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R. G. COTTAM ETAL

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ELECTROLYTIC PROCESS FOR PRODUCTION OF CHLORINE AND CAUSTIC

Filed July 11, 1961

2 Sheets-Sheet 1

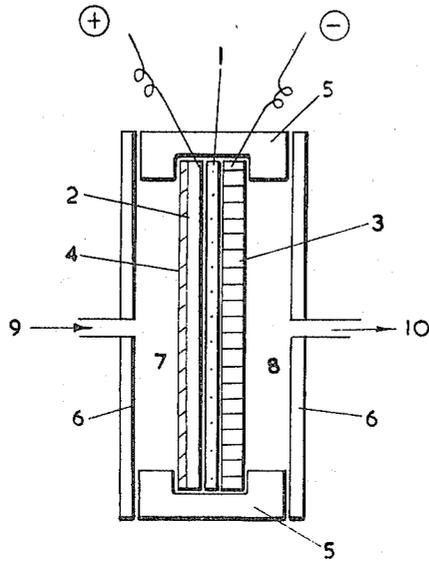


FIG. 1

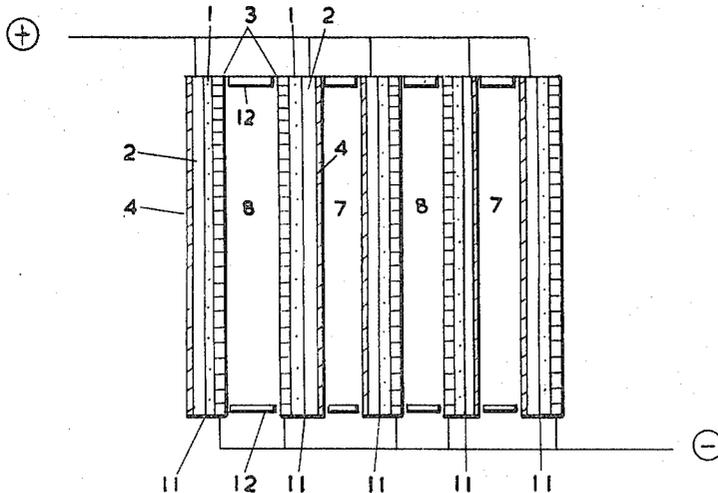


FIG. 2

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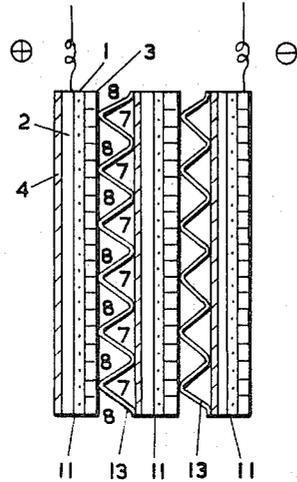


FIG. 3

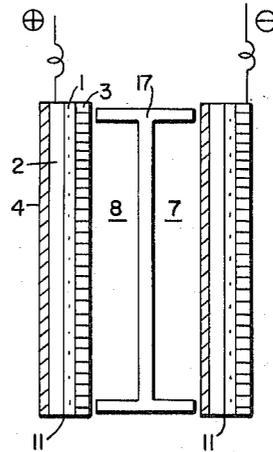


FIG. 5

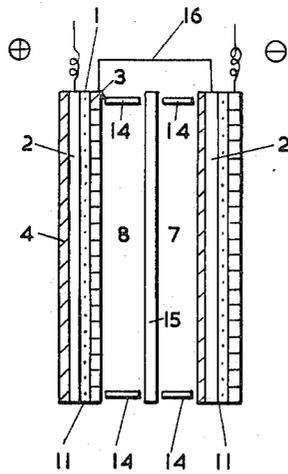


FIG. 4

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ELECTROLYTIC PROCESS FOR PRODUCTION OF CHLORINE AND CAUSTIC

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Claims priority, application Great Britain, July 11, 1960, 24,082/60

7 Claims. (Cl. 204-98)

The present invention relates to improvements in or relating to electrolytic cells and particularly electrolytic cells for the manufacture of chlorine and caustic alkali from aqueous solutions of an alkali metal chloride. Yet more particularly it relates to cells for the manufacture of chlorine and caustic alkali in which a porous diaphragm separates the anodes and cathodes of each unit cell.

