

(No Model.)

2 Sheets—Sheet 1.

E. HERMITE & A. DUBOSC.  
METHOD OF AND APPARATUS FOR ELECTROLYZING SOLUTIONS.  
No. 501,783. Patented July 18, 1893.

FIG. 4.

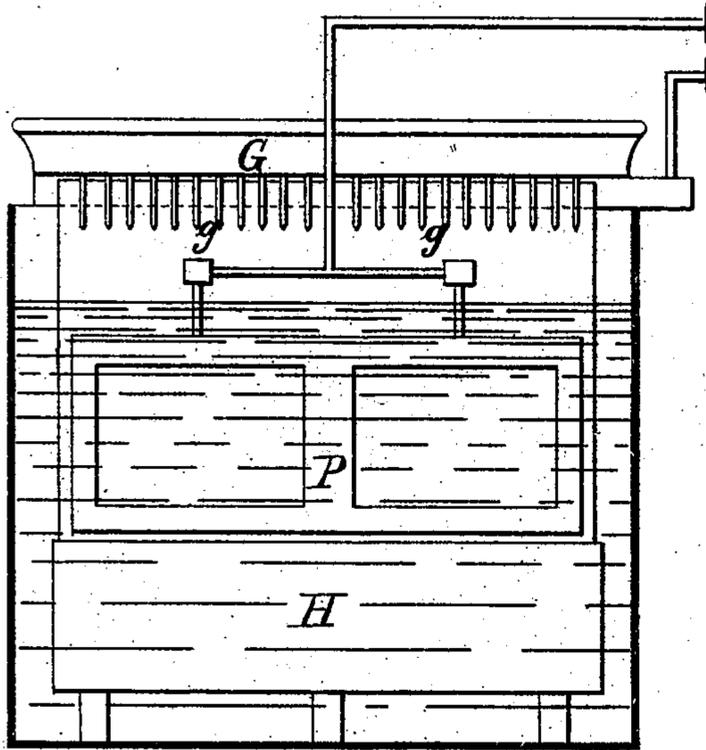


FIG. 1.

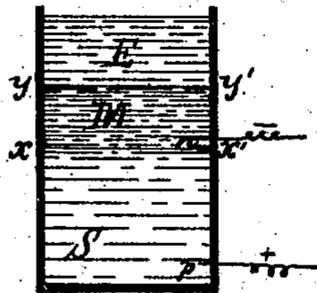
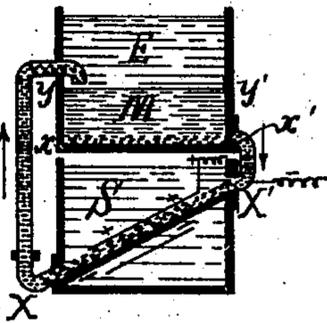


FIG. 2.



