

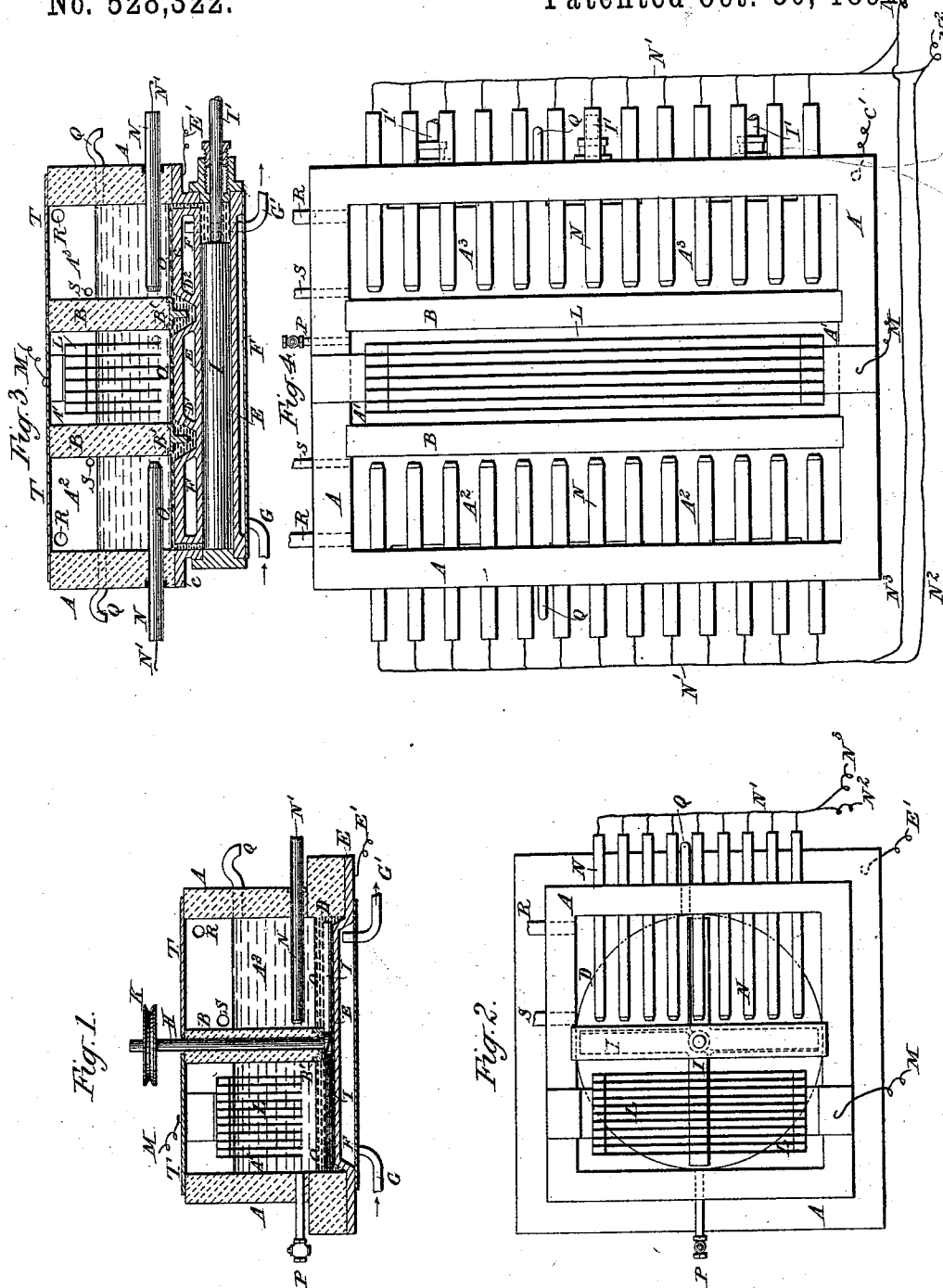
(No Model.)

H. Y. CASTNER.

PROCESS OF AND APPARATUS FOR ELECTROLYTIC DECOMPOSITION OF ALKALINE SALTS.

No. 528,322.

Patented Oct. 30, 1894.



