No. 665,426. Patented Jan. 8, 1901.

W. T. GIBBS.

ART OF OBTAINING CHLORATES BY ELECTROLYSIS.

(Application filed Sept. 9, 1895.)

(No Model.) 2 Sheets—Sheet 1.

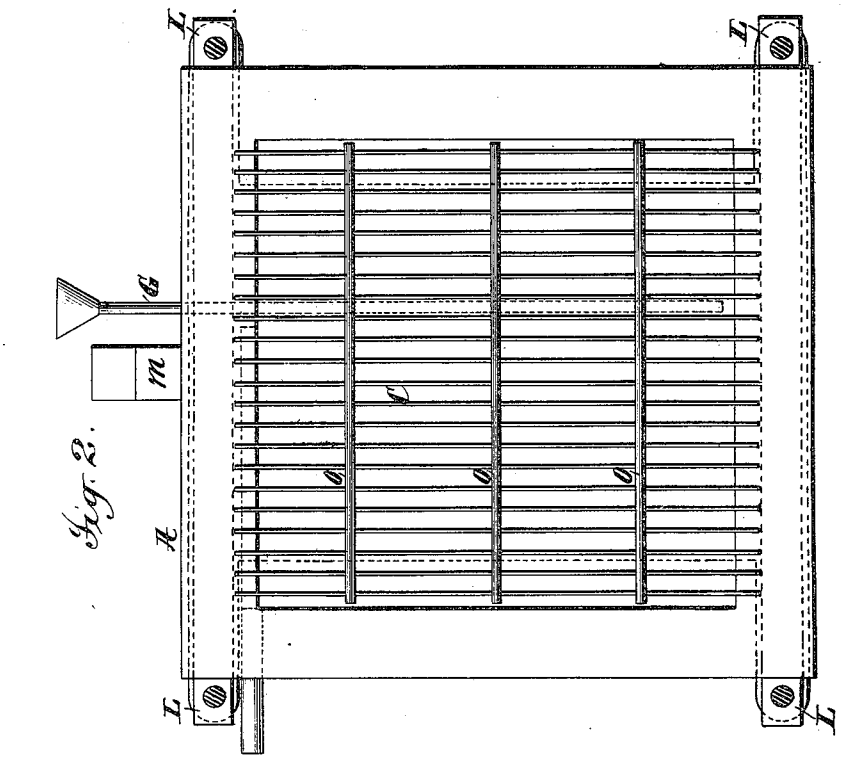


Fig. 2.

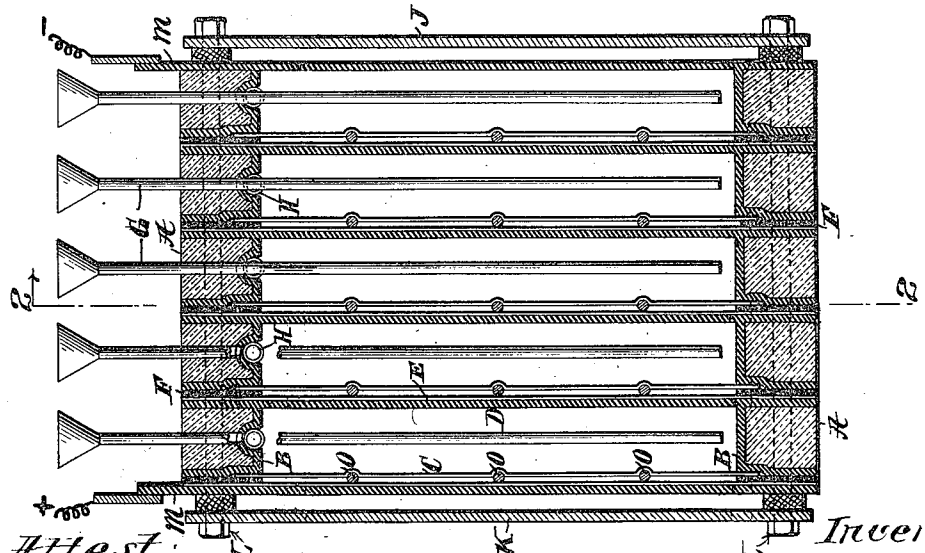


Fig. 1.

