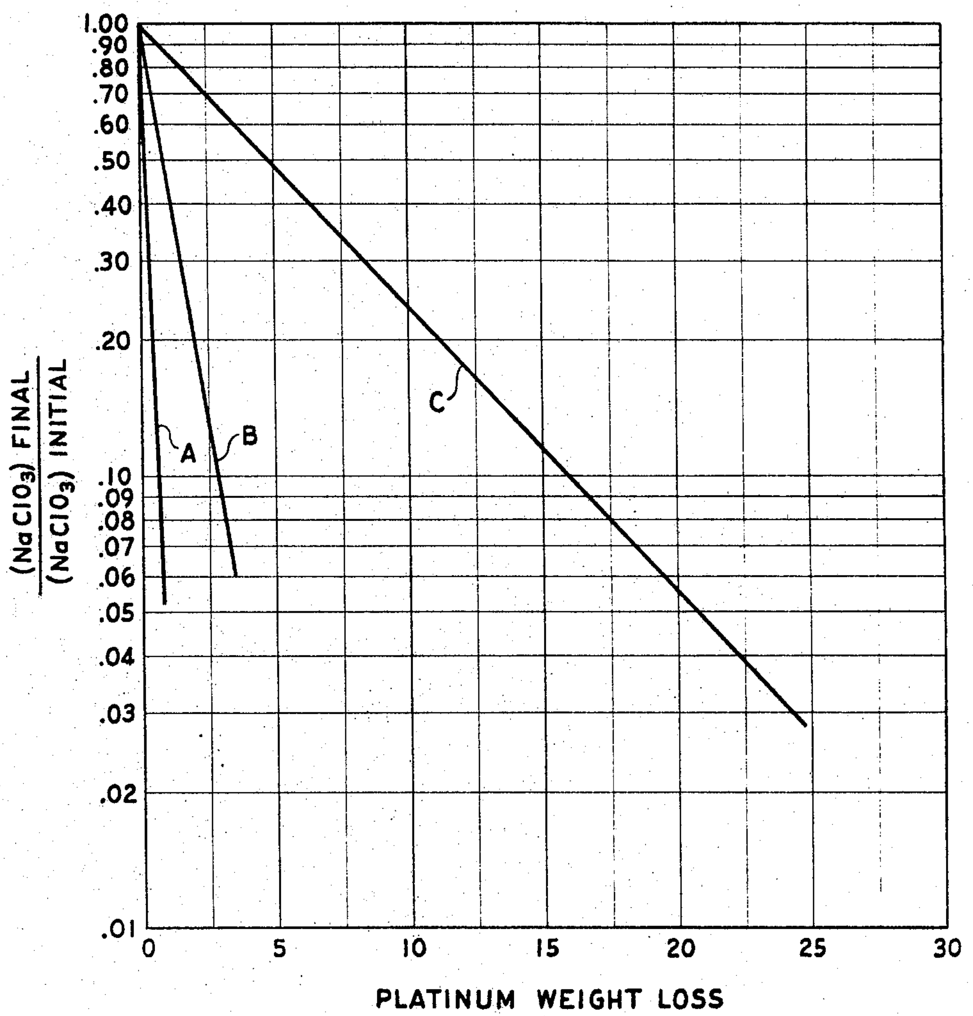
ELECTROLYTIC PREPARATION OF PERCHLORATES

Filed Nov. 25, 1964

FIG. 2

PLATINUM ANODE WEIGHT LOSS



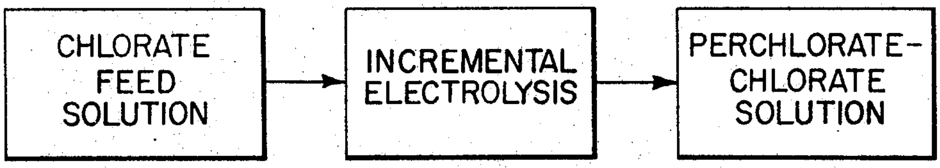


FIG. 1

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ELECTROLYTIC PREPARATION OF PERCHLORATES

Edward H. Cook, Jr., and Morris P. Gretheer, Lewiston, N.Y., assignors to Hooker Chemical Corporation, Niagara Falls, N.Y., a corporation of New York