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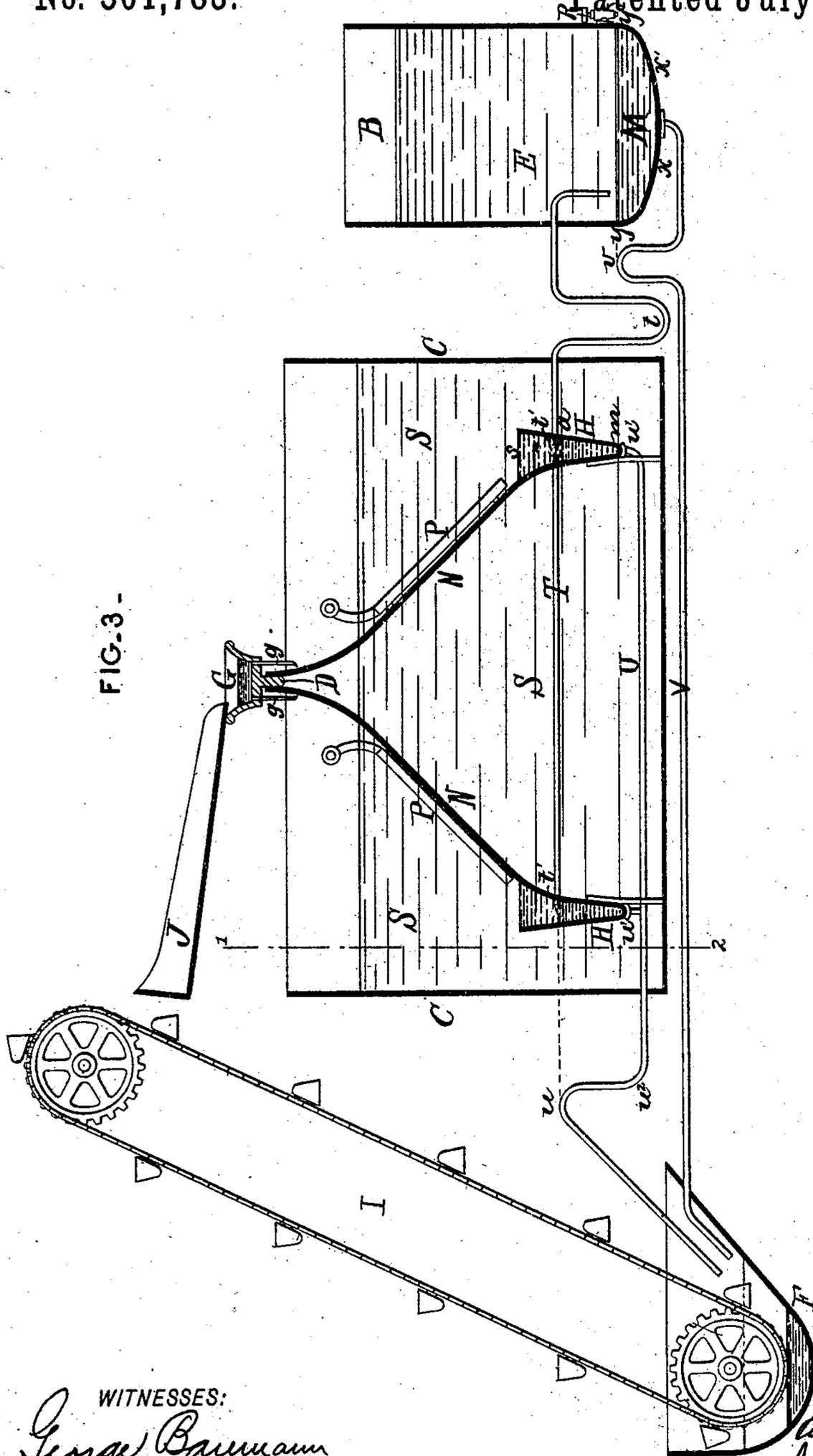


FIG. 3 -

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# UNITED STATES PATENT OFFICE.

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METHOD OF AND APPARATUS FOR ELECTROLYZING SOLUTIONS.

SPECIFICATION forming part of Letters Patent No. 501,783, dated July 18, 1893.

Application filed July 9, 1892. Serial No. 439,532. (No model.) Patented in France December 7, 1891, No. 217,887.

*To all whom it may concern:*

Be it known that we, EUGENE HERMITE, manufacturer, a citizen of the United States of America, residing at Paris, and ANDRÉ DUBOSC, manufacturer, a citizen of the Republic of France, residing at Rouen, France, have invented a new Method of and Apparatus for Obtaining Alkali and Earthy Alkaline Bases or Compounds Thereof by Electrolysis of Saline Solutions, (for which we have obtained a French patent, dated December 7, 1891, No. 217,887,) of which the following is a specification.