Attest:
Lyman White
S. V. Bourg

Inventor:
Wm T. Gibbs
By Philipp Thurman & Phelps
Attys

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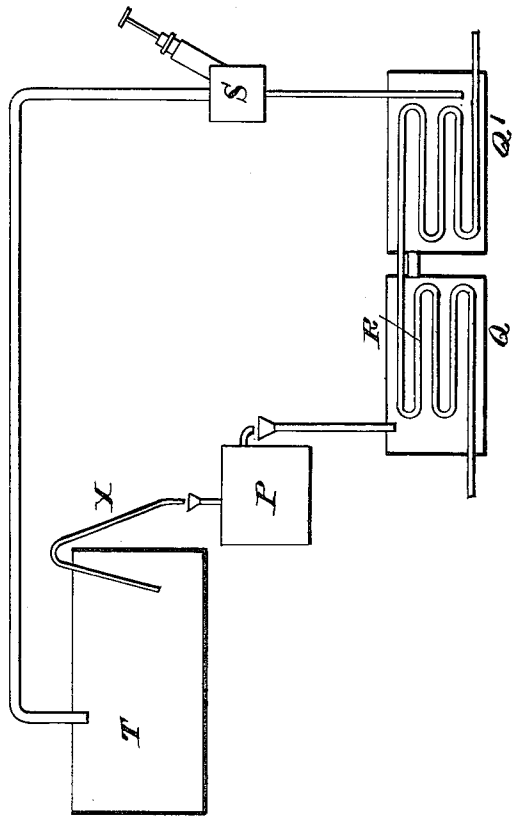
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(No Model.) 2 Sheets—Sheet 2.

Fig. 3.



Attest:
Susie White
A. V. Bourke

Inventor
Wm. T. Gibbs
By Philipp Munson & Phelps
Attys

UNITED STATES PATENT OFFICE.

WILLIAM T. GIBBS, OF BUCKINGHAM, CANADA, ASSIGNOR, BY DIRECT AND MESNE ASSIGNMENTS, TO THE NATIONAL ELECTROLYTIC COMPANY, OF NEW YORK.

ART OF OBTAINING CHLORATES BY ELECTROLYSIS.

SPECIFICATION forming part of Letters Patent No. 665,426, dated January 8, 1901.

Application filed September 9, 1895. Serial No. 561,911. (No specimens.)

To all whom it may concern:

Be it known that I, WILLIAM T. GIBBS, a British subject, residing at Buckingham, county of Ottawa, Province of Quebec, Dominion of Canada, have invented certain new and useful Improvements in the Art of Obtaining Chlorates by Electrolysis, fully described and represented in the following specification and the accompanying drawings, forming a part of the same.

My invention relates to the production of chlorates from the chlorids of alkaline and alkaline-earth metals, and has for its object increase in the efficiency and economy of such processes. In these processes this difficulty has been encountered and has proved very serious. Inasmuch as when a solution of mixed salts is submitted to electrolysis every salt present is to a greater or less extent decomposed, that salt, the production of which is the object of the process, will, as it accumulates in the liquid, be itself to a certain extent decomposed by the action of the current, and a portion of the current will thus be wastefully consumed. It has been usual to continue the electrolysis until the saturation of the bath became such that crystallization would occur in the cell itself or in another receptacle into which the liquid was drawn off and allowed to stand for that purpose. As the percentage of the salt in the bath increased the percentage of current wasted in attacking it also increased and the efficiency of the process diminished. While, therefore, the efficiency at the beginning might be good, that at the end was very low and the average showed a very large percentage of loss.