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Int. Cl. C01b *11/26, 11/18;* B01k *1/00*
U.S. Cl. 204—82 11 Claims

ABSTRACT OF THE DISCLOSURE

Alkali metal perchlorates are produced by incremental electrolysis of the corresponding chlorate by applying a decomposition voltage across the electrolyte in an electrolytic cell, passing the incrementally electrolyzed alkali metal chlorate solution to additional cells in series, said individual incremental electrolysis constituting the conversion ratio of initial chlorate concentration to final chlorate concentration falling within the range of less than 1.0 to 0.5. The incremental electrolysis of alkali metal chlorates within the conversion range specified, minimizes the consumption of platinum from an electrode.

This invention relates to the reduction of electrode consumption in electrolytic cells, and more particularly to a method of reducing the anode consumption during the electrolysis of alkali metal chlorates to alkali metal perchlorates.

In the production of perchlorates, considerable expense is incurred due to the consumption of anodes. A great effort has been made to find an anode material which is resistant to the perchlorate electrolysis environment. So far, only a few materials have been found which perform with reasonable success, but even these materials, of which platinum and lead dioxide are most frequently used, are decomposed at a rate which appreciably affects the cost of perchlorate manufacture. Because of the added cost and the contamination of the perchlorate product due to corrosion and erosion of the anode material, attempts have been made to reduce the anode consumption by controlling the temperature and other factors which have been thought to influence the corrosion rate.

It is known that low temperatures reduce anode losses. However, low operating temperatures result in high voltages which are also costly. Therefore, previous attempts to reduce anode consumption in perchlorate cells by changes in temperatures, current densities and so forth resulted in a compromise of the various factors involved. While such comprise conditions have been accepted for many years, they are not entirely satisfactory.

In addition to controlling various physical factors, the electrolyte flow, through perchlorate cells, has previously been essentially in parallel relation to the cells, that is, the electrolyte flows from a cooling tank to a bank of electrolytic cells having one to a hundred or more cells in a single tank. The electrolyte was circulated freely through the cell bank and then returned to the cooling tank. It has been proposed to operate these banks of cells by connecting two to about five cell banks to a single cooling tank and to thereby circulate the electrolyte through the cell banks freely or progressively. The present invention provides an improved process which greatly improves the efficiency of perchlorate cells.

It is an object of the present invention to provide a method for reducing the loss of anode material due to chemical corrosion in a perchlorate cell. It is another object of this invention to provide a process whereby platinum consumption is reduced in perchlorate cells by

a factor many times that experienced in conventional perchlorate cells. These and other objects will become apparent to those skilled in the art from the description herein.

In accordance with the invention a method of effecting the electrolysis of chlorates to perchlorates is provided comprising feeding an aqueous solution of alkali metal chlorate to an electrolytic cell applying a decomposition voltage across the cell, effecting an incremental electrolysis of alkali metal chlorate to alkali metal perchlorate in the cell, passing the incrementally electrolyzed alkali metal chlorate solution to additional cells in series, effecting additional incremental electrolysis therein, thereby effecting the production of alkali metal perchlorate.

The present invention provides a means of markedly reducing the anode consumption of electrodes during the conversion of alkali metal chlorates to alkali metal perchlorates.

The invention will be readily understood with reference to the drawings in which:

FIG. 1 is a flow sheet describing the process of the present invention; and

FIG. 2 graphically illustrates the improvements obtained in reduced platinum consumption by the process of the present invention.

The present invention is described more particularly with respect to platinum and platinum alloy anodes. However, in an effort to more clearly describe the invention, the description and examples will relate primarily to platinum alloys. Such description and examples are not to be understood as limiting the invention to platinum alloys.

The present invention resides in the application of a newly discovered principle to an electrolytic cell for the production of alkali metal perchlorates, especially sodium perchlorate. The principle discovered is that anode loss, such as the platinum loss, depends on the electrolytic conversion of chlorate to perchlorate and not on the quantity of chlorate converted to perchlorate.

