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ELECTROLYTIC ALKALI-CHLORINE DIAPHRAGM CELL

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FIG. 1

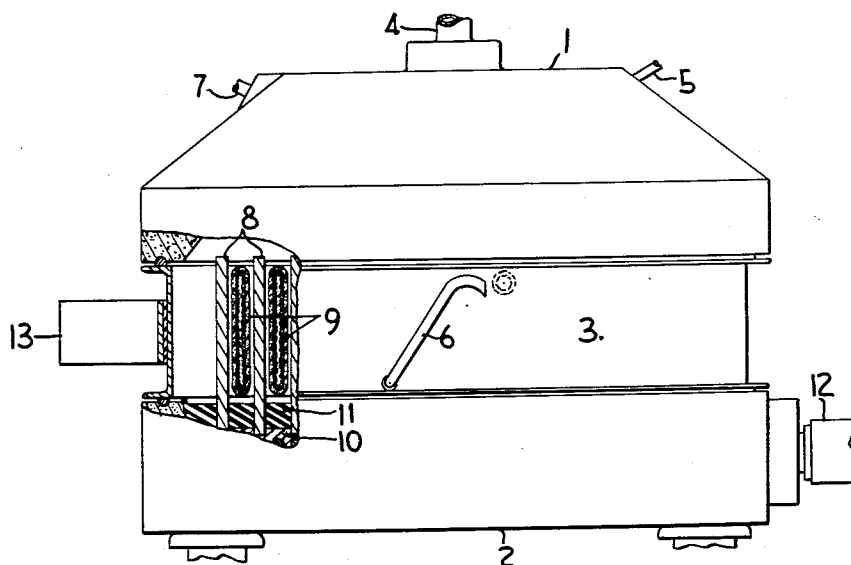
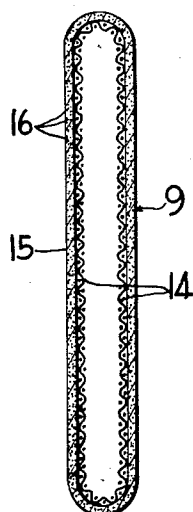


FIG. 2



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ELECTROLYTIC ALKALI-CHLORINE DIAPHRAGM CELL

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2 Claims. (Cl. 204-266)

This invention relates to a novel type of electrolytic cell such as suitable for production of alkali metal hydroxide and elemental chlorine, and also to the diaphragms used in such cells. It is known that chlorine and aqueous alkali metal hydroxide can be produced readily by electrolysis of alkali metal chloride brine in a diaphragm type cell. Such a cell consists essentially of a cell enclosure and an anode of chlorine-resistant electroconductive material, such as carbon, platinum or platinum coated titanium or the like, and a foraminous cathode, usually made of iron, within the enclosure. The anode and cathode are separated by means of a porous diaphragm of asbestos or like material, thus providing an anode compartment and a cathode compartment.

In the normal construction of such cells, the diaphragm is in direct contact with the cathode. Frequently, the diaphragm is deposited on the cathode by placing the cathode in an aqueous slurry of asbestos and causing the slurry to flow through the pores or mesh openings of the cathode until a porous sheet or layer of asbestos has been deposited upon the side of the cathode which in use is opposite the anode.

In operation of such a cell, the cell is filled with brine and an electrical potential is established between the anode and cathode. Chlorine is evolved at the anode and is withdrawn from the cell at a point above the liquid level in the anode compartment. Brine is fed into the anode compartment at a substantially continuous rate and the electrolyte flows through the pores of the diaphragm and through the cathode. In the course of this flow, alkali metal hydroxide is produced and hydrogen liberated at the cathode. The hydrogen is withdrawn from the cathode compartment which is behind the cathode at a point above the liquor level therein and aqueous alkali metal hydroxide is withdrawn from the cathode compartment at a lower level.

Typical electrolytic cells of this type which have found extensive commercial use are described in United States Letters Patent Nos. 1,862,245, granted June 7, 1932, and 1,866,065, granted July 5, 1932.

Cells typical of the type mentioned above are shown in the accompanying drawing in which:

FIGURE 1 is a side view of an alkali-metal-chlorine electrolytic diaphragm cell partially broken away and in section to show the anodes and cathode therein.

FIGURE 2 is an enlarged view of one of the cathode fingers of such a cell showing the asbestos diaphragm in place and impregnated with carbon particles according to the teachings of this invention.

In FIGURE 1 is shown an alkali-metal-chlorine electrolytic diaphragm cell having a top 1, a bottom 2, and intermediate cathode carrying section 3. Located at the top of the cell is a chlorine outlet 4 and a brine inlet 5. The cell is provided with a caustic outlet 6 and a hydrogen outlet 7, both of which are in communication with the interior of the cathode. As can be seen in the drawing, specifically FIGURE 1, the cell is provided with anode blades 8 and the cathode of the cell is divided into a plurality of cathode fingers 9. The anode blades are embedded in a lead base 10 which is covered with a mastic 11. Current is introduced into the cell through the negative bus bar 13. The conduction of current through the cell is accomplished by introducing the current through

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the bus bar 12 into the lead base 10 through the anode blades 8 through the cathode fingers 9 and out of the cell through the negative bus bar 13.

Turning now to FIGURE 2, there is shown an enlarged cross-sectional view of a cathode finger which shows the wire mesh screen 14 and the asbestos diaphragm 15 deposited thereon. Located in the asbestos diaphragm are carbon particles 16.

According to this invention it has been found that electrolytic cells of this character may be operated at lower voltage by use of an asbestos diaphragm in which elemental carbon particles are dispersed more or less uniformly. Such reduction in voltage is quite important since it affords a reduction in the amount of energy required per ton of chlorine and/or alkali metal hydroxide produced.

