

UNITED STATES PATENT OFFICE.

ARTHUR EDWARD GIBBS, OF NIAGARA FALLS, NEW YORK, ASSIGNOR TO
THE NATIONAL ELECTROLYTIC COMPANY, OF NIAGARA FALLS, NEW
YORK, A CORPORATION OF NEW YORK.

PROCESS OF PRODUCING SALTS OF OXYACIDS OF CHLORIN.

No. 827,721.

Specification of Letters Patent.

Patented Aug. 7, 1906.

Application filed March 26, 1904. Serial No. 200,044.

To all whom it may concern:

Be it known that I, ARTHUR EDWARD GIBBS, a subject of the King of Great Britain, residing at Niagara Falls, in the county of
5 Niagara and State of New York, have invented a Process of Producing Salts of Oxyacids of Chlorin, of which the following is a specification.

These salts have hitherto been produced
10 on a commercial scale by electrolyzing a solution of a chlorin by the use of platinum anodes in a cell without a diaphragm and crystallizing out the chlorate thus produced, the best results being obtained when the operation is conducted at temperatures of about
15 70° to 80° centigrade.

Taking the potassium salt as an example the reactions may be represented by the following equations:

- 20 1. $KCl = K + Cl$.
2. $K + H_2O = KHO + H$.
3. $2KHO + Cl_2 = KClO + KCl + H_2O$.
- 25 4. $3KClO + \text{heat in the electrolytic cell} = KClO_3 + 2KCl$.

The potassium chlorid splits up into potassium and chlorin, but the chlorin reacts at the moment of formation so quickly to form
30 (as in equation 3) potassium hypochlorite, with the potash made according to equation 2, that no chlorin is evolved. Three molecules of hypochlorite then decompose, forming chlorate and chlorid according to equation 4.

My invention results in producing chlorates at a current efficiency which may be as high as ninety-six per cent. or ninety-eight per cent., and the operation is conducted in
40 such a manner that carbon or graphite anodes may be used to advantage for the electrolytic step of the process. Such anode so far as I am aware have never before been used on a commercial scale in connection
45 with the production of chlorates. This enormously reduces the cost of plant necessary to produce these salts.

Hitherto in experimenting with graphite anodes for the production of chlorates two
50 principal causes have operated to break down or disintegrate such anode. First, the gas evolved at its surface breaks away parti-

cles of carbon, and in the case of oxygen combines with it chemically, forming an oxid of carbon, and, secondly, the high temperature
55 necessary to obtain a good efficiency tends to break up the graphite. To overcome the first difficulty, I reduce the amount of gas formed at the anode to a minimum by making use of the reaction between chromate and
60 chlorin discovered by me and described in my copending application, Serial No. 195,994, filed March 1, 1904, and which consists, essentially, in the simultaneous production of
65 bichromate and chlorate by acting upon a chromate with chlorin. By conducting this operation as described in the above application—i. e., by electrolyzing a solution of a
70 chlorid in the presence of a chromate in a diaphragm cell—only a very small quantity of gas is evolved at the anode, which when using graphite anodes adds greatly to their life. The second trouble is overcome by conducting the electrolysis at a comparatively low
75 temperature, preferably below 37° centigrade, removing the liquor from the neighborhood of the electrodes and heating. The following reactions occur in the cell at low temperature:

- 80 1. $KCl = K + Cl$.
2. $6K_2CrO_4 + 3Cl_2 = 3K_2Cr_2O_7 + 3KClO + 3KCl$.

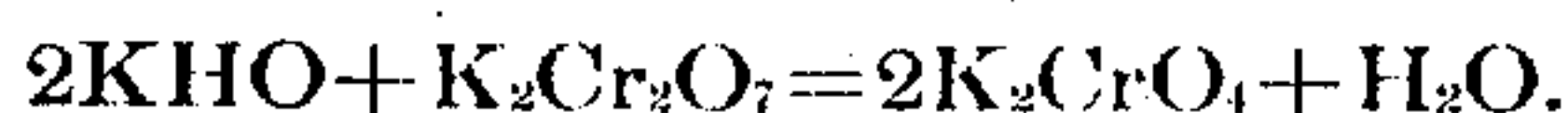
A portion of the hypochlorites split up in the cell even at the low temperature. The remainder do so when heat is applied, both reactions occurring according to equation 4,
85 page 1. I prefer to use a diaphragm-cell, as the output of product per horse-power hour is greatly increased thereby, owing to
90 eliminating the reducing action of the hydrogen at the cathode upon the chlorate or hypochlorite at the anode.