The kinetic theory for platinum losses is explained by the kinetic expressions developed for a batch operation; the rate of chlorate consumption, dc/dt depends only on the current and can be expressed as a zero order reaction in:

$$\text{rate}_1 = \frac{dc}{dt} = k'$$

wherein rate, or dc/dt, is the rate of chlorate conversion to perchlorate and k' is a constant depending on the current and current efficiency. k' is determined by using Faraday's law and current efficiency to determine production rate. The constant k' depends on both the total current and the current efficiency.

The rate of platinum consumption dp/dt, increases as the chlorate concentration in the batch decreases. Therefore, the rate is inversely proportional to the chlorate concentration C at any time. This is expressed as:

$$\text{rate}_2 = \frac{dp}{dt} = \frac{k''}{C}$$

The rate of platinum consumption is related to the decrease in chlorate concentration by the expression:

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{dc}{dp} = \frac{k'C}{k''} = kC$$

If C_0 is the initial concentration of sodium chlorate, and if C is the sodium chlorate concentration at a given time, and if P is the platinum weight loss at the same time, the following expression is developed:

$$\int_{C_0}^{C} \frac{dC}{C} = k \int_{0}^{P} dP$$

which on integrating results in:

$$\log\frac{C}{C_0}=kP$$

where the constant k still includes the current efficiency factor from k'.

This expression indicates that the platinum weight loss is related to the fraction of chlorate oxidized to perchlorate and is independent of the total amount of chlorate oxidized. Laboratory experiments have proven the expression to be true for constant current efficiencies. The expression developed, teaches that the logarithm of the ratio of the final chlorate concentration over the initial chlorate concentration is equal to the platinum loss, i.e.,

$$\log\frac{C}{C_0}=kP$$

In other words, as the ratio of C/C_0 approaches 1, the platinum loss approaches zero.

To apply the derived principle to reduce the platinum consumption in a perchlorate cell, the electrolysis in the cell is effected so that the fraction of chlorate converted to perchlorate is small with respect to any given cell, i.e., ratio $C/C_0 \rightarrow 1$. In this manner the log of the ratio of the final chlorate concentration over the initial chlorate concentration approaches zero.

To apply the discovered principles to an electrolytic cell for the production of perchlorates, a multi-cell, continuous process was developed wherein the current density, number of cells and feed rate are controlled so that within each cell, the sodium chlorate concentration within the cell approaches a state wherein the chlorate concentration is constant with respect to the cell. That is, the effected electrolysis in a given cell would be finite, but would approach zero. In a preferred embodiment, the arithmetic ratio of sodium chlorate concentration leaving a given cell over the sodium chlorate concentration entering the same cell ranges from less than 1.0 to 0.5, the ratio r being that at which anode losses are greatly reduced.

The process of the present invention was found to be most conveniently effected in a bipolar cell constructed so as to provide a continuous flow in stepwise fashion from one electrode to another. The electrolyte is controlled so as to proceed at a desired rate through the bipolar cell assembly. Although the process of the present invention can be utilized in monopolar cells, such applications are more readily and conveniently applied to bipolar cells. To effect the most desired results by way of reducing anode losses, the electrolysis is effected in a manner such that the average electrolysis per cell amounts to a conversion of about 5 to 10 grams per liter of sodium chlorate to sodium perchlorate, depending on the concentration of feed liquor going into the cell and the concentration of liquor leaving the cell. The preferred number of cells or incremental electrolysis used in the production of perchlorate by the present method is determined by the expression

$$\frac{C_0-C}{x}=N$$

wherein C_0 is the initial chlorate concentration in grams per liter, C is the final concentration of chlorate in grams per liter, x is the average electrolysis in per cell and N is the number of incremental electrolyses.

The concentration C_0, in any given cell can be varied for the particular process between about 900 to 10 grams per liter of $NaClO_3$. The concentration C can also be varied in the range of about 899 to 5 grams per liter of $NaClO_3$. The average electrolysis, x, in any one step or cell can be varied from a decomposition of sodium chlorate in an amount of about 0.1 to about 20 grams per liter per cell, 5 to 10 grams per liter per cell being preferred. The concentration of sodium chlorate in a feed solution to a cell series rather than an individual cell ranges from about 900 to about 100 grams per liter, the concentration being consistent with the solubility limits.