Witnesses.
A. N. Gibson
G. P. Kramer

Inventor
H. Y. Eastman
by Foster Freeman
att'y

UNITED STATES PATENT OFFICE.

HAMILTON YOUNG CASTNER, OF LONDON, ENGLAND.

PROCESS OF AND APPARATUS FOR ELECTROLYTIC DECOMPOSITION OF ALKALINE SALTS.

SPECIFICATION forming part of Letters Patent No. 528,322, dated October 30, 1894.

Application filed September 26, 1892. Serial No. 446,913. (No model.) Patented in England September 7, 1892, No. 16,046.

To all whom it may concern:

Be it known that I, HAMILTON YOUNG CASTNER, a citizen of the United States of America, residing at 115 Cannon Street, London, England, have invented a certain new and useful Improved Process of and Apparatus for the Electrolytic Decomposition of Alkaline Salts, of which the following is a specification, Letters Patent of Great Britain, No. 16,046, dated September 7, 1892, having been granted me for the same invention.

This invention has for its object the economical electrical decomposition of alkaline salts in solution or otherwise and is particularly applicable to the production of pure alkaline hydrates, and chlorine or hypochlorites from alkaline chlorides.

The electrical decomposition of haloid compounds of the alkali metals for the production of the corresponding halogens and alkaline hydrates has long been known, but, so far as I am aware, has never been commercially carried on for one or more of the following reasons:

First. The required use of a porous partition or diaphragm to separate the electrodes and the consequent products of the electrolysis necessarily interposes a considerable electrical resistance. Such electrical resistance increases relatively to the effectiveness of the chemical separation.

Second. As the chemical separation has never been perfect in a single cell, the intermingling of the two products of the electrical decomposition gives rise to a new series of products, which more or less interfere with the continuance of the electrical action besides meaning a direct loss in current efficiency.

Third. The caustic solutions produced contain more or less salt and are very dilute as the strong solutions more rapidly diffuse through the porous partition or diaphragm. Thus pure caustic cannot be obtained and the concentration and production of solid caustic materially increases the manufacturing cost.

Fourth. In the various kinds of apparatus which have been designed to overcome these many difficulties the parts are more or less complicated and thus both expensive and al-

most impossible to work practically on a large scale.

The present invention consists of a process of and apparatus for producing electrolytically from chloride of sodium, pure caustic soda and chlorine or hypochlorites or when treating other materials obtaining analogous products.

Briefly stated the invention may be said to consist in the employment of a body of mercury or other liquid metal or alloy between the compartments of a decomposing cell completely separating the materials therein and so placed that the current in its passage through the cell, must pass into and through the moving metal. Thus while the alkaline metal is being deposited in such liquid metal in the one compartment a like amount of the alkali metal is being set free in the other compartment thereby reducing the counter electromotive force, rendering it possible to carry on the electrical action continuously with a very high current efficiency and yielding at the same time where water is used in the second compartment a solution of pure caustic of any desired strength. Practically the moving liquid metal takes the place of a diaphragm as without interposing any appreciable resistance to the passage of the current it completely separates the products of the electrolysis. At the same time it allows the intervening space between the positive and negative electrodes to be reduced to a minimum and yet to have such space effectively occupied by salt and caustic solution.

In the accompanying drawings Figures 1 and 2 illustrate by sectional elevation and plan a simple form of electrolytic cell or apparatus with two compartments. Figs. 3 and 4 illustrate by sectional elevation and plan a three compartment apparatus or cell which will be found most suitable for carrying out the process on a commercial scale.

In Figs. 1 and 2 the square cell A is divided by an impervious partition B into two chambers A' A². The lower part of the cell is circular at D and the bottom is closed by metal plate E beneath which is a hollow chamber or water jacket F served by pipes G G' through which water or other cooling medium is caused to pass. The electrical connection

from bottom plate E is marked E'. Through partition B passes a spindle H fitted at the bottom with radial helical blades I and at the top with a driving pulley K. The negative electrodes L which are preferably of copper are clamped together and hung in chamber A' to which is secured the connection M. The positive electrode N passes into chamber A² and is joined to connection N' having two branches N²N³. Partition B is provided with a metal shoe at B' but such shoe does not touch the bottom of the cell. Mercury or other metal or alloy in a fluid state is shown at O. Compartment A' is provided with an outlet governed by tap P while the outlet for liquid from A² is indicated by Q and for gas by R and the inlet for liquid into A² by S. Both chambers or compartments are covered by glass or other plates T.