When the chlorin is produced electrolytically in the presence of a chromate at a temperature above 37° centigrade, the final result of the change at the anode may be expressed by the following equations:



The chlorate is therefore produced entirely by an anode reaction. This may be easily proved in using a diaphragm-cell when no chlorin is evolved until all the chromate has

been converted to bichromate. After or during the above change some or all of the alkali formed at the cathode or from an outside source may be allowed to react with the bichromate formed at the anode, producing chromate according to the following equation:



In this way the bichromate may be continually changed to chromate without the increase of either in solution while the chlorate formation proceeds. The presence of a chromium compound is not absolutely necessary to produce a high efficiency. I may have present a trace of a chlorid, the hydrate of the metal with which it is combined being sparingly soluble or insoluble in the solution—for instance, calcium chlorid—and conducting the electrolysis at a temperature preferably below 37° centigrade, raising the temperature of the solution after electrolysis. The calcium hydrate being practically insoluble is deposited at the cathode, leaving its chlorin free at the anode. This chlorin dissolves in the solution at the temperature at which the cell is operated and exerts a catalytic action, transforming the hypochlorite to chlorate when heat is subsequently supplied.

I may produce hypochlorites in a similar manner to the production of electrolytic bleach liquors and convert the hypochlorite to chlorate after electrolysis by heating the solution in the presence of chlorin or when mixed with chlorin or other suitable catalytic agent or carrier of oxygen.

My invention, therefore, is not limited to solutions containing chromates or bichromates, but is applicable to chlorid solutions alone or solutions containing a small amount of alkali, such solutions being capable after electrolysis with carbon or graphite anodes in contradistinction to hypochlorite solutions produced by other than electrolytic methods of direct and substantially quantitative conversion into chlorate by application of heat:

I claim—

1. The method which consists in electrolyzing a solution containing a chlorid with a carbon or graphite anode, at such temperature as to substantially avoid disintegration of the anode, and then heating the resulting solution out of contact with the anode to produce chlorate, substantially as described.

2. The method which consists in electrolyzing a solution containing a chlorid with a carbon or graphite anode, at a temperature below 40° centigrade, and then heating the resulting solution out of contact with the anode to produce chlorate, substantially as described.

3. The method which consists in electrolyzing a solution containing a chlorid and a compound of chromic acid with a carbon or graphite anode, at such temperature as to substantially avoid disintegration of the anode, and then heating the resulting solution out of contact with the anode to produce chlorate, substantially as described.

4. The method which consists in electrolyzing a solution containing a chlorid in a diaphragm-cell with a carbon or graphite anode, at such temperature as to substantially avoid disintegration of the anode, and then heating the resulting solution out of contact with the anode to produce chlorate, substantially as described.

5. The method which consists in electrolytically producing hypochlorites, then converting the same to chlorate by heating the solution in the presence of a chromic-acid compound out of contact with the electrodes, substantially as described.

6. The method which consists in heating a solution containing a hypochlorite and a compound of chromic acid, and thereby transforming the hypochlorite to chlorate; substantially as described.

In testimony whereof I have hereunto set my hand.

ARTHUR EDWARD GIBBS.

Witnesses:

LILLIAN GERTRUDE SMITH,
EMMONS BRYANT.

recognition in Letters Patent No. 827,721.

It is hereby certified that in Letters Patent No. 827,721, granted August 7, 1906 upon the application of Arthur Edward Gibbs, of Niagara Falls, New York, for an improvement in "Processes of Producing Salts of Oxyacids of Chlorin," an error appears in the printed specification requiring correction, as follows: In line 11, page 1, the word "chlorin" should read *chlorid*; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

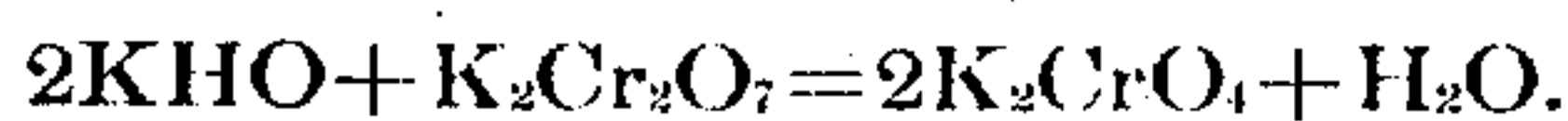
Signed and sealed this 28th day of August, A. D., 1906.

[SEAL.]

E. B. MOORE,

Acting Commissioner of Patents.

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3. The method which consists in electrolyzing a solution containing a chlorid and a compound of chromic acid with a carbon or graphite anode, at such temperature as to substantially avoid disintegration of the anode, and then heating the resulting solution out of contact with the anode to produce chlorate, substantially as described.

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