The electrolysis process can be varied so that the total electrolytic decomposition effected by the multitude of incremental electrolyses is any amount within the range of 900 to 5 grams per liter of sodium chlorate. For example, a decomposition of a feed liquor at 500 grams per liter to 200 grams per liter of sodium chlorate plus the formed sodium perchlorate can be effected, as well as any other partial decomposition within the range of 900 to 5 grams per liter. The number of incremental electrolysis employed for any degree of sodium chlorate decomposition is again determined by the equation

$$\frac{C_0-C}{x}=N$$

where N is in the range of about 20 to 130 and preferably 40 to 130, depending on the total change between the initial chlorate concentration and final chlorate concentration.

The incremental electrolysis is effected in individual cells composed of an anode and a cathode.

Since the sum of the anode consumption over a series of individual electrolyses is equal to the anode consumption for the total electrolysis, one would at first expect the anode consumption to be unchanged by the present process. However, a radical improvement in platinum consumption is realized which follows the developed theory. The developed theory states that anode consumption depends only on the degree of electrolytic conversion and not the quantity of chlorate converted to perchlorate. Therefore, in the present process, a constant concentration of chlorate feed liquor is continuously fed to each cell to effect an incremental electrolysis in each cell. Since the flow of feed liquor at the same concentration is infinite with respect to each cell, and the degree of electrolysis is small, the platinum consumption in grams per ton of perchlorate produced approaches zero. Therefore, in the present process, the platinum loss approaches zero as the average effected electrolysis per cell approaches zero. In this manner, the platinum loss per ton of perchlorate produced is greatly diminished by the present process.

As previously stated, the process of the present invention is readily effected in a bipolar cell assembly. Such a bipolar assembly is constructed so as to control the flow of electrolyte between bipolar electrode plates. By using smooth, bright platinum coated sheets for electrodes, one side of which serves as a positive pole, the other side as a negative pole, such electrode plates are arranged so as to form the sidewalls of a sealed chamber within the cell assembly. Preferably, the bipolar electrodes are surrounded by a non-conductive material such as slate, rigid polyvinyl chloride resin and the like, which form a seal between the electrode and the assembly walls. Thus, individual cells are formed within a bipolar cell assembly, the bipolar electrodes forming sidewalls for the cells and being held in place and insulated from the cell assembly by the non-conductive sealing material. A bipolar cell of this type is described by M. P. Gretheer, in Ser. No. 403,104, filed Oct. 12, 1964. To control the flow of electrolyte between adjacent cells, one or more holes are placed in the sealing material to permit unidirectional flow of electrolyte from one cell to another, progressively through the series of cells.

In a like manner, non-conductive inert partitions can be placed between pairs of positive and negative electrodes in a monopolar cell series to facilitate electrolysis while economizing space. The inert partitions are also constructed of slate, concrete and the like, or inert resins such as polyvinyl chloride, polyvinylidene chloride, polytetrafluoroethylene and the like. Again, one or more openings are placed in the partition to permit unidirectional flow of electrolyte through the cell series.

The flow rate through the cell assembly is in series, whether a bipolar cell assembly or a series of monopolar cells and is regulated in accordance with the current density and the cell efficiency so as to effect the total desired electrolysis in a single pass through the cell assembly or series of cells. In the normal operation of the cell, a current density of 0.75 to 4.5 or more amps per square inch is used. With a bipolar cell assembly operating at an average current of 1800 to 4000 amps, a flow rate of 0.5 to about 4 gallons feed solution per minute can be used. Such flow rates depend largely upon the capacity of the cell series and can reasonably be expected to be greater or less for cell assemblies of varying capacities. Greater operating currents will permit greater flow rates.