It is known that when an electric current is caused to pass through a solution of a salt of any alkali or alkaline earth metal base, the acid and the oxygen combined with the metal of the base pass to the positive pole and the metal passes to the negative pole. A certain amount of water is generally decomposed at the same time. The metal decomposes the water of the bath and becomes converted into oxide setting hydrogen free. The same theory applies to haloid salts such as chlorides. The chlorine and the oxygen resulting from the decomposition of the water pass to the positive pole and the base is reconstituted at the negative pole. It has been proposed long ago to utilize this principle in order to separate alkali and alkaline earth metal bases such as potash and caustic soda for example from their saline combinations. Nevertheless the essential part of the problem consists as may be imagined in separating the base from the acid as fast as the salt is decomposed in order to withdraw it from the influences of the acid and of the current and obviate recombination of the separated elements. With this object attempts have been made to utilize the two methods hereinafter described which have however yielded very inferior results in practice and have consequently been abandoned. These two processes are:—

I. *Separation of the base with the aid of porous membranes or partitions.*—The vessel containing the solution to be electrolyzed is divided into two compartments by a porous partition and an electrode is immersed in the liquid in each compartment. The base is collected in the compartment corresponding

to the negative electrode and the acid or oxygenized compound of chlorine in the other compartment. This method can never be employed in practice on account of two important disadvantages namely first the porous partitions present very considerable resistance to the passage of the electric current so that a high electro motive force is necessarily employed and the motive power is wasted. Moreover the porous partitions become clogged and are soon rendered useless. Second. When the base set at liberty at the negative pole is of a soluble nature such as soda and potash a great portion of the current passes to this base and decomposes it into metal and oxygen directly the quantity of base formed has attained a certain proportion thus occasioning considerable waste of motive power and rendering it impossible for the production to exceed certain limits. For these considerations we have abandoned the employment of porous partitions.

II. *Separation of the base by the employment of mercury.*—The bottom of the electrolyzing vessel is covered with a layer of mercury electrically connected with the negative pole of the source of electricity. The positive electrode is immersed in the saline solution which remains above the mercury. As fast as the salt is decomposed the metal passes to the negative pole constituted by the mercury and amalgamates with the latter. The acid or oxygenized compound of chlorine remains in the saline solution. When carried out in this way this process has never yielded practical results. In fact as fast as the proportion of metal in the amalgam increases the latter being in contact with the saline solution is decomposed by the latter so that the formation of amalgam stops in a very short time after which the energy of the current is expended to no useful purpose. Notwithstanding the inherent imperfections attending the employment of this process it occurred to us that if it were possible to automatically remove the amalgam of mercury as fast as it is formed from contact with the saline solution and from the influence of the electric current and to continually replace this amalgam by fresh or unamalgamated mercury this would have the effect of removing all the disadvantages men-

tioned and there would no longer be any obstacle to the mercury process acquiring considerable commercial value.

We think it desirable to set forth here in detail the data on which we have commenced and the conclusions which we have deduced therefrom in order to ascertain with precision the characteristics of our invention and determine the scope of the claims which it entitles us to establish.

In order to more clearly explain the principles whose application has enabled us to obtain the desired results we have represented in Figure 1 of the annexed drawings an imaginary apparatus which would be impossible in practice but which presents the advantage of facilitating the demonstration of our theory. In this drawing S represents a solution of any salts of any alkali or alkaline earth metal. M is a layer of mercury which must be imagined to be floating or suspended upon the surface of the saline solution and E represents the water or acid employed for removing the metal from the amalgam in order to form the base of the salt which is to be manufactured. The vessel is provided with two electrodes the + electrode being immersed in the solution S and the - electrode entering the lower part of the mercury. If it were possible to construct an apparatus of this description in practice it would give the desired results by reason of the following principle of action which forms the basis of all the practical apparatus derived from this imaginary arrangement.

