(No Model.) 2 Sheets—Sheet 1.

A. J. O. CHALANDRE.

ELECTROLYZING APPARATUS.

No. 511,682. Patented Dec. 26, 1893.

Fig. 1.

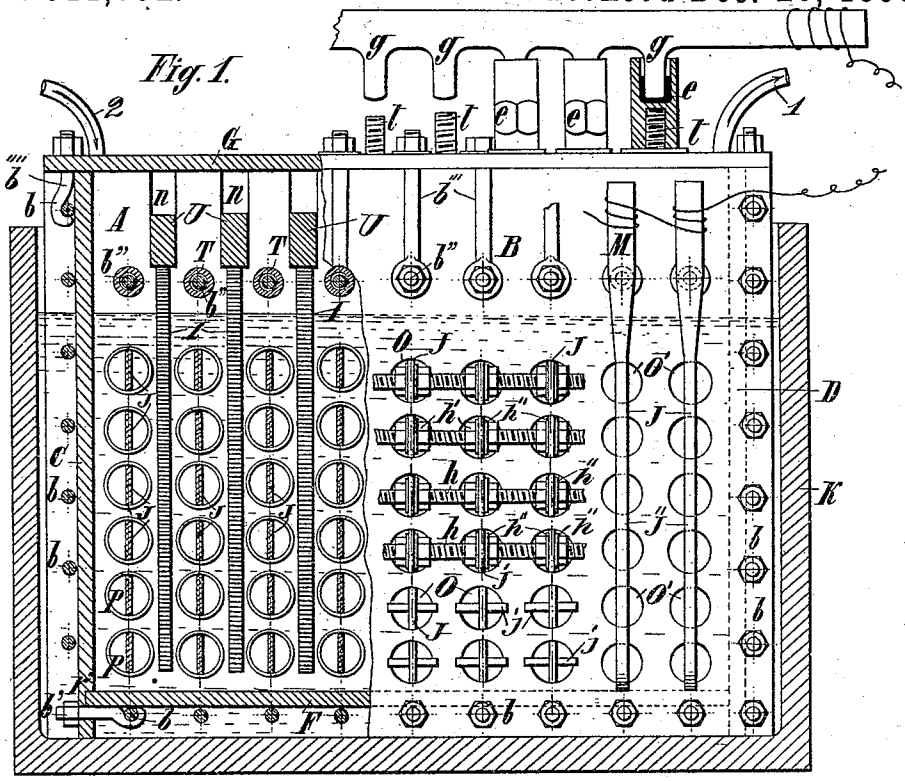
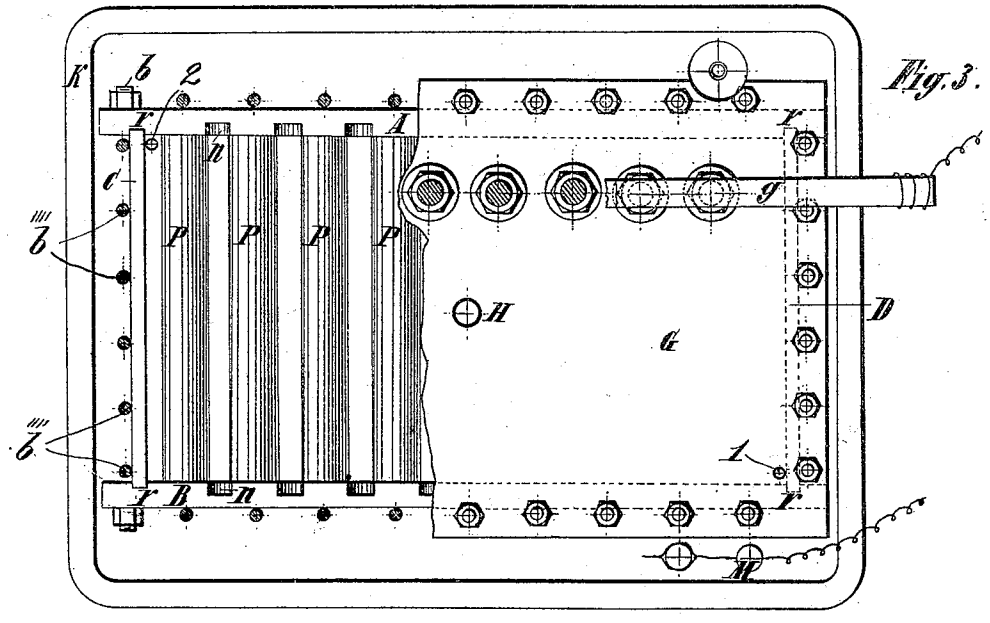


Fig. 3.