I have discovered that by making the flow of the liquid through the cell continuous it becomes practicable to remove the salt from the bath rapidly and continuously and while its percentage is still small, and thereby to greatly reduce the quantity of current lost in uselessly decomposing it. Thus whereas the degree of saturation usually heretofore employed in the practice of such processes has been upward of ten per cent. that employed in my process may be less than three per cent., and as a consequence the efficiency of the electrolysis is nearly doubled. Having removed the chlorate from the liquid, I replenish it with chlorid and return it in a continuous stream to the cell. I have also discovered that the chlorids of the alkaline and alkaline-earth metals can be electrolytically treated between metal electrodes separated from each other only by the solution and the necessary insulation—*i. e.*, without the use of a separating-diaphragm—with economy and success. It has been heretofore supposed that the hydrogen freed at the cathode would reduce or prevent the formation of the chlorates unless the electrodes were kept separate by a diaphragm or unless the hydrogen were consumed at the cathode—as, *e. g.*, by an oxid of copper electrode. It has also been considered desirable to thus separate the liberated hydrogen and chlorin to prevent the formation of hydrochloric acid and consequent diminution of the amount of chlorate produced. I have, however, discovered in the course of my experiments that these reactions do not occur in a substantially injurious degree when the percentage of chlorate is kept down to a low percentage by a continuous flow of the solution through the cell and that as a consequence I can employ metal electrodes in close proximity to each other. This is a great advantage, since the use of a diaphragm largely increases the resistance of the electrolytic cell, and consequently the expense of the production, while the use of a non-metallic electrode which will consume the hydrogen is attended with disadvantages which seriously interfere with the economy of the process. This discovery enables me to construct a cell having peculiar adaptations for my continuous process. I am enabled to place the electrodes in close and immediate proximity, and thus to use a current of large amperage and low voltage. The cell in which these electrodes are contained is necessarily of small cubical capacity, since the latter cannot be greater in proportion to the electrode-surface than will properly feed the electrodes by the action of diffusion, and therefore it is not adapted to the old discontinuous process.

In the first place its capacity is so small that the filling of the cell, the application of the current, and the emptying and the refilling of the cell would entail inconvenience which would make such use almost, if not wholly, impracticable, while if the solution passes through the cell in a continuous flow its capacity is ample.

Another very important advantage secured by the small size of the cell and the large amperage or density of the current I am enabled to use is that I can produce all the heat necessary to raise the temperature to the proper point for the decomposition of hypochlorites by the action of the current itself. Heretofore it has been usual on account of the large capacity of the cell employed in the manufacture of chlorates to supply this temperature by means of heat from an external source. This is very difficult to do practically because of the necessity of using apparatus for conveying the heat of the solution which will be resistant to the action of chlorin. In this connection, again, the continuous flow of the solution through the cell is of great consequence, for the reason that the large amount of current I am enabled to use in the small cell would, if the electrolysis were conducted in the usual discontinuous manner, heat the bath much higher than is permissible, while the continuous flow of the solution reduces and limits the development of heat to such a degree as is desirable for the process—namely, within the limits of 90° to 200° Fahrenheit, the preferable temperature being from 110° to 120° Fahrenheit. With this construction of cell and with a continuous flow I am enabled to use a current of two to four (preferably three) amperes per square inch of electrode-surface, which very greatly increases the capacity of the plant in proportion to its size over anything heretofore accomplished.

Another important advantage secured is that I am able to control and regulate the temperature of the solution in the cells by regulating the flow of the solution, which as it enters the cell is cold and causes an overflow of the hot solution. This is a much more convenient means of regulating the temperature than by regulating the supply of external heat on the one hand or than by regulating the density of the current used on the other hand, and this advantage is of greater value where a battery of cells such as is especially adapted to my process is employed than where single cells are used, for this reason, that where a single current is directed through a battery of cells if it were attempted to regulate the heat in the cells by changes in the density of current all the cells would be affected by each change, whereas the temperature of the solution in different cells may be different, owing to different conditions of locations of the cells in the battery or different internal conditions in the cell or in the supply and delivery pipes leading to and from each cell. The flow of the solution through each cell, however, can be separately and conveniently controlled, so as to properly limit and adjust the temperature in each cell separately from and independently of the others.