I. *Separation of the amalgam and of the mercury by means of the difference in their densities, the amalgam being lighter than the mercury and its relative lightness increasing in proportion to the amount of metal it contained.*—This being established the action of this apparatus would be as follows:—The electric current would decompose the saline solution in the usual way and the metal passing to the negative pole would form an amalgam on the under surface  $x x'$  of the mercury. But this amalgam directly it is formed being less dense than the mercury would ascend through the layer M and would accumulate on the upper surface  $Y Y'$  of the mercury where it would be decomposed by contact with the water and the base or solution of the base would be collected directly at E at the degree of concentration varying as required in accordance with the duration of the passage of the electric current. This apparatus thus complies with the conditions prescribed. The amalgam directly it is formed at  $x x'$  would ascend to  $y y'$  and would thus be withdrawn from contact with the saline solution acting at  $x x'$  and also from the direct influence of the current flowing between the two electrodes from  $p$  to  $n$  while the mercury which is amalgamated at  $x x'$  would be perpetually renewed and replaced by pure and active mercury. The great importance of being able to realize this theoretical ar-

angement in a practical manner will now be understood.

On referring to the imaginary arrangement represented in Fig. 1 it will be found that the parts situated above the line  $x x'$  can be constructed in practice. We can easily construct a vessel containing a layer of amalgamated mercury M underneath a layer of water E. The amalgam floating upon the top of the mercury transfers the metals to the water in order to form the base and the pure mercury descends to the bottom at  $x x'$ . The mercury being heavier than any imaginable saline solution the difficulty was to bring the lower layer of pure mercury into contact with the saline solution. We have arrived at this result by the aid of the method next hereinafter described which forms the complement of the principles hereinbefore set forth.

II. *Continuous flow of the lower layer of pure mercury and rapid passage of this mercury in a thin sheet into the saline solution over an inclined surface forming the negative electrode, facing the positive electrode, the amalgam formed being removed from the action of the solution and from the influence of the current immediately after its rapid passage over the said surface.*—A diagram illustrating this arrangement is given in Fig. 2 of the accompanying drawings. The lower layer of pure mercury at  $x x'$  flows over an inclined surface in a thin film or sheet at  $X X'$  passing rapidly through the saline solution S. At X the amalgam formed is removed in any suitable manner from the action of the solution of the current and is elevated from X to  $y$  by any suitable elevating apparatus. At M separation in order of density takes place as hereinbefore described in paragraph I. The water absorbs the metal to form the base and the disamalgamated mercury falls to the bottom whence it flows away and is amalgamated as stated in paragraph II afterward returning to M and thus keeping up a continuous circulation.

We have set forth at some length what may be termed the genesis of our method with the aid of diagrams in order to show clearly the essential principle of our apparatus and clearly defined our claims which cover all apparatus based upon the principle and on the method of operating as hereinbefore set forth.

The accompanying drawings illustrate by way of example an apparatus constructed according to our invention and enabling the same to be performed in practice.

In the said drawings Fig. 3 represents the apparatus in longitudinal section. Fig. 4 represents the apparatus in transverse section on the line 1—2 Fig. 3.

In the following description we have assumed, in order to obviate repetitions, that the invention is applied to the manufacture of caustic soda by the electrolysis of chloride of sodium but it must be clearly understood that the operation may be performed upon

any solution of a salt of an alkali or an alkaline earth metal as a base (potash, soda, ammonia, magnesia, alumina, &c.) either for the purpose of separating the base from the salt or for preparing therewith any other saline solution. In the first case the amalgam formed is decomposed with pure water and in the second case by a suitable acid. For example in preparing a carbonate a current of carbonic acid may be caused to pass through the water employed for decomposing the amalgam. The solution to be electrolyzed, indicated at S, is contained in a vessel C and the water E, employed for removing the sodium from the amalgam, in order to obtain the caustic soda, is contained in a tank B. The inclined electrodes are immersed in the solution in the vessel C. The negative electrode *n* is constituted by one, two or more plates N of iron, copper or other suitable metal. The upper surface of this electrode is amalgamated by known processes (by electrolytic action in the case of iron or by simple friction in the case of copper). The object of this amalgamation is to enable the mercury to spread over the electrode in a uniform layer. Without this precaution the mercury would run down in the form of globules and would be in a very bad condition for absorbing the metal separated from the solution. The plates aforesaid are connected to the negative pole of the source of electricity by a conducting bar D. At their lower extremities these plates are bent upward in such a manner as to form gutters H for the reception of the amalgamated mercury. The positive electrodes P made of platinum or other metal are placed facing or opposite to the negative electrodes in such a manner that the mercury flows down between the two.

