover. A layer of wire-gauze 29, fitting smoothly within the anode-compartment, rests upon the lead cathode, fixed lugs 30 extending from the walls to prevent it from dropping down in case the lead is withdrawn. The diaphragm—a floating layer 31 of any material which will resist the action of the molten salt and its products, such as broken magnetite—overlies the wire-gauze. In operation the lead and salt are preferably melted and maintained in a molten condition by the electric current. The molten lead passes under the anode, receives its charge of sodium, and overflows through pipe 19 at a level which is somewhat higher than that beneath the anode on account of the weight of the superincumbent diaphragm and salt.

The cell shown in Fig. 3 has a diaphragm consisting of granular electrically-conductive material 32, supported between concentric cups 33 34 of perforated material, such as sheet-iron. The granular conductive material may also be mixed with a small amount of an inert binder, such as a silicate of magnesium or calcium or ferrous hydrate, and molded into a self-supporting body.

The diaphragm 35 shown in Fig. 4 is a body of granular electrically-conductive material which substantially fills the electrolytic cell 36, a well being maintained around the cathode 37 by means of a perforated cup 38. The vessel here serves as the anode. This arrangement is especially suitable for the recovery of metallic sodium from any of its molten compounds, the sodium rising and floating upon the surface of the electrolyte in the cathode-well.

The cell shown in Fig. 5 has a horizontal anode 39 and cathode 40 in the upper and lower part of the cell, respectively, and upper and lower diaphragms 41 42. Each of these diaphragms is a horizontal layer floating between the electrodes. If the electrolyte be brine, the lower diaphragm may be of a material which will float upon the heavy caustic solution around the cathode and beneath the layer of brine around the anode. The lower diaphragm is shown as a rigid sheet, such as porous clay or silicated asbestos, having a peripheral flange 43, which extends down into a liquid seal 44 of an inert immiscible liquid, such as mercury or carbon disulfid or tetrachlorid. If the diaphragm material is of greater specific gravity than the electrolyte, it may be caused to float at the proper level by an air-chamber 45 in the flange 43. Separate floats or weights 46 may also be secured to the diaphragm. A granular material, such as an inert mineral of the proper specific gravity, or a lighter material, such as pumice or coke weighted with an insoluble inert mineral salt or a metallic deposit, may also be employed. The upper diaphragm 41 is a floating layer of material which is lighter than any portion of the electrolyte—such as pumice, sawdust, or cork—held in place by a sheet of wire-gauze 47, fixed horizontally above the layer.

While this diaphragm has been particularly described in connection with cells for effecting electrolytic decomposition, it is to be understood that it is equally as available for use in voltaic cells employing either an aqueous or molten electrolyte. For example, referring again to Fig. 3, the porous-cup diaphragm may contain a body of molten lead 48, serving as the positive or oxidizable electrode of a voltaic cell. The vessel 49, which may be of iron, serves as the negative electrode. The space between the porous cup and vessel is filled with a molten electrolyte and depolarizer 50, such as sodium manganate. An iron pipe 51 extends down into the molten lead and serves both as the negative terminal of the cell and as a means for introducing carbon monoxid, finely-divided carbon, or other reagent to reduce the lead oxid produced by the action of the cell. The depolarizer is reoxidized as it is reduced by the sodium ions by the injection of air through the iron tube 52 and perforated ring 53.

No claim is made herein to a cell for electrolyzing light-metal compounds having a depending partition which divides the cell into an electrolyzing and an oxidizing compartment, a liquid-metal cathode in contact with the lower edge of the partition, a diaphragm, such as broken magnetite, in the electrolyzing-compartment floating on the cathode and maintaining it at different levels in the two compartments, and means for oxidizing and removing the light metal from that portion of the cathode in the oxidizing-compartment, and thereby effecting an automatic circulation of the cathode, this invention constituting the subject-matter of application, Serial No. 85,099, filed December 7, 1901.

By the term "floating diaphragm," as used in the claims, is meant one which is supported by the liquid on which it rests, so as to rise and fall therewith unless held against upward movement.

I claim—

1. An electrolytic diaphragm, consisting of a poorly-conductive body of an electrically-conductive material, as set forth.

2. An electrolytic diaphragm, consisting of a body of an electrically-conductive material so subdivided or broken up by passages extending through it that it does not conduct as a body and therefore will not act as an electrode, as set forth.

3. An electrolytic diaphragm, consisting of a body of an electrically-conductive material traversed by tortuous interstices, as set forth.

4. An electrolytic diaphragm, consisting of a porous mass of particles of an electrically-conductive material, as set forth.

5. An electrolytic diaphragm, consisting of a porous mass of particles of an electrically-conductive oxid, as set forth.

6. An electrolytic diaphragm, consisting of a porous mass of particles of an anhydrous electrically-conductive oxid of iron, as set forth.