In Figs. 3 and 4 of the drawings the cell A has two partitions B B making three chambers A' A² A³ communicating at the bottom which is closed with metal casting C having channels D' D². In the metal bottom E are three barrels or cylinders having pistons I moved by rod I' in any convenient way. Mercury is drawn into and expelled from alternate ends of the cylinders causing circulation from compartment A² to A' and from A' to A³ or from A³ to A' and from A' to A² alternately. Bottom plate C has the connection E' fastened on it and a hollow water jacket F is provided for cooling purposes, the water for which enters and leaves by pipes G G'. Plates L are clamped together and supported in chamber A' and are in connection with wire M. The positive electrodes N N project into chambers A² A³ and are joined to connections N' having branches N²N³. The partition walls B B have metal shoes B' B' along the bottom edge dipping into mercury in channels D' D² in which the mercury level is shown at O. The outlet from A' is provided with a tap at P while the outlet from A² and A³ for liquid is indicated by Q and for gas by R while the liquid inlet is indicated by S the chambers having glass or other suitable covers T.

The operations of the process as carried on in the cell illustrated by Figs. 1 and 2 being most easily understood are first described. The cell being charged with mercury up to the level O as shown, this forms with the aid of the partition B and the metal shoe B' which is directly amalgamated by the mercury a complete means of separating the solutions placed therein. Compartment A' is charged with water and A² with a saturated solution of salt. The stirrer I is started slowly revolving and water is passed through compartment F by means of pipes G and G'. In carrying on the process it is necessary that the mercury should always contain a certain proportion of sodium. Should sodium not be present in the mercury, on the passage of the current through the cell, in the compartment A', hydrogen and oxygen will be

set free, the hydrogen passing off, the oxygen combining with the mercury. In the presence of sodium however no mercury is oxidized but the contained sodium being oxidized goes in solution as caustic. Thus to prevent the oxidation of the mercury and maintain the proper electrical and chemical action it is absolutely necessary that the alkali metal must always be present in the mercury; the fixed quantity being more or less regulated by the means employed for stirring. If the electrical efficiency of the passing current through this cell could be maintained at one hundred per cent. in both compartments then starting with mercury containing a small proportion of sodium, the quantity would remain constant, the chloride would be decomposed in A², chlorine being liberated and amalgam forming, while in A' hydrogen is set free, the sodium going in solution as caustic. From experiment I judge that it will be impossible to obtain one hundred per cent. efficiency in the passing of the current through A² owing to the partial decomposition of water or, what amounts to the same thing, owing to the deposited sodium recombining with the chlorine present to form chloride, or with the water to form caustic and consequently hypochlorite. This loss in efficiency will increase relatively with the percentage of sodium in the amalgam being used and also with any rise in temperature during the electrolysis. With proper stirring and regulated electrical action the amalgam can be kept at a uniform strength containing a minimum amount of sodium, and any increase of temperature due to the passage of the current may be prevented by the cold water flowing through F. Practically by this process and similar apparatus an efficiency of ninety per cent. can be obtained.

As the electrical efficiency in compartment A' is always one hundred per cent., to insure the presence of sodium in the mercury I proceed as follows, best explained by the following examples: The wires N' and E' are connected with the terminals of a dynamo and the current passed therefrom causes sodium to be deposited in the mercury and this is continued until an amalgam containing about .2% (two tenths of one per cent.) of sodium is obtained. Then N³ and M are made the connecting wires between the dynamo and the anode N and cathode L, the current passing for example being ninety amperes. N² and E' are also connected with the positive and negative poles respectively of a second dynamo which supplies a current of ten amperes. Thus while one hundred amperes are passing through N' only ninety are passing through M and the amalgam will remain at .2% (two tenths of one per cent.) of sodium while ninety per cent. of the theoretical yield for the combined or total current will be obtained as caustic in A' and a corresponding amount of chlorine will be produced in A². Without employing two sources of current

the same result may be obtained by passing the current say for one hour using the wires E' and N' and then changing and for nine hours using N' and M as the connections for the supply of the same current. Thus cells coupled in series have their connections so arranged as to allow this change to be made in turn and so allow a number of cells to be worked without varying the total difference of potential in the dynamo terminal. It is evident that cells coupled in parallel necessitate the use of two currents to maintain the presence of sodium in the mercury; the efficiency yield determining the proportion existing between the two currents. With cells coupled in series a single current only is required, the direction of passage through the cell being changed by time as fixed also by the efficiency.