It must be understood that the invention is not limited to electrodes of the shape represented in the drawings. In place of being flat or plane as shown they may be of a conical and continuous form for example.

The mercury is conducted to the higher part of the electrodes by means of a distributor constituted by a trough G communicating with one or more series of small tubes *g* having their lower extremities contracted and extending the whole length of the negative electrodes.

It now remains to describe the arrangements employed for producing the circulation of the mercury. For this purpose the combination of tubes or pipes T, U, V, is employed. The pipe T provided with a descending U shaped bend or trap *t* connects the tank B with the upper part of the mercury in the gutters H. The pipe U having an upward bend at *u* connects the lower parts of the gutters H with a collector F and the pipe V having an upward bend at *v* proceeds from the bottom of the tank B at *v'* and likewise communicates with the collecting vessel F. An elevating apparatus I (chain of buckets, noria, &c.) takes up the mercury from the collector F and dis-

charges it into a chute J from which it flows into the distributor G. The action of this apparatus is as follows: Let it be assumed that a suitable quantity of mercury has been introduced into the apparatus, that the electric current is supplied to the electrodes and that motion is imparted to the elevator I. The mercury flowing from the distributor G passes through the series of contracted tubes *g* and descends in the form of a sheet or film over the surfaces of the electrodes N. In its passage between the electrodes P and N the mercury gradually becomes charged with sodium resulting from the electrolytic decomposition of the saline solution after which it passes into the gutters H H. During the passage between the electrodes there is no danger of any appreciable decomposition of the amalgam formed the amalgam being decomposed with difficulty owing to the small proportion of metal which it contains and when this proportion has increased sufficiently to admit of the decomposition the amalgam passes into the gutters where it is secluded from the electric action exerted between the two electrodes. In order to protect it from contact from the saline solution sulphuret of carbon (or in general any liquid lighter than the amalgam and heavier than the saline solution) is poured into the gutters H on the top of the amalgam at *s* and separates the latter from the solution S. Separation in order of density takes place in the gutters in accordance with the principle hereinbefore set forth. The purest mercury descends to the bottom at *m* and the proportion of sodium in the amalgam increases toward the upper part the whole being covered by the layer *s* of sulphuret of carbon. The pipe T communicating with the gutters H at *t'* at a point over which the amalgam containing the greatest proportion of sodium is situated conducts this amalgam into the tank E. In order that the sulphuret of carbon at *s* floating upon the top of the amalgam may not flow away through the tube T the latter is provided with the U shaped bend at *t* which is always filled with the column of amalgam balancing the pressure of the liquid (amalgam, sulphuret, and solution in the vessel C) situated above the level *a*. The relatively pure mercury collected in the bottoms of the gutters at *m* escapes at *u' u'* and flows through the pipe U' into the collector F. The pipe U is provided with a bend at *u<sup>2</sup> u* so arranged that the column of mercury *u<sup>2</sup> u* balancing the pressure of the liquid (mercury amalgam, sulphuret and saline solution) above the level *u'* prevents the mercury from escaping through the orifices at *u'* until the said mercury by reason of its purity has acquired the necessary density. On the other hand the amalgam flowing into the tank B distributes itself in order of density at M on the bottom of this tank the mercury richest in sodium passing to the upper part at *y y'* where it is in contact with the water E which decomposes it and takes up the sodium to form the caustic

soda the exhausted amalgam sinking gradually so that the mercury at  $x x'$  is free from sodium. This mercury is discharged at  $v'$  through the pipe V (provided with a bend at  $v$  in order to preserve the level  $y y'$ ) and mixes with the mercury supplied from the gutters HH to the general collector F. From this collector the mercury is taken up by the elevator I and returned to the distributor G the operation being thus rendered continuous.