Cells of the diaphragm type are widely used for the production of chlorine and caustic alkali by the electrolysis of alkali metal chloride solution. In such cells the anodes, usually of graphite, and the cathodes, usually of iron or steel, are fixed and are spaced apart in the alkali metal chloride electrolyte. As current is passed through the electrolyte between anode and cathode, chlorine is evolved at the anode and alkali metal ions are discharged at the cathode and react at the cathode face with water from the electrolyte to form caustic alkali and liberate hydrogen. A porous diaphragm is placed in the anode-cathode gap in order to prevent as far as possible mixing of the hydrogen and chlorine and mixing of the caustic alkali with the incoming brine, which is fed to the anode side of the diaphragm. In operating cells of this type every effort is made to keep the anode-cathode gap small, since the resistance of the electrolyte in the gap to the passage of the electrolysis current raises significantly the operating voltage of the cell and consequently the energy consumption. In all known types of diaphragm cell, however, the anode-cathode gap cannot be reduced below a certain minimum distance; an average figure for the minimum gap in a commercial installation for example is approximately 1/2 inch. The diaphragm is commonly constructed of asbestos and is unsupported at least on the anode side, and if the gap between the anode and diaphragm is made too small the diaphragm tends to be disintegrated by the turbulence caused by the chlorine evolved from the anode; furthermore, mixing of the anode and cathode products can then also reach troublesome proportions. If the anode-cathode gap could be reduced, considerable savings in energy consumption would result.

We have now found surprisingly that in a diaphragm cell for the production of chlorine and caustic alkali the anode-cathode gap can be eliminated except for the thickness of the diaphragm itself and a thin anode-supporting member when a noble metal of the platinum group, namely platinum, rhodium or iridium, or an alloy consisting essentially of one or more of these metals (such metals and alloys being hereinafter called generically a "platinum metal") is employed as the working anode surface. In selecting alloys consisting essentially of one or more of the metals platinum, rhodium and iridium we do not exclude alloys which contain a small proportion of other

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metals, for instance the remaining metals of the platinum group.

According to the present invention, a cell for the manufacture of chlorine and caustic alkali by the electrolysis of alkali metal chloride solution consists essentially of a non-conducting porous diaphragm held between and in contact with a foraminated sheet metal cathode and a foraminated sheet titanium anode support, and an anode which is a coating of a platinum metal as hereinbefore defined on the said anode support. In order to economise on the use of expensive platinum metal, the anode coating is most suitably applied only to those surfaces of the anode support which are not in contact with the diaphragm.

The term "foraminated sheet" is intended to mean a perforate or reticulate sheet such as a multi-holed or perforated sheet, a gauze, or a sheet of expanded metal which, if desired, may be flattened. The term "titanium" includes a titanium alloy consisting essentially of titanium.

In an electrolytic cell according to the present invention the diaphragm is no longer unsupported even on the anode side, so that the effect of turbulence in the electrolyte owing to evolution of chlorine from the anode placed close to the diaphragm in causing mechanical damage to the diaphragm is minimised. Although both the foraminated titanium anode support and the foraminated cathode are in contact with the diaphragm, we have found surprisingly that very little mixing of anode and cathode products takes place through the diaphragm. Furthermore, since the anode and cathode are separated only by a distance approximately equal to the aggregate thickness of the diaphragm and the foraminated titanium anode support, and since the diaphragm and anode support can be quite thin, the resistance of the electrolyte to the passage of the electrolysis current between anode and cathode is very much lower than in conventional diaphragm cells. We have in fact found that a cell according to the invention can be operated at a current density three times greater than conventional diaphragm cells for the same cell voltage. The electrolytic cell of the present invention thus provides a very compact installation for the manufacture of chlorine and caustic alkali at high energy efficiency.