As regards the feature of my invention which consists in reducing, limiting, or regulating the temperature of the cell by means of continuous flow of the solution I intend to claim the same broadly, whether the source of heat be the current itself or wholly or partly external to the cell. I have also devised a peculiar construction of cell specially adapted for the production of these chlorates and preferably used in carrying out my process. It is necessary in these cells to use as an anode a material which is substantially resistant to the action of chlorin—as, for instance, platinum. The cost of this metal or equivalent material, however, makes impracticable the use of heavy sheets as electrodes, and the high resistance of platinum also unfits it for use alone as an anode. It is also extremely difficult to use thin sheets of platinum as electrodes, owing to their tendency to bend and warp, and consequently short-circuit. It is also disadvantageous to use compound plates made up of a cheap metal, which would, if used alone, be subject to disruption in the presence of chlorin plated or covered with resistant material, as platinum, for the reason that it is difficult to make such covering at the angles of the plate impervious to the action of chlorin, and such plates when used have been found to have less durability than is desirable. Furthermore, whatever the material of the electrodes the use of the usual connecting-rods causes much trouble and expense, since they are both inconvenient in themselves and continually liable to disintegration through accidental contact with the chemicals. I have overcome these difficulties by using for one side of each cell a plate of cheap metal—as, for instance, lead faced with platinum or other substance substantially resistant to the action of chlorin—causing the plate and facing to project beyond the other parts of the cell which inclose the solution, so that only the plain face of the plate will be exposed to the solution, and employing this platinum face as the anode of a single pair of electrodes contained in the cell, this being my preferred construction, it being understood that I do not limit myself to it. This facing of platinum or other resistant substance can be made very thin without disadvantage, since strength and rigidity are supplied to it by the metal backing, which cannot be reached by the solution. The difficulty of making connections is also avoided, since these are made through the wall of the cell, and the cell or cells being preferably closed and arranged as described chemical attack upon parts of the circuit other than the electrolyte is avoided. I have also devised a feature of construction which practically overcomes another difficulty ordinarily encountered in such processes—viz., polari-

zation of the cathode, caused by the adherence thereto of hydrogen bubbles. I have ascertained that an electrode composed of vertical wires or metallic rods effectually prevents polarization. The bubbles of hydrogen being spheres have the least possible contact with the cylindrical surface of the wires or rods. Consequently they do not adhere thereto, but roll up the wires to the top of the cell and there escape. In order to obtain the best results, these rods should be of metal and of small diameter, since there is no other material than metal which is equally suitable for the purpose, and if the diameter of the rods be large the surface approximates to a plane surface and has a tendency to hold the bubbles of hydrogen. I have found the best results to be secured by a small rod or wire, by which I mean a rod or wire having a diameter less than a quarter of an inch.

In order to facilitate the building up of a series or combination of cells which shall have any desired capacity, I cause the metal plate which serves as the backing for the anode of one cell to serve as the rear wall of another cell placed in contact therewith, and to simplify and protect the connections I provide in each cell an interior metallic connection between each cathode and this rear wall of the cell, as by lining the interior of the cell between the two in whole or in part with metal or making this part of the cell entirely of metal, providing mere conducting connections between the cathode and the rear wall. It will of course be understood that suitable insulation is provided between each pair of electrodes. This may be accomplished in any suitable manner—*e. g.*, when the cell is otherwise all of metal or lined with metal or provided with metallic connections, as above suggested, it may be conveniently effected by means of an insulating-gasket entirely separating those parts of the cell connected with the two electrodes, respectively, and held in place by a proper fastening or clamp placed upon the cell or series of cells. By this construction I secure a unit for use in constructing a series of cells, such unit containing an anode and a cathode belonging, respectively, to adjacent pairs of electrodes, which units when combined with interposed insulating-gaskets constitute a series of cells in which the path of the current lies entirely through the electrolyte and the cell-walls, exterior connections being wholly dispensed with, except at the two extremities of the series. This construction has great advantages in convenience and durability.

In the drawings annexed, Figure 1 represents a vertical cross-section of a series of cells made in accordance with my invention and set up for use. Fig. 2 is a side elevation of one of the cells seen on line 2 2 of Fig. 1, the point of view being to the left of Fig. 1; and Fig. 3 is a diagrammatic sketch of the cells, cooling-chambers, pump, and replenishing-vat as the same may be used in the practice of my continuous process.

I will first describe the construction of the cell preferably used in carrying out my process. Each cell consists of a frame A, (shown in vertical cross-section in Fig. 1 and in side elevation in Fig. 2,) which may be of metal, but which I prefer to make of wood, with metallic or other conducting resistant lining B, as shown, or which may be of other material not subject to attack by the solution. Upon one side of this frame are attached the rods or wires C, constituting a cathode, and on the other side a metallic plate D, faced with platinum E, constituting an anode. The cathode may be of copper, zinc, or other suitable metal, as likewise may be the lining B and the plate D. I prefer copper for the cathode and lead for the lining and the plate. It should be observed that it is not essential that the lining B be continuous over the entire surface of the frame A, it being sufficient if conducting connection is made between the cathode and plate D, and the material of the frame if subject to attack by the solution is suitably protected from the action of the contents of the cell. The successive frames are insulated from each other by means of gaskets F, of any suitable insulating material, which may be used to form a tight joint between successive frames. These gaskets are substantially of the same vertical cross-section as the frames.