The amount of carbon dispersed in the diaphragm is capable of rather wide range of variation from about 1 to about 60 percent by weight based upon the dry weight of asbestos therein. The carbon should be pulverulent, usually being below about 60 mesh in particle size. Carbon black of the type used for rubber fillers or reinforcing pigments, powdered graphite, and powdered carbon useful for filter aids or adsorbents, may be used for this purpose. The exact amount to be used depends upon the particle size of the carbon, the size of the asbestos fibers, and the degree of tightness that the fibers are interlaced. Thus, the diaphragm itself should be porous and permit ready flow of brine therethrough under a head of about 4 to 30 inches of saturated NaCl brine. If too much carbon is incorporated, the asbestos remaining is insufficient to provide the fibers necessary for a coherent sheet, and the diaphragm will gradually disintegrate in use. If too low in concentration, the carbon does not exert a noticeable effect upon the diaphragm and the cell. Usually, the elemental carbon content of the diaphragm is 1 to 40 percent by weight of the diaphragm, including the carbon.

The diaphragm herein contemplated may be prepared readily by forming a fluid aqueous slurry of asbestos and elemental carbon particles, immersing the cathode in such a slurry, and flowing the slurry through the pores or meshes of the cathode to deposit a carbon-containing asbestos sheet on the cathode in a manner similar to that normally used for depositing diaphragms on cathodes of alkali-chlorine cells. The diaphragms thus deposited are about $\frac{1}{16}$ to $\frac{3}{16}$ inch in thickness.

Alternatively, asbestos paper may be impregnated with an aqueous slurry of carbon particles and the carbon therein thus occluded or otherwise entrapped in the pores of the paper.

The carbon-containing diaphragm herein contemplated may be used in connection with a wide variety of electrolytic cells, including those disclosed in the above mentioned patents as well as those described in the following United States Letters Patent: 2,282,058, 2,409,912, 2,666,028, 2,681,884, 2,681,887, 2,742,420, 2,858,263, and 2,860,100.

The following examples are illustrative:

Example I

A laboratory electrolytic cell was used in these tests. The cathode was in the form of a vertical cylinder about $1\frac{1}{8}$ inches in diameter and was made of heavy iron screen. Anode rods depended downwardly from the cell cover and were disposed around the cathode, the space between the anode rods and the cathode being about $\frac{1}{2}$ inch.

A diaphragm was depended on the outside face of the cathode by forming an aqueous slurry of asbestos and a pulverulent carbon which is normally used as a filter aid and has a particle size such that about 70 percent

of this material has a particle size between 325 mesh and 150 mesh. This slurry contained about 1.6 percent by weight of asbestos (being a mixture of 2 parts by weight of short fibers, Quebec Asbestos Producers Association, Grade 4T, and 1 part by weight of long fibers, Quebec Asbestos Producers Association, Grade 3R) and 0.3 percent by weight of the carbon. The cathode was immersed in the slurry and the asbestos diaphragm deposited on the outside cathode surface by drawing the slurry through the cathode, ultimately establishing a pressure drop between the inside and the outside of the cathode of 28 inches of mercury.

The cell was then assembled and aqueous sodium chloride brine containing an average of 312 grams of NaCl per liter was fed into the anolyte compartment of the cell at a constant rate, evolved chlorine and hydrogen and sodium hydroxide solution being withdrawn in the conventional manner. The cell was operated at 185° F., with a pressure drop between the anolyte and catholyte of 11 inches of water, continuously for 19 days with an average current efficiency of 95.5 percent. The average pH of the anolyte was about 4.2 and the average voltage across the cell was 3.336 volts. The concentration of sodium hydroxide in the solution which was produced was 121 grams of NaOH per liter of solution.

In a control experiment using no carbon in the asbestos, the average voltage was 3.609 volts, the other conditions being substantially the same as those stated above in this example.

Example II

In this test the cells used were constructed substantially as disclosed in United States Letters Patent No. 2,409,912, granted October 22, 1946. The diaphragms were deposited using a slurry containing 1.6 percent by weight of asbestos and 0.35 percent by weight of the carbon described in Example I, and the cells were assembled and operated over a two-month period while feeding brine

containing on the average 322 grams of NaCl per liter of solution. The average voltage on these cells was 3.46 volts, about 0.1 volt lower than that required with the normal asbestos diaphragm.

Although the present invention has been described with reference to the specific details of certain embodiments thereof, it is not intended that such details shall limit the scope of the invention.

What is claimed:

1. In an electrolytic alkali chlorine cell having an anode, a foraminous cathode, a porous asbestos diaphragm in the form of a porous sheet on the cathode and between the anode and the cathode, thus providing an anode compartment between the anode and the diaphragm, means for feeding brine into the anode compartment, means for withdrawing evolved chlorine from the anode compartment, and means behind the foraminous cathode for withdrawing evolved hydrogen and alkali metal hydroxide, the improvement wherein the diaphragm has discrete carbon particles disposed within the asbestos diaphragm sheet said sheet having been formed by depositing the diaphragm on the cathode from an aqueous slurry of asbestos containing 1 to 60 percent carbon dispersed therein basis the dry weight of asbestos.

2. The apparatus of claim 1 in which the carbon particles are below 16 mesh in size and the diaphragm is between $\frac{1}{16}$ to $\frac{3}{16}$ inch in thickness.

References Cited in the file of this patent

UNITED STATES PATENTS

1,378,599	Michel	May 17, 1921
1,982,224	Michel	Nov. 27, 1934

FOREIGN PATENTS

16,437	Great Britain	Dec. 13, 1884
121,242	Austria	Feb. 10, 1931