In an electrolytic cell according to the invention the diaphragm may be constructed from a non-conducting porous material which is substantially inert to the electrolyte and the products of electrolysis, for example asbestos or an ion exchange resin. The preferred material is asbestos; for example one or more layers of asbestos paper or asbestos fabric may be employed or a diaphragm may be formed by depositing asbestos fibres from a slurry on to one side of the foraminated metal cathode material before assembling the cell. The cathode may consist of one or more layers of foraminated iron, steel or titanium sheet or it may be a coating of a platinum metal as hereinbefore defined on a foraminated sheet titanium metal support. In order to economise on the use of expensive platinum metal the cathode coating, when used, is most suitably applied only to those surfaces of the titanium sheet which are not in contact with the diaphragm.

The platinum metal anode material, and the platinum metal cathode coating if used, may be applied to the sup-

porting titanium metal in any known manner. For example a layer of platinum metal may be electrolytically deposited on the titanium surface or the platinum metal may be deposited by metal spraying or by painting the titanium structure with a conventional metallising solution and subsequently heating in the manner practised in the ceramic industry. It is preferred to deposit the anode coating of a platinum metal on the titanium by the painting and heating technique, since coatings produced in this manner have a low overvoltage for chlorine evolution. With certain methods of deposition a part of the titanium surface which will be in contact with the cell diaphragm may unavoidably receive a coating of the platinum metal. This is not objectionable but such deposit appears to serve no useful purpose and for reasons of economy we prefer to avoid it as far as possible.

An electrolytic cell according to the present invention may be operated as a unit cell or may be combined in various ways in a multi-cell arrangement. The construction of the unit cell and some useful multi-cell arrangements will be discussed with reference to the drawings accompanying the provisional specification, which are schematic representations not to scale. FIG. 1 shows schematically a horizontal section through a unit cell according to one embodiment of the invention. 1 is a diaphragm $\frac{1}{16}$ inch thick of asbestos fibres held between anode support 2, which is a sheet of expanded titanium metal, and cathode 3, which suitably may consist of a layer of steel gauze backed by a number of layers of expanded sheet steel, the gauze layer being in contact with the diaphragm. 4 is the anode, which is a coating of a platinum metal suitably carried on those surfaces of anode support 2 which are not in contact with diaphragm 1. The whole electrode and diaphragm assembly is held in carriers of resilient material 5, which together with side members 6 and the base and cover of the cell (not shown) enclose anode compartment 7 and cathode compartment 8. Clamping means (not shown) applied to side members 6 maintain pressure on resilient carriers 5 so that anode support 2 and cathode 3 are in close contact with diaphragm 1 and leakage of electrolyte and product gases between anode compartment 7 and cathode compartment 8 around the edges of the electrode and diaphragm assembly are prevented. In operation, alkali metal chloride solution is fed continuously as shown at 9 to anode compartment 7 under sufficient pressure to maintain anode compartment 7 full of electrolyte and to cause percolation of electrolyte through the electrode assembly and diaphragm into cathode compartment 8. Causticised electrolyte is withdrawn continuously from cathode compartment 8 as shown at 10. Current of the polarity shown is supplied to the cell through anode support 2 and cathode 3. Exits (not shown) are also provided in or near the top of the cell for the removal of chlorine and hydrogen gas from anode compartment 7 and cathode compartment 8, respectively. Causticised electrolyte may be allowed to drain freely from cathode compartment 8 or this compartment may be maintained full of electrolyte. We prefer to operate with a filled cathode compartment as this ensures the same pressure of electrolyte on all areas of the diaphragm and an even electrolyte percolation rate over the whole area.

FIG. 2 shows how any number of unit cells may be combined for feeding in parallel with electric current. 5 unit cells 11 are illustrated in FIG. 2 and it will be seen that these are arranged so that neighbouring pairs have cathodes and anode alternately facing so that cathode and anode compartments are formed alternately between pairs of cells, the neighbouring cells being spaced apart from each other by insulating spacers 12. 1, 2, 3 and 4 are diaphragms, anode supports, cathodes, and anodes, and 7 and 8 are anode and cathode compartments respectively, as in FIG. 1. Current of the polarity shown is fed to anode supports 2 and cathodes 3.