The electrodes used in the present invention are of any suitable anode material for perchlorate electrolysis. Therefore, the anode may be of lead dioxide or more preferably platinum or platinum alloys. The cathode can also be of platinum or platinum alloys in addition to other electrically conductive metals such as copper, nickel, steel, silver and the like metals and alloys thereof. Since the cathode normally is not subjected to severe corrosion, less expensive material can be used. Normally, only the anode face is of a corrosion resistant material such as lead dioxide or platinum, the face being preferably supported by a conductive material such as titanium or tantalum. The conductive metal serves as a backing to supply the needed structural strength to the platinum face, thereby reducing the quantity of platinum required. In this manner only a very thin coating of platinum is required to form the anode face.

As in conventional perchlorate electrolyses, it is preferred to control the temperature of the electrolyte during electrolysis within a temperature of 20 degrees centigrade to 80 degrees centigrade. However, because of the lower platinum consumption by the present process, if it should be found to be desirable to operate at higher than normal temperatures, such operation can be effected by the present process at much lower platinum losses than would be expected by conventional methods. Normally, it is preferred to conduct the electrolysis at a temperature within the range of about 24 to 60 degrees centigrade.

The following examples illustrate certain preferred embodiments of the present invention. Unless otherwise indicated, all parts and percentages used herein are by weight and all temperatures in the examples and claims are in degrees centigrade unless otherwise indicated.

Example 1

FIG. 2 illustrates graphically the relation between platinum weight loss in grams per ton of sodium perchlorate produced and of the ratio of the final chlorate concentration over the initial chlorate concentration at a designated temperature. The graph substantiates the known fact that operating temperature directly effects the anode weight loss but that the weight loss is also dependent on the ratio of chlorate concentration. Line A on FIG. 2 was drawn from data obtained at a temperature of 24±2 degrees centigrade, line B was obtained from data taken at 44±2 degrees centigrade and line C was taken from data taken at 60±2 degrees centigrade. The graph illustrates that independent of temperature, as the ratio of the sodium chlorate final concentration over the sodium chlorate initial concentration approaches one, the platinum loss approaches zero. Therefore, as the incremental electrolysis per cell approaches zero, the platinum anode loss per ton of sodium perchlorate produced approaches zero. Again, the developed theory is experimentally proven to be correct in showing that platinum loss is independent of the volume of sodium chlorate decomposed to sodium perchlorate but rather dependent on the degree of decomposition.

The graph further illustrates that temperature strongly influences the platinum loss so that it is readily seen in studying FIG. 1 that lower operating temperatures are preferred. However, lower operating temperatures increase the voltage such that the anode saving is achieved at decreased power efficiencies which normally do not justify the saving. Therefore, it is most preferable to operate in a temperature range of 40 to 80 degrees centigrade. The present incremental electrolysis is most effective in reducing anode loss in this preferred temperature range. Thus, at a temperature of 44±2 degrees centigrade, and incrementally electrolyzing the sodium perchlorate so as to maintain the arithmetic ratio at 0.7, the platinum loss would be 0.5 gram per ton of sodium perchlorate produced compared to about 4 grams per ton by conventional methods. Again, when operating at 60±2 degrees centigrade and maintaining the ratio of the chlorate concentration at 0.7, the platinum loss would be 2.5 grams per ton of sodium perchlorate produced compared to about 20 grams loss by conventional methods.

Examples 2 through 5

To demonstrate and prove the effect of incremental electrolysis of sodium chlorate to sodium perchlorate, experimental cells were constructed and operated in accordance with the present invention. Data was collected during the electrolysis by observing the electrolysis within individual cells. The cells were constructed so as to pass a large volume of liquor through the cell and effect an incremental electrolysis within each cell prior to passing the liquor to another cell, the flow being continuous with respect to each cell. The volume of liquor passing through each cell was in a liquor-volume ratio to cell-volume of 135 to 370 liquor-volumes per cell volume. The liquor passing through the observed cell was at a concentration of 660 grams per liter of sodium chlorate in water. The liquor was fed at a controlled rate through the cell. The anode and cathode used in the cell were of 90 percent platinum and 10 percent iridium. Electrolysis was effected by passing a decompositon voltage through the cell at an anode current density of 1.6 amperes per square inch. The cell temperature was controlled at 45 degrees centigrade. By increasing or decreasing the rate of flow through the cell, the amount of sodium chlorate being electrolyzed to sodium perchlorate could be controlled. Table I tabulates the results of the experiments and the measured platinum iridium loss.