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(No Model.) 2 Sheets—Sheet 2.

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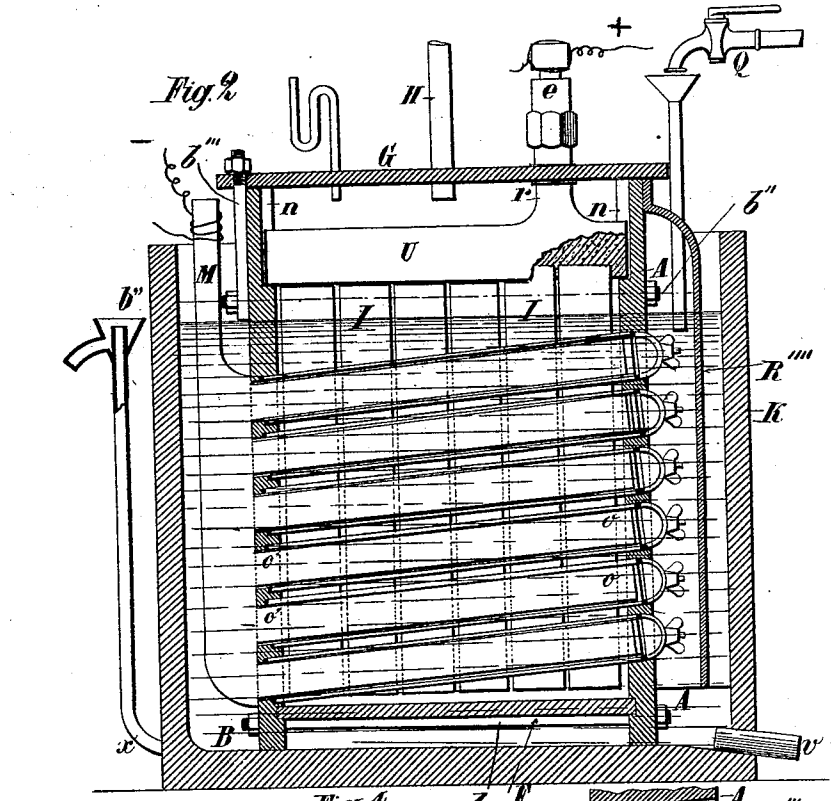


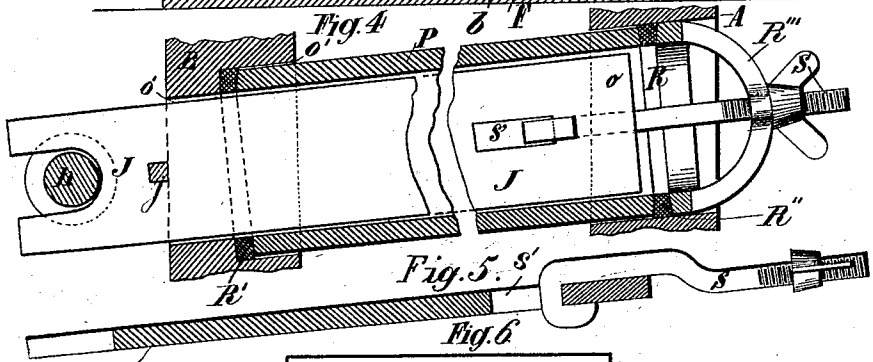
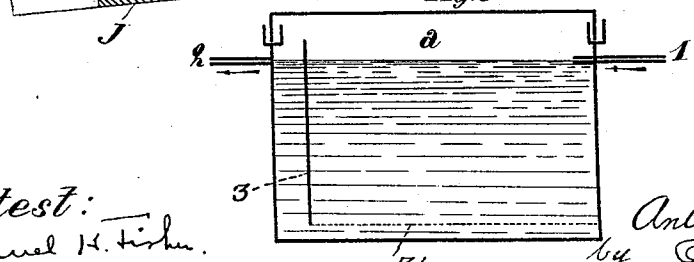


Fig. 5.