Supply-tubes G are provided for the introduction of the solution to be subjected to the electrolytic process, and vents H are provided at the tops of the cells for the discharge thereof and of the liberated gas. In order that the cells may be kept always full, these vents are placed just above the inside level of the top of each cell, the frame being recessed for that purpose, and this recess is continued inward, as shown in dotted lines in Fig. 2, in order to permit access of the solution to the vent.

When erected for use the frames are placed side by side, with a gasket between each two, as shown in Fig. 1, and are preferably clamped together by means of two end plates J K, connected by bolts L. The plates J K are separated from the cells by insulating material. The left-hand cell of the series is closed by a simple plate *m*, faced with platinum. The platinum face on the metal back of the right-hand cell is omitted.

Each pair of electrodes is separated by the corresponding gasket. To prevent short-circuiting by bending of the wires, horizontal insulating-rods O are provided between the electrodes, these rods being supported by curved portions of the wires, or other suitable support or other appropriate insulating means may be employed.

Referring now to the diagram Fig. 3, P represents the electrolytic cells overflowing into cooling-chambers Q Q', which may be one, two, or more in number. These cooling-

chambers are shown as provided with cooling-coils R. The use of such coils is an advantage, since it secures the precipitation of a greater proportion of the chlorate in solution; but their use is not essential to my process. S is a pump for returning the depleted solution to the replenishing-vat T, where it meets a fresh supply of chlorid and is fed by the siphon X or other connection again into the cell.

The flow of the solution through the cells is, as I have stated, continuous, and the rate of flow and quantity of electric current used are so proportioned that the solution as it leaves the cell shall have a small percentage of chlorate. This percentage is preferably less than three per cent., and I have found the results to be excellent when it was as low as one and one-half to one and three-quarters per cent.

The capacity of the cell advantageous for use in my process is from two to four cubic inches per square inch of electrode-surface. If a greater amount of liquid in proportion to the electrode-surface is present in the cell, it is difficult to maintain the requisite degree of heat by the action of the current, and the application of external heat to the cell is difficult and expensive, and, further, the presence of a larger amount of solution than that indicated interferes with the proper diffusive action in the cell. While these dimensions are preferable, I do not limit myself to them.

By the term "close proximity" of the electrodes I intend to indicate the closest proximity which it is practicable to obtain between insulated electrodes—as, for instance, one-sixteenth to one-eighth of an inch. I do not, however, limit myself to such close proximity except in those claims in which the electrodes are specified as being in close proximity.

It is an advantage that the flow of the liquid should be continuous through the crystallizing-chambers and the replenishing-vat back to the cell, as well as through the cell itself; but continuous flow is not essential to this part of the process, and I intend to claim in this patent the feature of continuous flow through the cell whether or not such flow is continuous through the remainder of the apparatus.

I do not, of course, limit myself to any special dimensions of apparatus; but I may mention that I have found a convenient size for the cells to be twenty-six by eighteen inches with a thickness of three inches, the electrodes being about one-eighth of an inch apart.

The action of the apparatus as above described is that adapted to the manufacture of potassium chlorate and other chlorates which are less soluble in water than the corresponding chlorids. In the manufacture of sodium chlorate and of such other chlorates as are more soluble than the corresponding chlorids the separation of the chlorates is effected by causing the chlorid to crystallize in the cooling-vats and the subsequent evaporation of the chlorate solution, a continuous flow of the electrolyte being maintained through the electrolytic cell or cells.

It will be understood that the present invention is not limited to the use of apparatus of the specific form shown and described, but that while the use of such apparatus is preferred the carrying out of the process claimed herein by any other suitable form of apparatus is within my invention.

The cell and series of cells shown and described herein form the subject-matter of another application filed October 8, 1900, Serial No. 32,440½.