7. An electrolytic diaphragm, consisting of a porous mass of particles of ferroferric oxid, as set forth.

8. An electrolytic diaphragm, consisting of a loose, granular body of particles of electrically-conductive material, as set forth.

9. An electrolytic diaphragm, consisting of a loose, granular body of particles of an electrically-conductive oxid, as set forth.

10. An electrolytic diaphragm, consisting of a loose, granular body of particles of an anhydrous electrically-conductive oxid of iron, as set forth.

11. An electrolytic diaphragm, consisting of a loose, granular body of particles of ferroferric oxid, as set forth.

12. A floating electrolytic diaphragm, as set forth.

13. A floating electrolytic diaphragm of granular material, as set forth.

14. A floating electrolytic diaphragm of granular, electrically-conductive material, as set forth.

15. A floating electrolytic diaphragm of a granular electrically-conductive oxid, as set forth.

16. A floating electrolytic diaphragm of granular, ferroferric oxid, as set forth.

17. An electrolytic cell having a liquid electrode and a diaphragm floating on said electrode, as set forth.

18. An electrolytic cell having a liquid electrode and a diaphragm of granular material floating on said electrode, as set forth.

19. An electrolytic cell having a liquid electrode and a diaphragm of granular, electrically-conductive material floating on said electrode, as set forth.

20. An electrolytic cell having means for heating a solid electrolyte to the temperature of fusion, and a diaphragm of particles of an electrically-conductive material, as set forth.

21. An electrolytic cell having means for heating a solid electrolyte to the temperature of fusion, and a diaphragm of particles of ferroferric oxid, as set forth.

22. An electrolytic cell having an electrode of fusible metal, means for heating the electrode to the temperature of fusion, and a diaphragm arranged to float upon said electrode, as set forth.

23. An electrolytic cell having an electrode of fusible metal, means for heating the electrode to the temperature of fusion, and a diaphragm of particles of electrically-conductive material arranged to float upon said electrode, as set forth.

24. An electrolytic cell having an electrode of fusible metal, means for heating the electrode to the temperature of fusion, and a diaphragm of particles of ferroferric oxid arranged to float upon said electrode, as set forth.

25. A floating diaphragm and a retainer of foraminous material adjacent to the diaphragm, as set forth.

26. An electrolytic cell having a floating foraminous sheet of conducting material the openings of which are filled with liquid metal, serving as a surface for discharge of the ions, as set forth.

27. An electrolytic apparatus, comprising a containing vessel, a liquid-metal electrode, a second electrode, a chamber for the second electrode having its lower end in contact with the liquid-metal electrode, and a diaphragm within said chamber and floating on the liquid-metal electrode, as set forth.

28. An electrolytic apparatus, comprising a containing vessel, a liquid-metal cathode, an anode, an anode-chamber having its lower end in contact with the cathode, and a diaphragm of loose granular material within the anode-chamber and floating on the cathode, as set forth.

29. An electrolytic apparatus, comprising a containing vessel, a liquid-metal cathode, an anode, an anode-chamber having its lower end in contact with the cathode, a diaphragm within the anode-chamber and floating on the cathode, and means for preventing the diaphragm from dropping out of the anode-chamber, as set forth.

30. An electrolytic apparatus, comprising a containing vessel, a liquid-metal cathode, an anode, an anode-chamber having its lower end in contact with the cathode, a diaphragm of loose granular material within the anode-chamber and floating on the cathode, and means for preventing the diaphragm from dropping out of the anode-chamber, as set forth.

31. An electrolytic apparatus, comprising a containing vessel, a depending partition partly dividing the vessel into two compartments, a liquid-metal cathode extending beneath both compartments and in contact with the lower edge of the partition, an anode in one compartment, and a diaphragm in the anode-compartment and floating on the cathode, as set forth.

32. An electrolytic apparatus, comprising a containing vessel, a depending partition partly dividing the vessel into two compartments, a liquid-metal cathode extending beneath both compartments and in contact with the lower edge of the partition, an anode in one compartment, and a diaphragm of loose granular material in the anode-compartment and floating on the cathode, as set forth.

33. An electrolytic apparatus, comprising a containing vessel, a depending partition partly dividing the vessel into two compartments, a liquid-metal cathode extending beneath both compartments and in contact with the lower edge of the partition, an anode in one compartment, a diaphragm of loose granular material in the anode-compartment and floating on the cathode, and means for preventing the diaphragm from dropping out of the anode-chamber, as set forth.

In testimony whereof I affix my signature in presence of two witnesses.

EUGENE A. BYRNES.

Witnesses:
C. A. NEALE,
GEO. M. COPENHAVER.