Nov. 23, 1965 **J. H. COLLINS ET AL** **3,219,563**

MULTI-ELECTROLYTIC CELL COMPRISING A PLURALITY OF DIAPHRAGM-FREE UNIT CELLS AND THE USE OF SAME FOR PREPARING ALKALI METAL CHLORATES

Filed June 2, 1961 2 Sheets-Sheet 1

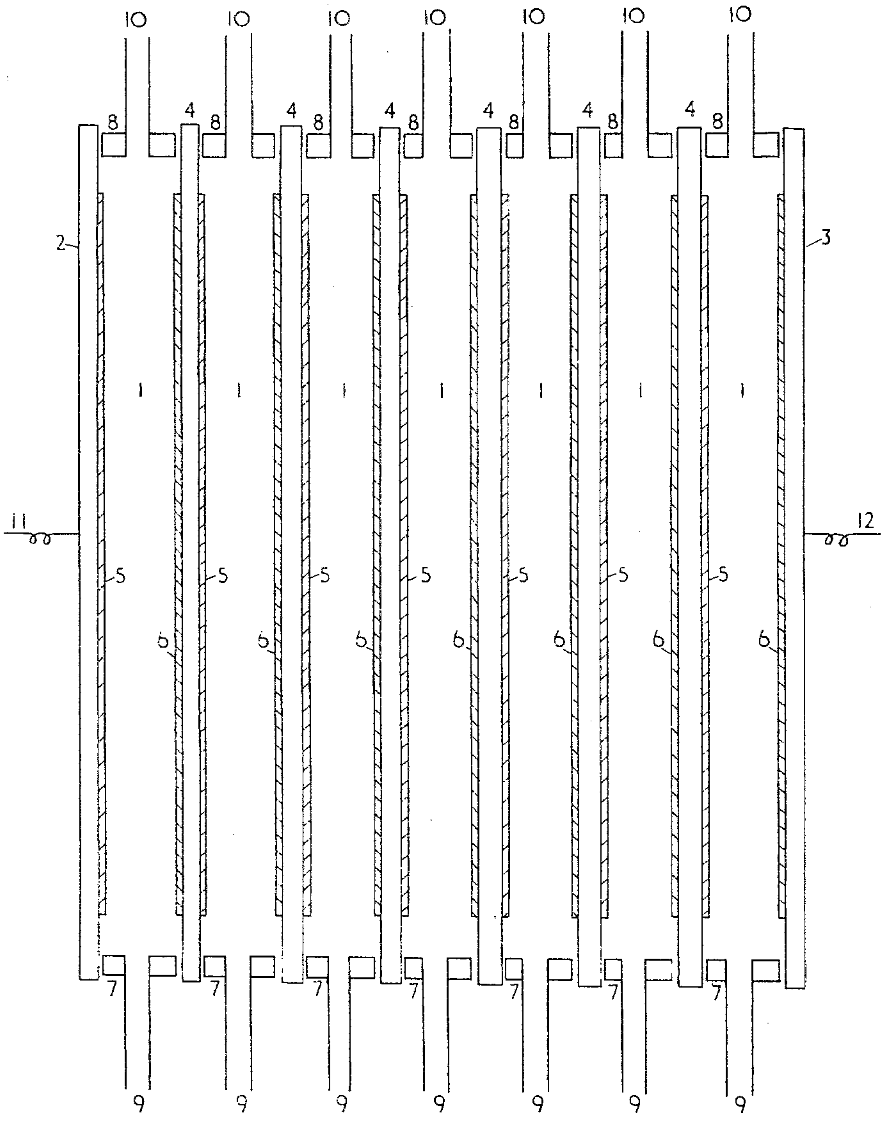

FIG. 1

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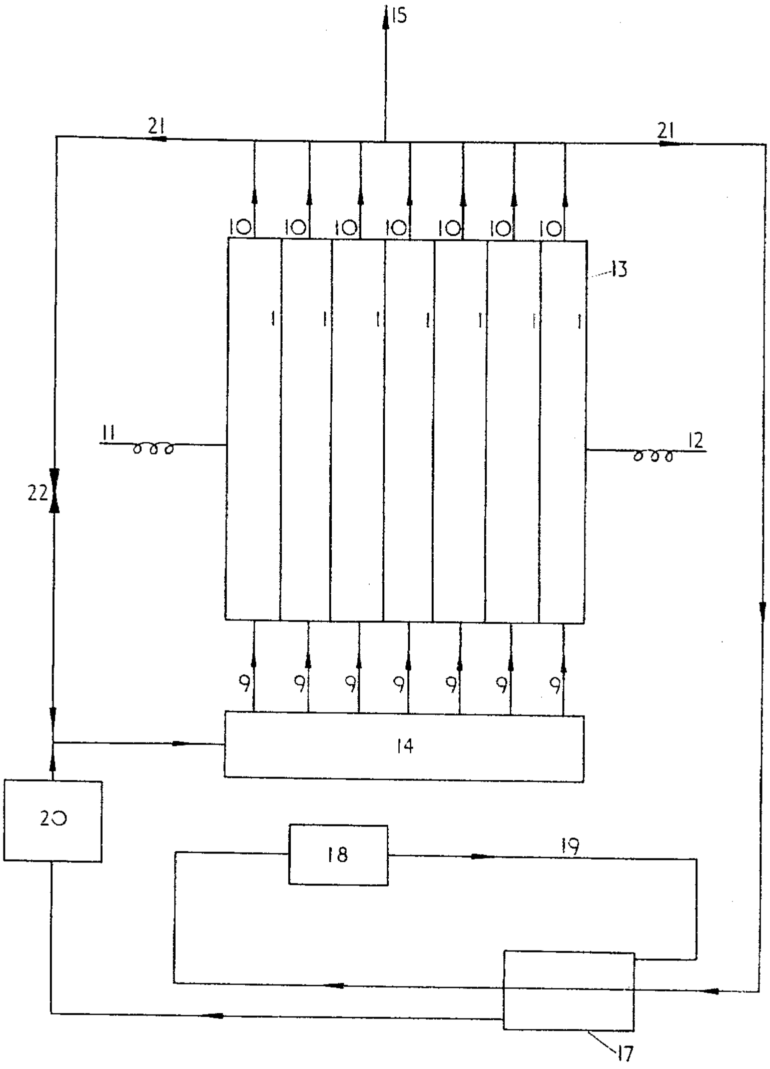

FIG. 2

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3,219,563
Patented Nov. 23, 1965

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MULTI-ELECTROLYTIC CELL COMPRISING A PLURALITY OF DIAPHRAGM-FREE UNIT CELLS AND THE USE OF SAME FOR PREPARING ALKALI METAL CHLORATES

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Filed June 2, 1961, Ser. No. 114,354
Claims priority, application Great Britain, June 22, 1960, 21,851/60
12 Claims. (Cl. 204—95)

This application is a continuation-in-part of Serial No. 796,856, filed March 3, 1959.

The present invention relates to improvements in or relating to multi-electrolytic cells. More particularly it relates to multi-electrolytic cells, comprising a plurality of unit electrolytic cells, for the manufacture of alkali metal chlorates from aqueous solutions of alkali metal chlorides.

It is known to produce chlorates of alkali metals by electrolysis of alkali metal chloride solutions in single unit cells in which the anodes are of graphite, the cathode is of iron or steel and there is no diaphragm between the anodes and the cathodes. Blocks of magnetite and sheets of platinum have also been employed as anode materials but because the maximum current density possible with magnetite is low and because of the prohibitively high capital cost of platinum sheet anodes, graphite anodes are almost universally employed. The use of graphite anodes, however, imposes heavy costs upon the process because of the high rate of anode wear. The pH of the electrolyte in cells producing chlorates is relatively high so that oxidation of the graphite by discharge of hydroxyl ions is severe. High rates of wear lead not only to heavy replacement costs for anodes but also to progressively increasing cell voltage, because of the increasing anode-cathode gap, and thus to excessive energy consumption. Furthermore, the maximum anode current density achievable with an acceptable rate of anode wear is limited to about 1.5 kA/m.^{2} even when steps are taken to cool the cell and when cooling is not resorted to the anode current density may be as low as 0.2–0.5 kA/m.^{2}.