TABLE I

	Grams Per Liter $NaClO_3$ Converted to $NaClO_4$ in a Single Cell	Rate of Liquor Volume to Cell Volume	Grams Platinum Iridium Anode Loss Per Ton of $NaClO_4$ Produced
Example Number:			
2	5.5	180 to 1	0.80
3	13.0	135 to 1	1.20
4	16.9	370 to 1	1.56
5	19.5	170 to 1	2.86

As a means of comparison with conventional sodium perchlorate cells, conventional processes result in platinum losses, at the stated temperature, ranging from as low as 3.11 grams platinum to 6.22 grams platinum loss per ton of sodium perchlorate produced, with the average platinum anode loss being in excess of 4.0 grams per ton of sodium perchlorate produced. In the present process, as particularly illustrated in Examples 2 and 3, the platinum anode loss is greatly reduced by incremental electrolysis. Thus, in the preferred incremental range the anode loss is greatly reduced over any other known process.

The examples further illustrate that as the grams per liter of sodium chlorate electrolyzed in any given cell decreases so that the function of the log of the ratio of $NaClO_3$ final/$NaClO_3$ initial approaches zero, the grams of platinum loss per ton of sodium perchlorate produced also decreases.

Examples 6 through 18

Additional experiments were conducted to show the relationship between the volume of electrolyte passed through a cell and the increment of electrolysis effected within the cell. A laboratory cell was designed to study the rate of platinum consumption during the electrolysis of sodium chlorate to sodium perchlorate. Electrodes were fabricated from one inch by one inch by 0.003 inch coupons of 90 percent platinum, 10 percent iridium. Electrical wire connections were welded to the coupons using 22 gauge platinum-iridium wire of identical alloy as the coupon.

Three electrodes were placed face to face in each cell. The electrodes were positioned one inch apart and emerged into the electrolyte so as to have an effective anode surface to two square inches and a corresponding cathode face. The center electrode was connected to a source of electrical current in a manner such that it became the anode, and the two end electrodes served as the cathode.

Solutions of sodium chlorate were electrolyzed batchwise and observations were made at temperatures ranging from 22 degrees centigrade to 62 degrees centigrade. Current densities were varied from 1.0 to 1.7 amperes per square inch of anode surface. The electrolyte solution volume range from 300 cubic centimeters to 2000 cubic centimeters. Table II lists the data obtained in a series of tests run at a temperature of 45 degrees centigrade. Also noted, is a comparison between the calculated platinum loss and the experimentally observed loss.

TABLE II

	Solution Volume (cc.)	pH	Current Density, (a./in.^{2})	$NaClO_3$ final/ $NaClO_3$ initial	Platinum-iridium Anode Loss (mg.)	
					Experimental	Calculated
Example Number:						
6	800	6.0	1.6	0.724	0.6	0.35
7	500	6.0	1.6	0.509	0.7	0.73
8	500	6.0	1.6	0.086	2.6	2.66
9	500	6.0	1.6	0.136	2.0	2.17
10	500	6.0	1.6	0.117	2.2	2.33
11	500	10.0	1.6	0.533	0.9	0.86
12	500	10.0	1.6	0.068	2.8	2.92
13	2,000	6.0	1.6	0.571	0.8	0.61
14	500	6.0	1.6	0.574	0.7	0.60
15	500	10.0	1.6	0.506	0.9	0.74
16	500	10.4	1.6	0.607	0.5	0.54
17	900	6.0	1.7	0.268	1.7	1.43
18	300	6.0	1.0	0.624	0.6	0.51

The above-tabulated results clearly show the relation between the amount of anode loss and the amount of sodium chlorate electrolyzed to sodium perchlorate. The data further shows that the absolute loss of platinum is independent of the solution volume and therefore lower further reductions in platinum loss per ton of sodium perchlorate produced are attainable by increasing the solution volume. Both experimental values and the values calculated according to the equation

$$\text{Log } 10 \frac{\text{final chlorate concentration}}{\text{initial chlorate concentration}} = k'(\text{platinum weight loss})$$

are tabulated for 45 degrees centigrade in which k has a constant value of −0.4.