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UNITED STATES PATENT OFFICE.

ANTOINE JOSEPH OUTHENIN CHALANDRE, OF PARIS, FRANCE, ASSIGNOR TO THE SOCIETY OUTHENIN CHALANDRE FILS ET CIE., OF SAME PLACE.

ELECTROLYZING APPARATUS.

SPECIFICATION forming part of Letters Patent No. 511,682, dated December 26, 1893.

Application filed September 13, 1893. Serial No. 485,404. (No model.)

To all whom it may concern:

Be it known that I, ANTOINE JOSEPH OUTHENIN CHALANDRE, a citizen of the Republic of France, and a resident of Paris, in said Republic, have invented certain new and useful Improvements in Electrolyzing Apparatus, of which the following specification is a full, clear, and exact description.

This invention relates to an electrolyzing apparatus or cell intended more particularly for the electrolysis of sea salt or chloride of sodium with a view to the production simultaneously of caustic soda in solution and of chloride of lime in powder or in liquid form, and in this latter case free from salt. It can, however, be utilized for any analogous operation, that is to say for the treatment of substances generally in the electrolytic way.

The accompanying drawings, which form a part of this specification illustrate what is considered the best mode of carrying the invention into effect, and represent apparatus in accordance therewith.

Figure 1 is a longitudinal vertical section of the new or improved electrolyzer, the section being taken on different planes at the two ends of the apparatus. Fig. 2 is a cross section of the same. Fig. 3 is a plan of the apparatus, a portion of the cover for the anode compartment being broken away. Figs. 4 and 5 are detail views, and Fig. 6 is a view in section of a salt vat used in connection with the apparatus illustrated in the other figures.

The containing vessel K (Fig. 1) is a tight vessel, of a material which is not attacked by the liquid which it contains, or which is protected from attack by the application of an appropriate varnish. Its dimensions are a little larger than the anode compartment which it contains, and correspond with the amount of the work to be done. It is, moreover, the amount of work which determines the dimensions and the number of apparatus or cells to be employed. These are, according to circumstances, connected in series or in parallel in the electric circuit.

The cathodes are of metals not attacked by the electrolyte—wrought or cast iron, for example, in the case of sea salt—and the anodes of carbon or platinum. The total surface of the electrodes corresponds with the work to be done.

The anode compartment, apart from the different openings provided in its walls, as explained below, consists of a close box of plates held together by metallic bolts exteriorly arranged. In case inner bolts are also used they are arranged to have no exposed part liable to attack by the gases or liquids of the compartment.

The plates forming sides of the box, are of ebonite, glass, porcelain or pottery. These materials can be employed together or separately. In the inner surfaces of the side plates A and B, are grooves r to receive the end plates C and D and the bottom F. Outside of these grooves are holes for the threaded bars or exterior bolts b which hold the plates together. The joints are made tight by means of strips of rubber or of suitable cement placed in the grooves of the plates A and B. A tight joint between the bottom F and the ends C and D, is insured in an analogous manner by means of grooves r' with rubber or cement packing, and exterior bolts b'. (See left end of Fig. 1.) The joints can be arranged otherwise than shown, but the principle of the attachment and joining remains always the same in this that the bolts are exterior to the box or compartment of the anodes. When the box is of certain dimensions and the side plates A and B in several parts, or when such an arrangement is thought desirable, the plates may be cross connected at the upper part by tubes T traversed each by a bolt or threaded bar b'' with an exterior nut at each end, (Figs. 1 and 2.) Rubber washers are interposed between the ends of each tube T and the inner faces of the plates A and B to prevent the gases or liquid of the anode compartment from penetrating to the interior of the tube T (which is of unattackable material, ebonite, glass, &c.) and corroding the bar b''. The screwing up of the exterior nut on each bar insures at the same time a tight joint at the ends of the tube T and a firm cross connection of the plates A and B. There may be as many cross connections with their tubes T as may be desired.