In British application Serial No. 845,043 there is described and claimed a multielectrolytic cell adaptable for the production of chlorine, a hypochlorite or a chlorate from aqueous solutions of an alkali metal chloride and comprising a plurality of unit electrolytic cells and wherein an inert partition separates the anode of one unit electrolytic cell from the cathode of an adjacent unit electrolytic cell, characterised in that the inert partition is an electroconducting chemically inert partition of titanium metal sheet. It is also stated in the said British application that in each unit cell of the multielectrolytic cell the anode may be, inter alia, a layer of a platinum metal, namely ruthenium, rhodium, palladium, osmium, iridium or platinum, or an alloy of two or more of such metals, which is on one side of each titanium metal sheet partition.

We have now found that when a multielectrolytic cell comprising a plurality of unit electrolytic cells as claimed in British application Serial No. 845,043 and in which there is no diaphragm between each pair of anodes and cathodes is employed for the production of an alkali metal chlorate by electrolysis of aqueous solutions of an alkali metal chloride, a surprisingly high current density can be used economically when the anode in each unit electrolytic cell is a layer of a platinum metal on one side of the titanium metal sheet. This is especially so when the cathode in each unit electrolytic cell of the multielectrolytic cell is bare titanium as described in British application Serial No. 845,043 or is a layer of a platinum metal or of iron or of steel on the face of the next titanium metal sheet opposed to the anode. It is preferred, however, that the cathode should comprise a layer of a platinum metal, which may be applied to the titanium metal sheet by any of the methods disclosed in the aforementioned British application, since we have found that a platinum metal cathode layer minimises the cell voltage needed and does not suffer from the corrosion found with iron and steel cathode layers when the cell is taken off load. It is also preferred that the anode layer of the platinum metal in each unit cell should be electrolytically deposited on the titanium surface since such an electrolytically deposited layer of the platinum metal provides the lowest and most stable cell voltage. We have furthermore found that when alkali metal chlorate is produced in multielectrolytic cells of the type herein described the gap between anode and cathode may advantageously be made very narrow, suitably about 3 mm., thus further assisting in the reduction of cell voltage.

We have found that when alkali metal chlorate is produced by electrolysis of alkali metal chloride solution according to the present invention a current density approximately 3–14 times greater than in prior art chlorate cells fitted with graphite, magnetite or platinum anodes may be employed at high energy efficiency. For example in a multielectrolytic cell working according to the present invention at a current density of approximately 3.5 kA/m.^{2} the energy consumption is at least as low as in the prior art low-current-density chlorate cells.

According to the present invention therefore, there is provided a modification of that form of the multielectrolytic cell claimed in British application Serial No. 845,043 in which there is no diaphragm between anode and cathode in each unit cell, especially useful for the production of an alkali metal chlorate from aqueous solutions of an alkali metal chloride, wherein the anode in each unit electrolytic cell is a layer of a platinum metal on one side of the titanium metal sheet partition and the cathode is a layer of a platinum metal or of iron or of steel on the face of the next titanium metal sheet partition opposed to the anode.

Further, there is provided a process for the manufacture of an alkali metal chlorate by the electrolysis of an aqueous solution of an alkali metal chloride using that form of the multielectrolytic cell claimed in British application Serial No. 845,043 wherein in each unit cell the anode is a layer of a platinum metal on one side of the titanium metal sheet separator and there is no diaphragm between anode and cathode, which is characterised in that the current density employed is at least 2 kA/m.^{2} and preferably between 2 and 4 kA/m.^{2}.

By the term "a platinum metal" is meant a noble metal of the platinum group or an alloy of two or more such metals as defined in British application Serial No. 845,043.

In carrying out the process according to the invention, electrolysis may be carried out continuously, an aqueous solution containing alkali metal chloride being passed through the cell at high temperature, suitably 70–80° C., and the effluent liquors may be cooled or concentrated to promote crystallisation of the chlorate produced in the cell. It is preferred to have a small concentration of a chromate in the liquor fed to the cell, suitably 2–10 g./l. of an alkali metal chromate, in order to promote chlorate production as is known in the art. An especially advantageous method, which is made possible because of the high electrolyte temperatures which can be employed in the present process, is to operate the cell in conjunction with a continuous crystallisation and resaturation system, whereby the chlorate is recovered without recourse to evaporation and simply by cooling the cell effluent liquor, and the liquor is subsequently resaturated with alkali metal chloride and reheated for return to the cell. The temperature at which resaturation is carried out will depend on the solubility relations of the salts involved. For example, when manufacturing sodium chlorate the resaturation with sodium chloride is best carried out at elevated temperature, suitably about 70° C. in order to achieve the maximum solubility of the chloride, and the crystalliser may be operated at about 20° C. On the other hand, when manufacturing potassium chlorate, resaturation must be carried out at a lower temperature because of the steeper solubility curve for potassium chloride, otherwise on cooling the cell effluent liquor for crystallisation of potassium chlorate sufficient potassium chloride may still be present in solution to deposit this salt along with the chlorate in the crystalliser. In the case of the potassium salt it is convenient to carry out resaturation at the crystalliser temperature, suitably about 20° C., and then to reheat the resaturated liquor before return to the cell. Heat may be conserved by operating the cooling/crystallising-resaturation/reheating cycle on the heat-exchanger principle.