The apparatus hereinbefore described fulfills all the conditions hereinbefore set forth and presents moreover the advantage of being automatic and continuous in its action.

It is possible to obtain in the vessel E either caustic soda, potash or ammonia at any degree of concentration; for this purpose it is simply necessary to prolong sufficiently the duration of the operation. The soda may be drawn off through a cock R arranged above the level  $y y'$  of the mercury or in any other suitable manner.

We claim as our invention—

1. As an improvement in the method of obtaining alkali or alkaline earth metal bases or compounds thereof, by the electrolysis of saline solutions, the mode herein described, consisting in subjecting a thin sheet of mercury to electrolysis in a saline solution thereby forming an amalgam of the metal of the base, and separating the amalgam, as it is formed, from the saline solution by a layer of liquid lighter than the amalgam and heavier than the saline solution, all substantially as set forth.

2. The method of obtaining alkali and alkaline earth metal bases or compounds thereof by the electrolysis of saline solutions, consisting in subjecting a thin sheet of mercury to electrolysis in a saline solution thereby forming an amalgam of the metal of the base, separating the amalgam, as it is formed, from the saline solution, by a layer of liquid lighter than the amalgam and heavier than the saline solution and permitting the mercury to separate from the amalgam by the difference in densities, substantially as set forth.

3. An apparatus for obtaining alkali and alkaline earth metal bases or compounds thereof by electrolysis, the said apparatus comprising a vessel for the saline solution and provided with a positive electrode and with an inclined plate or plates forming the negative electrode and bent up at the bottom to form a gutter, in combination with a collector for the reception of disamalgamated mercury, a distributing device to spread the mercury in a thin sheet over the negative electrode, an elevating device to carry the mercury from the collector to the distributing

device, a tank in which the amalgam is brought into contact with the water employed for exhausting it, and a system of pipes connecting the gutter on the negative electrode with the said tank and with the said collector, all substantially as set forth.

4. In an apparatus for obtaining alkali and alkaline earth metal bases or compounds thereof by the electrolysis of saline solutions, the combination of a vessel for the saline solution, with an inclined metallic plate provided at the lower end with a gutter, the said plate forming the negative electrode, and a positive electrode facing the negative electrode, substantially as and for the purpose set forth.

5. In an apparatus for obtaining alkali and alkaline earth metal bases or compounds thereof by the electrolysis of saline solutions, the combination of a vessel for the saline solution, provided with a metallic plate, forming the negative electrode and terminating at its base in a gutter with a distributing device at the upper part of the said negative electrode, the said device consisting of a trough provided with a series of tubes contracted at their lower extremities, all substantially as and for the purposes set forth.

6. In an apparatus for obtaining alkali and alkaline earth metal bases or compounds thereof by the electrolysis of saline solutions, the combination of a vessel for the saline solution, provided with positive and negative electrodes, the negative electrode formed of an inclined metallic plate terminating at its base in a gutter to hold mercury, amalgam and a liquid lighter than the amalgam and heavier than the saline solution, an exhausting tank, and a collector for the pure mercury, with a pipe T opening communication between the said tank and the said gutter at a suitable height from the bottom of the gutter, a pipe U connecting the bottom of the gutter with the collector, and a pipe V connecting the bottom of the tank with the collector, the said pipes T, U, V, being provided with suitable bends for maintaining constant the levels of the mercury, of the amalgam, and of the aforesaid liquid in the said gutter, and the level of the amalgamated mercury in the tank, all substantially as set forth.

In testimony whereof we have signed our names to this specification in the presence of two subscribing witnesses.

EUGENE HERMITE.  
ANDRÉ DUBOSC.

Witnesses:

C. A. CARLIER,  
GEORGES TRUEBOST.