After charging and starting the apparatus as before mentioned the current being passed as described in either of the foregoing examples, chlorine is given off in compartment A² and escapes through the opening R into any suitable collecting apparatus. The solution which is kept at saturation, by the addition of salt from time to time, may be removed and replaced by a fresh solution free from hypochlorites when necessary, while the solution so removed is treated either to separate or decompose the hypochlorite and then again returned to the cell, or if desired this operation may be made continuous. Some advantage is also gained by employing salt solutions free of calcic sulphate an impurity always occurring in common salt. Unless it is removed from the solutions the proportion of this impurity gradually increases to such an extent as to materially decrease the current efficiency.

The oxidation and solution of the sodium in the compartment A' generates a certain amount of electrical energy or practically the electromotive force necessary to decompose sodium chloride into its elements less the electromotive force gained by the oxidation and solution of the metal to caustic and represents the actual counter electromotive force of the cell, a result being equivalent to the direct electrolysis of sodium chloride solution into caustic soda, hydrogen, and chlorine, with the advantage of separating the products completely by the interposition of a substance that offers no appreciable electrical resistance and allows the electrodes to be brought almost in direct contact. At the commencement of the operation owing to the weak caustic solution in A' being a poor electrical conductor the resistance will be high but as this solution becomes concentrated the electrical resistance will fall considerably. In running continuously after the solution in A' reaches a certain strength it is kept so by allowing water to flow slowly into the compartment, in proportion to the caustic being produced, while a uniform strength caustic solution is being drawn off at P. In this way

without disturbing the liquid level of the compartment a continuous flow of caustic solution is maintained.

In Figs. 3 and 4 which represent a larger and more economical apparatus the same principle is employed the advantages being in the double compartment for salt solution, the comparatively small quantity of mercury needed and the improved method of keeping the mercury in motion. The three compartments shown are the same size the depth of mercury being about one-eighth of an inch. Thus the same weight of mercury is in each compartment and the combined capacity of the three small piston pumps I is made equal at a single stroke to the space occupied by the mercury in each compartment. For example, if the size of a cell requires for a depth of one-eighth of an inch thirty pounds of mercury or ten pounds per compartment then the combined capacity of the three small pumps per stroke is made ten pounds and in reality forty pounds of mercury are used in each complete cell. At each stroke of the three pumps which move very slowly the mercury or amalgam completely changes its position and as the pumps are moving constantly during the electrolysis the mercury is continuously flowing from a compartment in which there is a chloride solution into a compartment in which there is a caustic solution and vice versa. The carbons which are used as anodes slowly disintegrate and may be moved inward as required, new ones being substituted from time to time. The solutions are treated as before mentioned. The strong caustic liquor being evaporated produces pure caustic soda, a product at present unknown in commercial quantities.

The above arrangement of apparatus and parts thereto are described merely to fully illustrate the process and the character of the apparatus necessary to carry out the idea of a moving body of liquid metal as the means of separating the two solutions in an electrolytic cell during electrolysis, completely doing away with a porous diaphragm of any kind heretofore always thought necessary in similar electrical processes.

In discharging the alkali metal in the compartment A' by the action of an electric current passed successively through the alkaline amalgam and an electrolyte capable of oxidizing the alkali metal and dissolving the oxide so formed, it is understood that the alkaline amalgam or alloy is kept in constant motion and this agitation in contact with the solution forming the electrolyte in A' aids to a small degree in depriving the alkaline amalgam or alloy of its alkali metal in the form of a soluble alkaline salt.