By way of example the invention will be further discussed with reference to the drawings accompanying the provisional specification. FIG. 1 shows schematically (not to scale) in vertical cross section one form of multielectrolytic cell according to the invention. FIG. 2 shows one arrangement of apparatus suitable for carrying out the process according to the invention for the manufacture of sodium chlorate on the aforementioned continuous resaturation principle.

In FIG. 1 the multielectrolytic cell is shown as comprising seven unit electrolytic cells 1, but it must be understood that it may comprise a smaller or larger number of unit cells. The multielectrolytic cell has titanium end plates 2 and 3, and between each pair of unit cells 1 are titanium sheet metal partitions 4. Anodes 5 are thin layers of a platinum metal carried on the internal surface of end plate 2 and on one face of each of titanium partitions 4. Cathodes 6 are preferably thin layers of a platinum metal on the internal surface of end plate 3 and on the face of each of the titanium partitions 4 opposite to the anodes. Cathode layers 6 may however be layers of iron or steel or may be omitted entirely so that the bare titanium faces of end plate 3 and partitions 4 form the working cathode surfaces. The anodes 5 and cathodes 6 are spaced apart at a distance of approximately 3 mm. from each other by insulating separators 7 and 8 placed between the ends of each pair of titanium sheets, the whole assembly of sheets and insulating separators being held together in a liquor- and gas-tight manner by clamping means (not shown). Channels 9, passing through the lower set of insulating separators 7, are used for feeding electrolyte to each unit cell, and channels 10, passing through the upper set of insulating separators 8, are used for removing the electrolyte and hydrogen gas from each unit cell. The electrolyte may alternatively be fed to and removed from the unit cells in some other manner, for example through channels cut in the titanium end plates 2 and 3 and titanium partitions 4 near the bottom and top respectively. 11 and 12 are current leads to the anodic and cathodic titanium end plates 2 and 3 respectively.

In FIG. 2, 13 is a multielectrolytic cell of the type shown in FIG. 1 comprising, in the case shown, seven unit electrolytic cells 1. In the manufacture of sodium chlorate using the apparatus of FIG. 2, feed electrolyte is saturated with sodium chloride at a temperature of approximately 70° C. in saturator 14 and passes continuously from 14 by lines 9 to each of the unit cells 1, where sodium chlorate and hydrogen are produced by electrolysis. Spent electrolyte leaves unit cells 1 by lines 10 together with the hydrogen evolved in the cells. Hydrogen is removed at 15 and spent electrolyte passes along line 16, is cooled in heat exchanger 17 and then flows through crystalliser 18, where sodium chlorate crystals are deposited. Mother liquor leaves crystalliser 18 by line 19, is reheated partly in heat exchanger 17 and then in heater 20 and returned to saturator 14. Line 21 is provided for a secondary flow of spent electrolyte from the cells 1 to the saturator 14 without passing through the crystalliser as a means of adjusting the chloride/chlorate content of the electrolyte entering and leaving the cells. The flow through line 21 is controlled by valve 22. It will be understood from the foregoing discussion that the apparatus shown in FIG. 2 may also be employed for the continuous production of potassium chlorate provided that the heating means are repositioned so that the saturator works at low temperature and the saturated electrolyte is afterwards heated before being fed to the cells.

The following table illustrates the efficient production of sodium and potassium chlorates by the process according to the invention. In the multielectrolytic cell employed the anodes were electrodeposited layers of platinum and the cathodes were layers of platinum deposited by the painting and firing process as practised in the ceramic industry.