FIGS. 3, 4 and 5 show various ways in which unit cells according to the invention may be combined in a bipolar series arrangement. FIG. 3 shows three unit cells 11, in each of which the component parts 1, 2, 3 and 4 are as in FIG. 1. Neighbouring cells are spaced apart by corrugated titanium sheets 13, which also act as current connections between the cells and provide anode compartments 7 and cathode compartments 8 on opposite sides of each corrugated sheet. FIG. 4 shows a combination of two unit cells 11 spaced apart from each other by insulating spacers 14 and separator 15 to provide anode compartment 7 and cathode compartment 8. Separator 15 may be an insulating material such as concrete or very suitably it may be a sheet of titanium metal. 16 is the current connection from the anode support 2 of one unit cell to the cathode 3 of the next unit cell. The arrangement of FIG. 5 is similar to that of FIG. 4 but has the advantage that the need for the external current connection 16 of FIG. 4 has been eliminated by replacing spacers 14 and separator 15 of FIG. 4 by the combined member 17 which is constructed of titanium so that titanium member 17 now acts as spacer, separator and current connection between the two unit cells 11 shown. It will be understood that any number of unit cells 11 may be combined in a bipolar arrangement in the manner of FIGS. 3, 4 or 5.

By way of further illustrating the usefulness of the invention the following table illustrates the high current loading and high energy efficiency achievable when operating a unit cell according to the invention for the electrolysis of sodium chloride solution.

Cell voltage (average) -----	3.85 volts.
Anode current density -----	4 ka./m ² .
Sodium chloride feed concentration -----	305 g./l. NaCl (approx.).
Catholyte concentration (average) -----	141.1 g./l. NaOH.
Chlorine current efficiency --	95.5%.
Chlorine gas analysis ---	{ Cl ₂ --- 98.4%.
	{ O ₂ --- 1.6%.
Energy consumption per ton of chlorine -----	3,096 kwh.

The electrode and diaphragm assembly of this unit cell was constructed in the following manner—

Anode support: 20-gauge titanium metal sheet expanded to 62 mesh per foot, and then flattened to 58 mesh per foot.

Anode: Platinum metal applied by painting on those surfaces of the expanded titanium metal anode support which are not in contact with the diaphragm to give a deposit of 47.4 g. of platinum metal per m².

Cathode: One sheet of 25-gauge steel wire gauze with 24 mesh per inch, in contact with the diaphragm, backed by 5 sheets of 20-gauge steel expanded to 7 mesh per inch.

Diaphragm: Asbestos fibre layer $\frac{1}{16}$ inch thick deposited on the cathode gauze layer under vacuum from a slurry of asbestos fibre in causticised cell liquor.

What we claim is:

1. A process for the manufacture of chlorine and caustic which comprises passing an alkali metal chloride solution into an electrolytic cell from the anode side, electrolyzing said alkali metal chloride solution in said cell, withdrawing caustic solution from the cathode side of said cell and withdrawing chlorine from the anode side of said cell, said cell comprising a non-conducting porous diaphragm held between and in contact with a foraminous sheet metal cathode and a foraminous sheet titanium anode support, and an anode which is a coating of a platinum metal on said anode support.

2. A process according to claim 1 wherein the cathode comprises a coating of a platinum metal on a titanium support.

3. A process according to claim 2 wherein the platinum

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metal cathode is coated on those surfaces of the titanium support which are not in contact with the diaphragm.

4. A process according to claim 1 wherein said platinum metal anode is coated on those surfaces of the titanium anode support which are not in contact with the diaphragm. 5

5. A process according to claim 1 wherein the diaphragm comprises asbestos.

6. A process according to claim 1 wherein the cathode comprises a member of the group consisting of iron and steel. 10

7. A process according to claim 1 wherein the cathode comprises titanium.

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