The cover G of glass, porcelain, ebonite, &c.,

hermetically closes the anode compartment at the top by the aid of rubber or cement interposed between the edges of the vertical sides A B C D of the box and the under face of the cover. The cover is held in place and clamped by exterior bolts. These bolts in sufficient number may be held by engaging the four vertical plates of the box or projections therefrom, or they may engage the plates A and B and catch under the top bars *b* of the ends C and D. The bolts can be otherwise disposed, but whatever arrangement may be adopted, they should be exterior to the anode compartment. As shown eye bolts *b'''* engage at the bottom the ends of cross bolts *b''* at the sides and hook bolts *b''''* the upper cross bolt *b;* and both sets of bolts have nuts at their upper ends which confine the cover G.

The anode compartment is provided with a porous diaphragm or diaphragms so arranged as on one side to be in contact with the liquids in said compartment, and on the other side to be in contact with the liquid in the containing vessel K.

The openings *o* and *o'* are formed in the side plates A and B in a number of parallel vertical rows, an opening *o* in plate A corresponding with an opening *o'* in plate B at a lower level so that the common axis of the two holes is slightly inclined to the horizontal, (Figs. 2 and 4.) Each pair of holes receives a diaphragm formed by a tube of porcelain of suitable thickness and porosity of a round or flattened section open at both ends. The mounting of these tubes is illustrated in detail in Fig. 4. In certain cases tubes of flattened sections are more advantageous for reasons of compactness and electrical resistance.

Each porous tube P is supported at the opposite ends by the plates A and B. It is introduced through the opening *o*, whose diameter is a little greater than that of the tube, and its lower end bears against a soft rubber washer R' placed in the counterbored end of the opening *o'*. A second rubber washer R'' is then placed on the other end of the tube P in the opening *o*. On this washer a clasping ring R provided with an arch R''' bears. A hook bolt S passes through the middle of the arch and is provided with a wing nut which presses the ring R against the washer at the adjacent end of the porous tube P. The hook of bolt S engages the cathode J, (Figs. 4 and 5,) which is anchored against endwise motion by means of the pin *j*, passed through a hole in the cathode and bearing at the ends against the outside of the plate B. At *s'* the cathode has a slot for the introduction of the hook of bolt S. By means of the bolt S and its nut the porous tube P and its washers are so confined as to make a tight joint between the ends of the said tube and the plates A and B respectively. All the porous tubes being arranged as described, the liquid in the anode compartment is separated from the liquid in the containing vessel K while electrical communication is established through the porous walls of the tubes P. The vertical space occupied by these tubes is such that they are completely immersed in the electrolyte. The described mounting of the porous tubes very much simplifies their replacement in case of need; it insures in all cases a tight joint where such is necessary. The tubular form of these diaphragms is advantageous on account of the solidity and hardness which can be given them, their comparatively large surface preventing too great electrical resistance.

The anodes are placed perpendicularly between the vertical rows of tubes P as at I, Figs. 1 and 2. They are constructed of special carbons, in the form of sticks or plates secured in a leaden head U, by casting in an appropriate mold. The heads U extend slightly beyond the carbons to form at each end a support for upholding the anodes by resting upon the bottoms of the short grooves *n* in the side plates A and B. The leaden heads are arranged to occupy the space above the liquid level so as not to be bathed by the liquid. The application of a suitable varnish, as a varnish with a base of bitumen of Judea or of gum lac, sufficiently protects the metal of the heads against the action of the gases which fill the space above the liquid in the anode compartment.

Each head is provided with a conductor for external connection, applied in casting and consisting of a copper pin *t* embedded partly in the metal of the head. This pin passes through the cover G. The lead in proximity to the cover receives a soft rubber washer and to assure at this point the tightness of the anode compartment, such washer is clamped by means of a special nut *e* engaging the pin *t* which is threaded for this purpose. The nut is closed at the upper end and a certain space is allowed between the end of the bar *t* and the bottom of the hole in the nut so as to allow the nut to be screwed down to clamp the washer. This nut, moreover, constitutes the terminal of the anode properly speaking, and is provided according to a known mode with a mercury cup into which dips a part *g* of the principal conductor from the corresponding pole of the dynamo. This arrangement establishes at all times the good condition of the electrical connection. The anode terminals are arranged in the same line and are placed on the opposite side of the apparatus from the cathode terminal or terminals M.