Product	Cell Voltage	Cell Load, kA/m.^{2}	kWh/ton of Product
Sodium Chlorate	3.33	2.0	5,920
Do	3.62	3.5	6,430
Potassium Chlorate	3.7	3.5	6,100

What we claim is:

1. A process for the manufacture of alkali metal chlorate by the electrolysis of an aqueous solution of alkali metal chloride which comprises uses a multi-electrolytic cell having a plurality of diaphragm-free unit electrolytic cells, each of said cells having an anode and a cathode with the cells arranged so that a partition carries the anode of each cell and the cathode of the next cell, said partition comprising an inert titanium metal sheet separating the anode of one unit electrolytic cell from the cathode of an adjacent unit electrolytic cell, the anode in each unit cell comprising a layer of a platinum metal on one side of the titanium metal and the cathode in said unit cell comprising a layer of a metal selected from the group consisting of a platinum metal, iron and steel on the side of the next titanium metal sheet opposed to the anode of said unit cell, and employing an anode current density of at least 2 kA/m.^{2}.

2. A process according to claim 1, wherein the cell is operated at an electrolyte temperature of 70–80° C.

3. A process according to claim 2, wherein electrolyte is continuously passed through the electrolytic cell and alkali metal chlorate is obtained from the effluent liquor by cooling said liquor and separating alkali metal chlorate crystals from the cooled mother liquor.

4. A process according to claim 3 wherein the cell effluent liquor is cooled to approximately 20° C. before separating alkali metal chlorate crystals from the cooled mother liquor.

5. A process for the manufacture of sodium chlorate according to claim 3, wherein the mother liquor after separation of sodium chlorate crystals therefrom is reheated to approximately 70° C., saturated with sodium chloride at that temperature, and then returned to the cell.

6. A process for the manufacture of potassium chlorate according to claim 3, wherein the mother liquor after separation of potassium chlorate crystals therefrom is saturated at its existing temperature with potassium chloride and is then reheated to approximately 70° C. and returned to the cell.

7. A process according to claim 1 wherein the cathode is a layer of platinum and the anode current density is between 2 and 4 kA/m.^{2}.

8. A process for the manufacture of alkali metal chlorate by the electrolysis of an aqueous solution of alkali metal chloride which comprises employing an anode current density of at least 2 kA/m.^{2} in a diaphragm-free, multielectrolytic cell, said cell comprising a plurality of

diaphragm-free unit electrolytic cells, each such unit cell having an anode and a cathode, the unit cells being so arranged that a partition carries the anode of each unit cell and the cathode of the next cell, said partition comprising an inert titanium metal sheet, the anode of each cell comprising a layer of a platinum metal on one side of the titanium separating sheet and the cathode of said unit cell being the bare titanium face of the next titanium metal sheet facing the anode in said unit cell and carrying the anode for the adjacent unit cell.

9. A process according to claim **8** wherein the anode current density is between 2 and 4 kA/m.^{2}.

10. A multielectrolytic cell comprising a plurality of diaphragm-free unit electrolytic cells, each of said cells having an anode and a cathode with the cells arranged so that a partition carries the anode of each cell and the cathode of the next cell, said partition comprising an inert titanium metal sheet separating the anode of one unit electrolytic cell from the cathode of an adjacent unit electrolytic cell but in electrical conducting relationship with respect to both the anode and the cathode carried thereby, the anode in each unit cell comprising a layer of a platinum metal on one side of the titanium metal sheet and the cathode in said unit cell comprising a layer of a metal selected from the group consisting of a platinum metal, iron and steel on the side of the next titanium metal sheet opposed to the anode of said unit cell.

11. A multielectrolytic cell comprising a plurality of diaphragm-free unit electrolytic cells, each of said cells having an anode and a cathode with the cells arranged so that a partition carries the anode of each cell and

the cathode of the next cell, said partition comprising an inert titanium metal sheet separating the anode of one unit electrolytic cell from the cathode of an adjacent unit electrolytic cell but in electrical conducting relationship with respect to both the anode and the cathode carried thereby, the anode in each unit cell comprising a layer of a platinum metal on one side of the titanium metal sheet and the cathode in said unit cell comprising a layer of a platinum metal on the side of the next titanium metal sheet opposed to the anode of said unit cell.

12. A multielectrolytic cell according to claim **11** wherein the anode and cathode in each unit cell are separated by a gap of about 3 mm.

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