What I claim is—

1. The process of obtaining chlorates from the chlorids of alkaline or alkaline-earth metals which consists in subjecting the chlorid in solution while flowing continuously through a cell to the action of an electric current between two electrodes insulated from each other, but otherwise separated only by the liquid, the density of the current used being such as to maintain the solution in the cell at a temperature suitable for decomposing hypochlorites, substantially as set forth.

2. The process of obtaining chlorates from the chlorids of alkaline or alkaline-earth metals which consists in subjecting the chlorid in solution while flowing continuously through a cell to the action of an electric current between two electrodes in close proximity and insulated from each other, but otherwise separated only by the liquid, the density of the current used being such as to maintain the solution in the cell at a temperature suitable for decomposing hypochlorites, substantially as described.

3. The process of obtaining chlorates from the chlorids of alkaline or alkaline-earth metals which consists in subjecting the chlorid in solution while flowing continuously through a cell to the action of an electric current between two electrodes insulated from each other, but otherwise separated only by the liquid, the density of the current used being such as to maintain the solution in the cell at a temperature high enough for the decomposition of hypochlorites, and the flow of solution being such as to prevent the temperature from rising above 200° Fahrenheit or thereabout, substantially as set forth.

4. The process of obtaining chlorates from the chlorids of alkaline or alkaline-earth metals which consists in subjecting the chlorid in solution while flowing continuously through a cell to the action of an electric current between two electrodes insulated from each other, but otherwise separated only by the liquid, the density of the current used being such as to maintain the solution at a temperature high enough for the decomposition of hypochlorites, and controlling the temperature of the solution in the cell by regulating the flow of the solution, substantially as set forth.

5. The process of obtaining chlorates from the chlorids of alkaline or alkaline-earth metals which consists in subjecting the chlorid in solution while flowing continuously through each of a series of cells to the action of an electric current passing through the cells in series, between two electrodes in each cell insulated from each other, but otherwise separated only by the liquid, the density of the current used being such as to maintain the solution in all the cells at a temperature high enough for the decomposition of hypochlorites, and controlling the temperature of the solution in each separate cell by regulating the flow of the solution, substantially as set forth.

6. The process of obtaining chlorates from the chlorids of alkaline or alkaline-earth metals which consists in subjecting the chlorid in solution while flowing continuously through a cell to the action of an electric current, between two electrodes insulated from each other, but otherwise separated only by the liquid, the capacity of the cell being from two to four cubic inches per square inch of electrode-surface, and the current employed being from two to four amperes per square inch of electrode-surface, the density of the current and the flow of the liquid being so adjusted that the solution is maintained at a temperature suitable for the decomposition of hypochlorites, substantially as set forth.

7. The process of obtaining chlorates from the chlorids of alkaline or alkaline-earth metals which consists in subjecting the chlorid in solution in a cell to the action of an electric current between two electrodes insulated from each other, but otherwise separated only by the liquid, imparting heat to the solution in the cell by suitable means, and reducing the temperature of the solution by maintaining the continuous flow thereof through the cell, whereby is maintained in the cell a temperature suitable for the decomposition of hypochlorites, substantially as described.

8. The process of obtaining chlorates from the chlorids of alkaline or alkaline-earth metals which consists in subjecting the chlorid in solution while flowing continuously through a cell to the action of an electric current between two electrodes insulated from each other, but otherwise separated only by the liquid, imparting to the cell by suitable means heat sufficient to raise the temperature of the solution to a degree high enough for the decomposition of hypochlorites, and regulating the temperature by regulating the flow of the solution through the cell, substantially as set forth.

9. The process of obtaining chlorates from the chlorids of alkaline or alkaline-earth metals which consists in subjecting the chlorid in solution while flowing continuously through each of a series of cells to the action of an electric current between two electrodes in each cell insulated from each other, but otherwise separated only by the liquid, imparting heat to the solution in each cell by suitable means sufficient to raise the temperature thereof to a degree suitable for the decomposition of hypochlorites, and regulating the temperature of the solution in each cell by regulation of the flow of the solution through the cell, substantially as set forth.

In testimony whereof I have hereunto set my hand in the presence of two subscribing witnesses.

WM. T. GIBBS.

Witnesses:
M. H. PHELPS,
A. L. KENT.