The cathodes are strips or sheets—of iron, for example—of suitable cross section. They are arranged with their flat faces vertical or parallel with the planes of the anodes. Their width is a little less than the interior diameter of the porous tubes P which they enter freely. According to arrangement they have notched ends and are introduced through the openings *o* until the notched ends fit over the bar *h*, (Fig. 4.) A pin *j* is then passed through each cathode and holds the same from end-

wise motion by contact with the side plate B when the hook bolt S has been engaged and its nut is screwed down. The replacement of a cathode or its removal for putting in place a porous tube is thus very easy. The connection with the dynamo of these cathodes is made through the notched ends by means of the bars *h*, which are of metal and are provided with screw threads, and a pair of nuts *h'* and metal washers *h''* for each of the cathodes. The nuts and washers are strung on the rod and are screwed together sufficiently to leave between them a space to receive the cathodes when this is inserted through the openings *o o'*. When this has been done the nuts are screwed up so as to strongly clamp the cathode. The bars *h* are arranged horizontally and they can be connected with a single conductor by solder or otherwise, and it is the principal conductor which is connected with the corresponding pole of the dynamo outside of the liquid. Another arrangement consists in making all the cathodes of the same vertical or horizontal row in one piece of cast or wrought iron and is illustrated by the two vertical rows, the right of Fig. 1. Each of these pieces then represents a sort of comb whose teeth enter the corresponding tubes and whose back J'' is prolonged outside of the liquid as at M to permit the connection with the exterior electrical conductor. (See Figs. 1 and 2.) In this case, since the cathodes are constructed or forged in one piece they are introduced through the openings *o'* in the side plate B and each of them has projections to bear against said plate and take the place of the pin *j* employed with the bands or sheets of Fig. 4. The opposite end of each tooth of the comb is slotted as at *s'* in the case of the strips, to receive the hooks of the hook bolts S. One or the other of these arrangements will be used according to circumstances. The first may be inconvenient in certain liquids, on account of the connections with each cathode being in the electrolyte, but it is simpler than the second and better adapted for the removal or renewal of the cathodes; whichever arrangement may be used the cathodes serve as anchors for clamping the washers of the porous tubes P so as to make the joints tight. The cathodes are upheld in either case from the anode compartment and form with this latter an arrangement which can be removed as a whole from the contained vessel K for cleaning, inspection, or repair.

The anode compartment can be provided with handles or other means for moving it.

The cover G is provided with a pipe H for carrying off the gases liberated during the working of the apparatus. There may be also applied thereto a thermometer for enabling the temperature of the electrolyte bath surrounding the anodes to be kept constant; a manometer to indicate the tension of the gases of this electrolyte; a gage for enabling the level of the liquid to be controlled, &c.

Two tubes 1 and 2 are shown as arranged to pass through the cover G with suitable joints for maintaining a given concentration of the electrolyte within the compartment by circulating mechanically the electrolyte through an independent vat containing the salt to be decomposed. This vat is constructed of glass, porcelain or other material not attacked by the liquid to be contained therein. It is separated into two unequal compartments by a vertical division *z* extending to a perforated false bottom *z'* (Fig. 6). It is hermetically closed by a cover with a hydraulic joint permitting when necessary the introduction of the salt into the larger compartment *a*. The liquid withdrawn from the upper portion of the electrolyte by the tube 1, enters the vat, and flows out by the other tube 2, after passing through the mass of salt in the compartment *a* by which it is saturated. The vat is so placed that the liquid drawn off by the tube 2 flows by gravity through the same to the bottom of the anode compartment. To avoid an accumulation of the gases, in the space at the top of the salt vat this space may be connected by a small pipe with the escape pipe H from the anode compartment.