In the foregoing when mention of sodium chloride is made it is apparent that potassium chloride could be substituted. It is also apparent that the process and apparatus are adapted to the formation of other salts as well as hydrate according to the treatment in

the final compartment, that instead of chloride of the alkali metals being used, other salts of the alkali metals may be substituted in the first compartment, that hypochlorites may be formed directly therein instead of allowing the chlorine to escape; that in place of carbon anodes any other suitable material capable of resisting the action of chlorine may be substituted and that the same principle may be applied to the electrolysis of fused salts using a molten metal such as lead, tin or the like or an alloy of various metals in place of mercury. It has long been known that sodium amalgam can be made by electrolyzing a solution of the hydrate or chloride using mercury as a cathode. It is also evident that to produce a rich amalgam (say one-half to one per cent.) the mercury must be stirred else a large part of the sodium deposited on the surface of the mercury would be oxidized and return to the solution actually meaning a loss in efficiency.

I am aware that various and special means have been suggested for producing amalgams and then by subsequent and separate treatment to produce caustic and mercury for reuse but such suggestions can only refer to a distinct form of apparatus to carry out a process long known of using mercury as a cathode.

What I claim is—

1. In a process for the electrolytic decomposition of salts of alkali metals, passing an electric current through a solution of the same to a moving body of a liquid metal or alloy which forms part of the electric circuit, forming thereby an alkaline amalgam or alloy and decomposing same by passing an electric current successively through the alkaline amalgam or alloy and an electrolyte capable of oxidizing the alkaline metal and dissolving the oxide so produced.

2. In a continuous process for the electrolytic decomposition of salts of alkali metals, passing an electric current through a solution of the same to a liquid metal or alloy, then transferring the alkaline amalgam or alloy so formed to a point where it acts as an anode and decomposing it while it still forms part of the main electric circuit.

3. In a continuous process for the electrolytic decomposition of salts of alkali metals, passing an electric current through a solution of the same to a liquid metal or alloy, continuously passing the alkaline amalgam or alloy so formed to a point where the alkaline metal is oxidized and removed while the amalgam is acting as an anode for said current and returning the amalgam to the point at which it acts as a cathode for said current.

4. In a process for the electrolytic decomposition of the salts of alkali metals, passing an electric current through a solution of same to a moving body of liquid metal or alloy, in which the alkali metal is deposited, moving the alkaline amalgam or alloy so formed and then separating the alkali metal therefrom

in the form of an alkaline salt or hydrate by causing said alkaline amalgam or alloy while it is in motion to act as an anode for the current in the presence of an electrolyte.

5. In a process for the electrolytic decomposition of the salts of alkali metals, mechanically separating two different electrolytes, one of which contains the salt to be decomposed, electrically connecting said electrolytes by means of a liquid metal or alloy in contact with both, and passing an electric current through the electrolyte containing the salt being decomposed to said liquid metal or alloy, and from the liquid metal or alloy to and through the second electrolyte.

6. In a process for the electrolytic decomposition of the salts of alkali metals, decomposing the alkaline amalgam or alloy, as produced by passing an electric current through a solution of the salt being decomposed, while the amalgam is in the main electrical circuit by causing said amalgam or alloy to act as an anode in the presence of a second electrolyte, whereby the caloric energy stored or contained in the amalgam is set free in the form of electrical energy which is employed in carrying on the process.

7. In a continuous process for the electrolytic decomposition of the salts of alkali metals, mechanically separating two different electrolytes, one of which contains the salt to be decomposed, electrically connecting said electrolytes by means of a liquid metal or alloy in contact with both, and passing a given quantity or volume of electric current through the electrolyte containing the salt being decomposed to said liquid metal or alloy, and passing a lesser quantity or volume of current from said liquid metal or alloy to and through the second electrolyte.

8. In an electrolytic apparatus, the combination of two or more compartments, containing fixed electrodes and second electrodes formed of a liquid metal or alloy, openings between said compartments and mechanical means for causing the said liquid metal or alloy to flow through such openings from the bottom of one compartment to another compartment.

9. In an electrolytic apparatus, the combination of compartments containing fixed electrodes and second electrodes formed of a liquid metal or alloy, and openings between said compartments constantly filled by said liquid metal or alloy, which forms part of the electric circuit and at the same time seals the materials being decomposed in one compartment from mixing with those being produced in another compartment.

In testimony whereof I have hereunto set my hand in the presence of two subscribing witnesses.

HAMILTON YOUNG CASTNER.

Witnesses:

ALLEN PARRY JONES,
WILLIAM TRIMMER.