While there have been described various embodiments of the present invention, the methods and elements described are not intended to be understood as limiting the scope of the invention as it is realized that changes therein are possible. It is intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner. It is intended to cover the invention broadly in whatever form its principles may be utilized.

What is claimed is:

1. A method of effecting the electrolysis of chlorates to perchlorates comprising feeding an aqueous solution of alkali metal chlorate to an electrolytic cell, applying a decomposition voltage across the cell, effecting an incremental electrolysis of alkali metal chlorate to alkali metal perchlorate in the cell, passing the incrementally electrolyzed alkali metal chlorate solution to additional cells in series, effecting additional incremental electrolyses therein, said individual incremental electrolyses are in an amount wherein the arithmetic ratio of chlorate final over chlorate initial ranges from less than 1.0 to 0.5, thereby effecting the production of alkali metal perchlorate and minimizing anode consumption.

2. A method of effecting the electrolysis of sodium chlorate to sodium perchlorate comprising continuously feeding an aqueous solution of sodium chlorate to a series of electrolytic cells, applying a decomposition voltage across the cells, effecting an incremental electrolysis of sodium chlorate to sodium perchlorate in the cells in an amount wherein the arithmetic ratio of chlorate final over chlorate initial in each cell ranges from less than 1.0 to 0.5, progressively passing the incrementally electrolyzed sodium chlorate solution through the series of cells, effecting an incremental electrolysis in each cell and producing sodium perchlorate in an amount equal to the sum of the increments thereby minimizing anode consumption.

3. The method of claim **2** wherein the sodium chlorate feed solution comprises 100 to 900 grams sodium chlorate per liter of feed solution.

4. The method of claim **2** wherein the incremental electrolysis per cell is a decomposition of sodium chlorate in an amount of 0.1 to 20 grams per liter.

5. The method of claim **2** wherein the electrolysis is effected in a series of about 20 to 130 incremental electrolyses.

6. A method of reducing anode consumption in a perchlorate cell as in claim **1** comprising feeding a solution of sodium chlorate progressively through a series of 20 to 130 electrolytic cells, passing a decomposition voltage across the cells, effecting an incremental electrolysis of sodium chlorate to sodium perchlorate in each cell prior to passing the feed solution to the next cell in series.

7. The method of claim **6** wherein the incremental electrolysis in each cell results in a decomposition of 0.1 to 20 grams of sodium chlorate per liter of feed solution.

8. A method of reducing anode consumption in a perchlorate cell comprising feeding a solution of sodium chlorate through a series of electrolytic cells at a decomposition voltage and flow rate such that an incremental electrolysis is effected in each cell in an amount where the arithmetic ratio of the sodium chlorate concentration leaving a given cell over the sodium chlorate concentration entering the same cell ranges from less than 1.0 to 0.5.

9. The method of claim **8** wherein the number of cells used in the electrolysis is equal to the total decomposition of sodium chlorate effected divided by the electrolysis effected in a single cell.

10. A method of reducing anode consumption in perchlorate production comprising feeding an aqueous solution of 900 to 100 grams per liter of sodium chlorate to 40 to 130 electrolytic cells in series, applying a decomposition voltage across the cells, effecting a flow rate to effect the decomposition of 0.1 to 20 grams per liter of sodium chlorate in each cell, progressively passing the sodium chlorate feed solution through the cell series, thereby effecting a decomposition of sodium chlorate and production of sodium perchlorate equal to the sum of the individual electrolyses.

11. The method of claim **10** wherein the decomposition in each cell is effected in an amount of 5 to 10 grams of sodium chlorate per liter of feed solution.

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JOHN H. MACK, Primary Examiner

H. M. FLOURNOY, Assistant Examiner

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(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,475,301 Dated October 28, 1969

Inventor(s) Edward H. Cook, Jr. et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

The second inventor's name should be spelled ---Grotheer---;

Column 4, line 60, reference should be made to ---M.P. Grotheer---;

Column 7, Table II, Example II, last column, delete "0.86" and inse
---0.68---.

SIGNED AND
SEALED
MAY 12 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents