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ELECTROLYTIC METHOD

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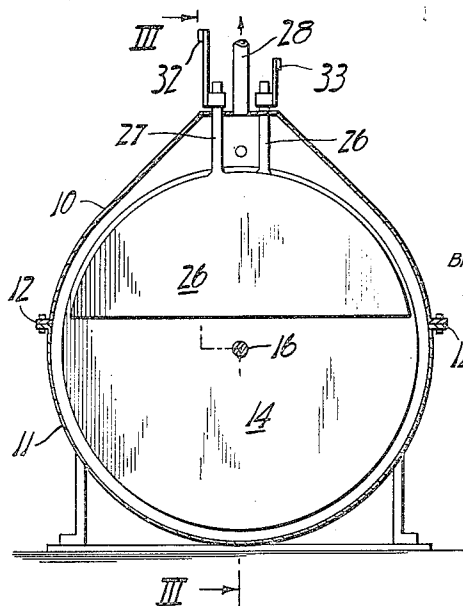


Fig. 2.

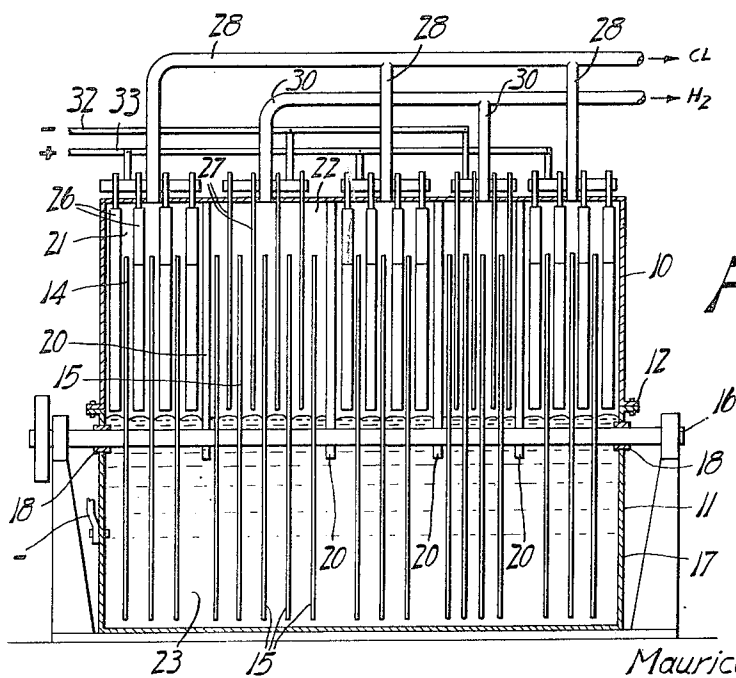
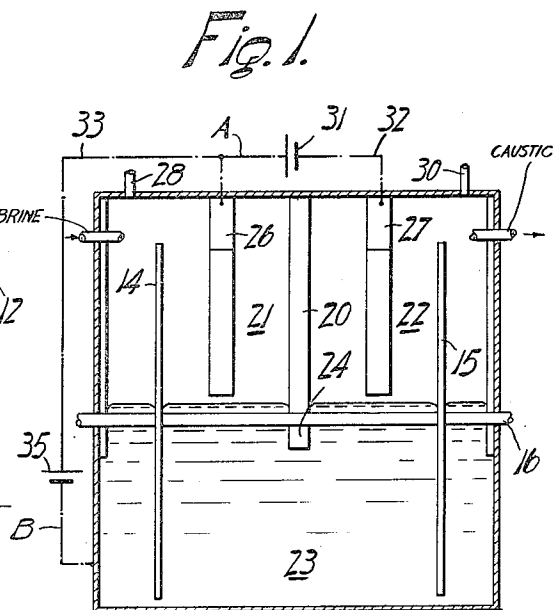


Fig. 3.

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ELECTROLYTIC METHOD

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8 Claims. (Cl. 204—99)

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The present invention relates to electrolytic cells for use in the manufacture of chlorine and alkali metal hydroxides, wherein an alkali metal amalgam provides the alkali metal in the production of the hydroxide. The invention relates more particularly to a cell of this type provided with amalgam anodes inclined with respect to the surface of the amalgam and to the process of preparing alkali metal hydroxides therein.

For nearly a half century, elemental chlorine and caustic soda have been prepared by the electrolysis of brine solutions in an amalgam cell of the rocking type provided with a fluid amalgam cathode which is supplied with sodium by electrolysis, the amalgam being subsequently treated with water, whereby the sodium of the amalgam was changed to sodium hydroxide with the liberation of hydrogen gas. This type of cell is commonly known as a Castner cell, and its operation is commonly known as the Castner process. Various modifications and improvements of this cell have been proposed and reference is made to the United States patents, 2,248,137 of Maurice C. Taylor et al. and 2,336,045 and 2,423,351 of Maurice C. Taylor.

Many of the modifications depended upon mechanical circulation of the amalgam but, in essence, the basic concept of Castner has been followed. This particular basic type of cell possesses an advantage in that caustic soda of high purity can be manufactured therein which is eminently suitable for satisfying the demands of certain chemical industries wherein high purity caustic is a requisite. The caustic soda may be produced of substantially any strength desired, from about 10 per cent to 75 per cent. The end product, requiring no purification, can be shipped as it discharges from the cell or after mere concentration.

More recently, proposals have been made to electrolyze brine solutions in so-called vertical amalgam cells, the amalgam so produced being withdrawn and passed through towers, wherein the amalgam is reacted with water with the production of caustic soda. This particular type of cell has been described in U. S. Department of Commerce Publication P. B. 33,222.

Whereas considerable floor space is required for the installation of an amalgam chlorine cell of the original Castner type, and of its various modifications, this requirement has been considerably reduced in installations employing vertical amalgam cells. However, energy is required for circulation of amalgam and, in both types of installations, overall energy consumption is higher than the diaphragm cells.

It is an object of the present invention to provide an amalgam chlorine cell of the so-called vertical amalgam type provided with vertical amalgam anodes.

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It is also an object of the invention to provide an amalgam-chlorine cell which is compact, which requires a minimum of floor space, and a minimum of forced circulation of amalgam.

It is also an object of the invention to provide a completed cell wherein the inefficiency of the anode compartment may be compensated for.

In the drawings, Fig. 1 is a diagrammatic vertical section through a simplified form of the improved cell illustrating the basic elements thereof; Fig. 2 is a lateral section through the improved cell of the present invention, and Fig. 3 is a section in line III—III of Fig. 2.

Referring more specifically to the drawing, the cell is preferably made in a generally cylindrical outline having an upper removable portion or shell 10 and a lower portion or shell 11, which portions may be attached by suitable flanges 12 and their cooperating assembly gaskets. The cell is preferably made of steel or other engineering material resistant to the chemicals of the cell. When the shells 10 and 11 are fabricated from steel, it should be lined in whole or in part by materials which resist the action of brine and of chlorine as, for instance, rubber or other suitable chlorine resisting lining material. The portion of the lower shell 11 in contact with alkali metal amalgam, need not be lined. Disposed laterally of the cylindrical cell are a series of metal discs 14 and 15 mounted upon shaft 16, which shaft extends through the end wall 17 of the cell by way of a suitable stuffing box 18, which shaft is actuated by any suitable driving mechanism not specifically shown. Between the discs 14 and 15 is positioned an impervious partition 20 which extends from the top of the cell downwardly and terminates above the bottom thereof, thus dividing the upper portion of the cell into separate compartments, the compartment at the left being the "anode" or brine compartment 21, and that shown at the right of partition 20 being the "cathode" or caustic compartment 22. The bottom portion of the cell is filled with amalgam 24 which extends above the lower terminus 24 of partition 20.

A suitable electrode 26 is positioned within the anode compartment 21 and a suitable electrode 27 is positioned within the cathode compartment 22. These electrodes are connected to a suitable source of current 31 through bus bars 32 and 33.

Generally, electrode 26 will be made of graphite, as is conventional in usual amalgam-chlorine cells operating on the Castner principle, and electrode 27 in contact with caustic soda may be of iron. Other metals which do not react rapidly with alkali metal hydroxides may be used as, for instance, Ni, Pt, Ti, Zr, stainless steel or graphite. It is desirable to use metals having a low hydrogen over-voltage for best efficiency.

An improved operating procedure is to provide an iron electrode at 27 electroplated with iron and tungsten. For example, a cathode electroplated with an iron-tungsten alloy containing 50% tungsten and the balance iron, is especially suitable.

In operation, brine, which is approximately saturated, and for purposes of illustration the brine will be considered as sodium chloride, although the invention is applicable to alkali metal chlorides generally, is fed to anode compartment 21, which will contain up to 311 grams of sodium chloride per liter and, in operation, the cell temperature may rise to 80 to 90° C.

In operation, the main electrolyzing current is supplied at a voltage which may vary from about 3.0 volts at 0.07 ampere per sq. cm. to about 3.6 volts at 0.2 ampere per sq. cm. Usually, the operating current density is about 0.2 ampere per square centimeter, depending upon the sodium concentration in the amalgam, and the speed of rotation of discs 14 and 15. In the drawing these discs are shown attached for convenience to a common shaft, although this is not a necessary feature of the invention as they may be rotated separately and independently at variable speeds.

Under the conditions set forth above, chlorine gas is liberated in compartment 21 at electrode 25 and is withdrawn through discharge ducts 28. Sodium is discharged at the amalgam surface coating disc 14 and is absorbed in the amalgam, thereby increasing its sodium content. Under the operating conditions specified, a minimum of hydrogen is liberated in compartment 21 and is generally less than 1 per cent by volume as a contaminant of the chlorine. The amount of sodium in the amalgam may vary from about 0.1% to about 0.5% or higher and may reach about 0.8%.

The operation of compartment 22 is in essence as follows: The compartment being filled with aqueous sodium hydroxide provides hydroxyl ions which, under the influence of the current combine with the sodium of the amalgam to produce sodium hydroxide. Hydrogen gas is liberated at the surface of electrode 27 and withdrawn through duct 30. Rotation of disc 15 within and through amalgam 23 provides a thin film of amalgam upon the disc which film, during rotation of the disc, passes through the aqueous caustic soda of compartment 22 providing sufficient time interval for the depletion of the sodium from the amalgam and formation of caustic soda. The speed of rotation of disc 15 is adjusted to result in an exposure time varying from about 5.0 seconds to about 0.7 second. In this compartment the film of sodium amalgam is exposed to electrolysis under conditions where it acts as an anode.

It is the intention of the invention to provide a continuously renewed film of amalgam acting as an anode, which film is carried by a sheet member angularly disposed to the surface of the amalgam to which the film will adhere and to move the amalgam film acting as an anode, through aqueous caustic at such a rate and to electrolyze at such a current density as to deplete the amalgam of alkali metal to a point such that mercury oxide begins to form only as the carrier member again enters the pool of amalgam.

With a main circuit A connected to the electrodes 26 and 27, and an auxiliary circuit B connected between the amalgam 23 and the electrode in the brine compartment from a separate source of current 35, the amalgam acts as a cathode

in the brine compartment 21 and as anode in the caustic compartment 22.

Thus, by means of the present invention, the amalgam is made to serve as cathode for the alkali metal chloride electrolysis on the brine side of the cell, and as anode for the electrolysis to form the hydroxide on the caustic side of the cell in a very practical and efficient manner. By the provision of the auxiliary circuit B, the operation can be made continuous, as this circuit tends to raise the amount of alkali metal added to the amalgam to an amount relatively equal to that of the removal of alkali metal from the amalgam at the anode surface. To permit the efficiency of the brine compartment to drop below that of the caustic compartment would ultimately result in an undue depletion of the amalgam in alkali metal with consequent formations of mercury oxide at the anodic surface of disc 15 and ultimate failure of the operation.

An alternative method of compensating for the inefficiency accompanying the deposition of sodium in the amalgam is to periodically interrupt the circuit by disconnecting the negative pole of the current supply from the electrode 27 and attach the same to the amalgam lead. By such operation, sodium tends to build up in the amalgam. When the sodium content in the amalgam reaches a value of about 0.4%, the negative lead may be again connected to electrode 27 and electrolysis of the amalgam resumed. When the sodium content in the amalgam is depleted to about a concentration of 0.15% in the amalgam, due to the relative inefficiency of the operation in the brine compartment, the negative lead is again connected to the amalgam, and so on. If the efficiency of deposition of sodium in the brine compartment is 94% and the current is maintained constant, the time for which the negative lead is connected to electrode 27 will be about 15 times as long as the time for which it is connected to the amalgam.

A form of commercial cell is illustrated in Figs. 2 and 3 having multiple electrodes in both the brine compartment 21 and the caustic compartment 22. These compartments are separated by the partition 20 and by the amalgam 23. In the form shown, there are four partitions 20, the anode or brine compartment having four graphite electrodes 26 and three discs 14 adjacent thereto for carrying amalgam therein and receiving metallic sodium liberated at the surfaces thereof. Chlorine discharged at electrodes 26 is withdrawn through conduits or ducts 28. Brine is suitably fed into each brine compartment above the surface of the amalgam by intake ducts and caustic removed through ducts not specifically illustrated.

In the cathode or caustic compartment 22, four tungsten-iron electrodes are illustrated at 27 and five discs at 15 placed adjacent thereto. These discs, when rotated, carry a film of amalgam from the pool of amalgam 23 into the aqueous caustic solution in compartment 22 where, under the influence of the current, the amalgam acts as an anode and metallic sodium of the amalgam is changed to sodium ion in the presence of water, hydroxyl being formed concurrently and hydrogen gas is liberated and is withdrawn separately from the chlorine through ducts or conduits 30.

By employment of the present invention, there is a saving in energy lost in the conventional amalgam cells. The vertical disc, or equivalent arrangement of film acting as anode, makes possible a juxtaposition of electrodes in a practical manner whereby the primary electrolyzing

energy can be applied to the chlorine-producing electrode on the brine side of the cell and to the hydrogen-producing electrode on the caustic side of the cell. The somewhat lower efficiency of the brine electrolysis is made up by applying the additional current to this compartment as shown in circuit B in Fig. 1.

What is claimed is:

1. In the method of producing chlorine and alkali metal hydroxide by electrolyzing an aqueous solution of alkali metal chloride in contact with a continuous body of mercury to produce alkali metal amalgam, the improvement which comprises exposing the amalgam as an anode to the action of water to produce alkali metal hydroxide and hydrogen, the amalgam being so exposed in a continually renewable film angularly inclined to the surface of the main body of amalgam, and connecting the cathode lead of an auxiliary electrical circuit to said continuous body of mercury, and the anode lead of said circuit to the electrode in the alkali metal chloride compartment at which chlorine is discharged to raise the amount of alkali metal introduced into the mercury and increase the production of alkali metal amalgam.

2. Method in accordance with claim 1 wherein the alkali metal is sodium.

3. Method in accordance with claim 1 wherein the alkali metal content in the main pool of amalgam is maintained in the limits 0.1% and 0.8%.

4. Method in accordance with claim 1 wherein the chlorine and hydrogen are separately collected.

5. In the method of producing chlorine and sodium hydroxide by electrolyzing an aqueous solution of sodium chloride in contact with a continuous body of mercury to produce sodium amalgam containing from 0.1% to 0.5% sodium, the improvement which comprises exposing the amalgam as an anode and carried upon a sheet member inclined angularly to the surface of the main body of amalgam to the action of water in an aqueous caustic soda solution to produce hydrogen and additional caustic soda, and connecting the cathode lead of an auxiliary electrical circuit to said continuous body of mercury, and the anode lead of said circuit to the electrode in the alkali metal chloride compartment at which chlorine is discharged to raise the amount of sodium introduced into the mercury in that compartment of the cell to equal the amount being electrolyzed into the caustic soda solution.

6. In the method of producing chlorine and sodium hydroxide by electrolyzing an aqueous solution of sodium chloride in contact with a continuous body of mercury to produce sodium amalgam containing from 0.1% to 0.5% sodium, the improvement which comprises exposing the amalgam as an anode and carried upon a sheet member inclined angularly to the surface of the main body of the amalgam to the action of water in an aqueous caustic soda solution to produce hydrogen and additional caustic soda, connecting the cathode lead of an alternative electrical circuit to said continuous body of mercury, and the anode lead of said circuit to the electrode in the alkali metal chloride compartment at which chlorine is discharged to raise the amount of sodium introduced into the mercury in that compartment of the cell to equal the amount being electrolyzed into the caustic soda solution, and

intermittently disconnecting the cathode lead of the principal electrical circuit from the electrode in the caustic soda compartment, and connecting said cathode lead to the mercury body.

7. In the method of producing chlorine and sodium hydroxide by electrolyzing an aqueous solution of sodium chloride in contact with a continuous body of mercury to produce sodium amalgam containing from 0.1% to 0.5% sodium, the improvement which comprises exposing the amalgam as an anode and carried upon a sheet member inclined angularly to the surface of the main body of the amalgam to the action of water in an aqueous caustic soda solution to produce hydrogen and additional caustic soda, connecting the cathode lead of an auxiliary electrical circuit to said continuous body of mercury, and the anode lead of said circuit to the electrode in the alkali metal chloride compartment at which chlorine is discharged to raise the amount of sodium introduced into the mercury in that compartment of the cell to equal the amount being electrolyzed into the caustic soda solution, and intermittently disconnecting the cathode lead of the principal electrical circuit from the electrode in the caustic soda compartment, and connecting said cathode lead to the mercury body and maintaining the latter connection until the sodium content of the amalgam approaches 0.5%.

8. A cell for producing chlorine and caustic soda comprising two compartments separated from each other by an impervious partition extending from one side towards the opposite side thereof, a continuous body of amalgam in said cell cooperating with said partition to complete the seal between said compartments, an aqueous alkali metal chloride maintained in one compartment and an aqueous alkali metal hydroxide maintained in the other compartment out of contact with each other, an electrode in each compartment electrically connected to a source of direct current to form a cell, and a mechanically actuated means for exposing said amalgam in a thin film as an anode to the action of said aqueous alkali metal hydroxide whereby the alkali metal therein is changed to alkali metal hydroxide which is retained in the hydroxide already present in the cell, the mercury being returned to the amalgam, said means being disposed angularly to the surface of the main pool of amalgam, and an auxiliary electric circuit having its cathode lead connected to said continuous body of amalgam and having its anode lead connected to the electrode in the alkali metal chloride compartment at which chlorine is discharged to raise the amount of alkali metal introduced into the amalgam in that compartment.

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