The following is the operation of the apparatus for say the industrial electrolysis of chloride of sodium and the production first of a solution of pure salt-free caustic soda and second, of chlorine, chlorine products and oxygen suitable for the manufacture of liquid or powdered chloride of lime, or under certain conditions of the chlorites, chlorates, &c., of different bases. The anode compartment (being placed in the exterior containing vessel K) is filled with a saturated solution of salt to such a level as to cover the tubular diaphragms P, without reaching the anode heads U; and the space around the anode compartment and inside the tubes P is filled with ordinary water to which can be added a little soda in order to diminish the resistance at the beginning of the operation. By suitably closing the circuit of the dynamo through the electrolyzer the separation of the elements of the salt commences at once and the normal operation is very soon established. It is not necessary to refer to the long known action of the electric current upon a solution of sea-salt; but it may be observed that the decomposition takes place at the same time as that of the salt and of the water which serves as its vehicle. On the cathode there is therefore a disengagement of hydrogen from the electrolytically decomposed water and also from that which is decomposed chemically by the liberated sodium, which latter forms the caustic soda without admixture of salt and of a concentration growing more and more as often soda is formed. When the solution of soda attains the desired strength it is drawn off by the outflow *x* on the introduction of ordinary water through the supply pipe Q. The inclination of the porous tubes facilitates the escape of the hydrogen, which escape takes place

almost entirely on the side of the plate A. A suitable arrangement may be adopted to collect this gas if thought desirable. Such an arrangement is shown in Fig. 2, consisting of a chamber R'''' open at the bottom and closed at the top and lateral edges against the side plate A, and extending into the liquid so as to inclose all the openings *o*, by which the gas escapes after passing through the tubes P and clamping rings R. From this chamber the gas can be withdrawn into any suitable receiver. At its upper part there may be a manometer by which to control the pressure; moreover, the supply pipe for the introduction of the water to keep the liquid in the containing vessel at the proper strength and volume may enter this chamber. It is so shown in Fig. 2. This water will flow through the porous tubes P becoming more and more saturated with soda as it flows. On the anodes there is a disengagement of oxygen from the water and of chlorine from the salt. These gases escape as they are formed by the pipe H, which is to be connected with an absorption chamber containing hydrate of lime in powder or milk of lime in case the production of calcium hypochlorite is sought. The escape of the gases is controlled in accordance with the indications of the manometer before mentioned. The supply of gases is regularly maintained by keeping up the concentration of the electrolyte in the anode compartment. It is necessary to maintain the level of the liquid in the anode compartment by adding water from time to time to replace that decomposed by the action of the current. The level is regulated by the aid of a gage or level indicator.

As advantages of the new or improved apparatus described may be mentioned first the large surface obtained for the electrodes in a reduced space; second, the ready facility of inspection or repair, all the elements being of the same type or duplicates of one another; and third, the complete separation of the electrolyzed elements.

I claim as my invention or discovery—

1. The cell composed of a containing vessel, electrodes therein, a compartment with porous diaphragms set within the containing vessel and composed of plates held together by exterior fastenings, and electrodes in said compartment, substantially as described.

2. The compartment provided with porous diaphragms in the form of open ended rigid porous tubes each set in and opening at its opposite ends through the walls of said compartment, substantially as described.

3. The compartment provided with porous diaphragms in the form of open ended porous tubes set in vertical rows in and opening through the walls of said compartment and arranged with both ends of said tubes below the liquid level substantially as described.

4. The compartment provided with porous diaphragms in the form of inclined open ended porous tubes, substantially as described.

5. The combination with the compartment walls, of porous tubes opening at their opposite ends through said walls, packing rings interposed between the walls and the tubes and a clamping device arranged exterior to the compartment for compressing said rings to form tight joints, substantially as described.

6. A cell provided with vertical rows of porous tubes set in and opening through the walls of an electrode compartment, and also provided with electrodes in said compartment, and opposing electrodes in said tubes, substantially as described.

7. A cell provided with vertical rows of horizontal disposed electrodes within porous tubes, substantially as described.

8. A cell provided with vertically arranged electrodes and opposing electrodes horizontally disposed in vertical rows within porous tubes, between the first named electrodes, substantially as described.

9. A cell provided with an electrode compartment, a containing vessel, and a gas chamber for the electrodes and exterior to the compartment bathed by the liquids of the containing vessel, substantially as described.

10. A cell provided with an electrode compartment with open ended rows of porous tubes, electrodes in said tubes, and a gas chamber inclosing the ends of said tubes, substantially as described.

In testimony whereof I have signed this specification in the presence of two subscribing witnesses.

ANTOINE JOSEPH OUTHENIN CHALANDRE.

Witnesses:

CLYDE SHROPSHIRE,

EDOUARD BARBARY.