M. C. TAYLOR.

PROCESS OF MAKING CHROMOUS CHLORID.

APPLICATION FILED DEC. 15, 1919.

1,369,204.

Patented Feb. 22, 1921.

2 SHEETS—SHEET 1.

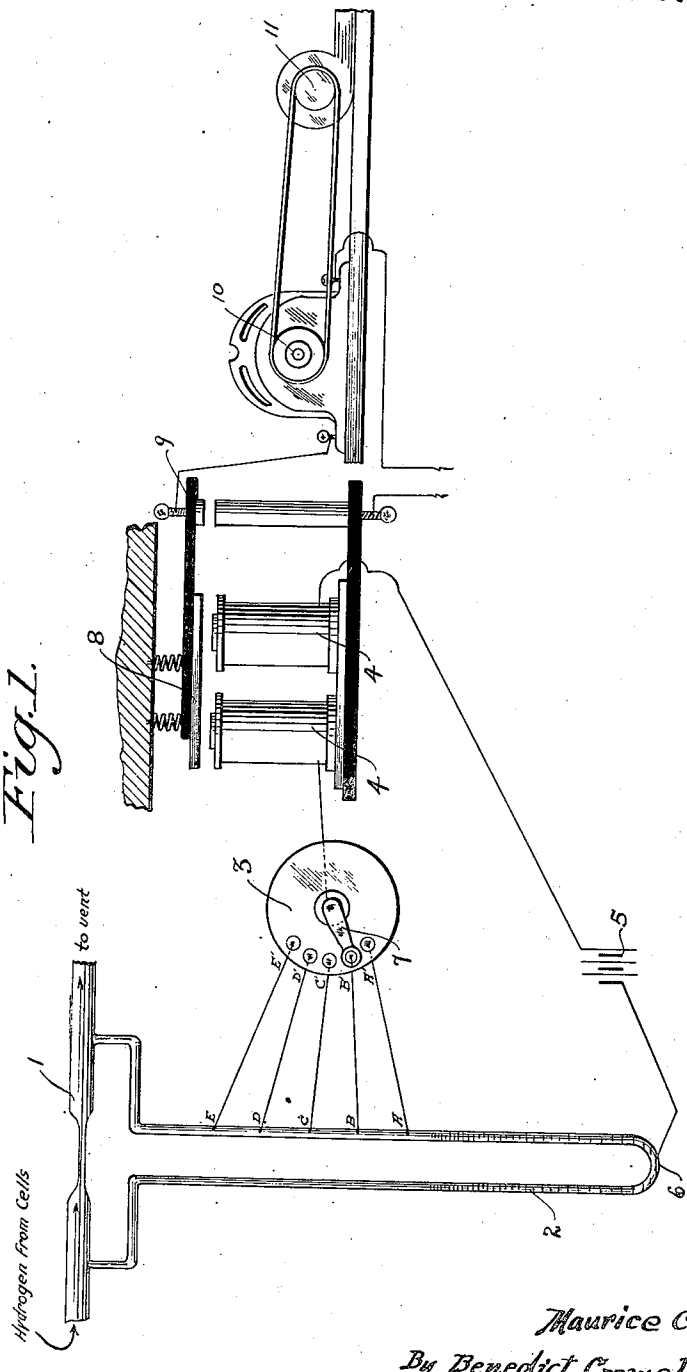


Fig. 1.

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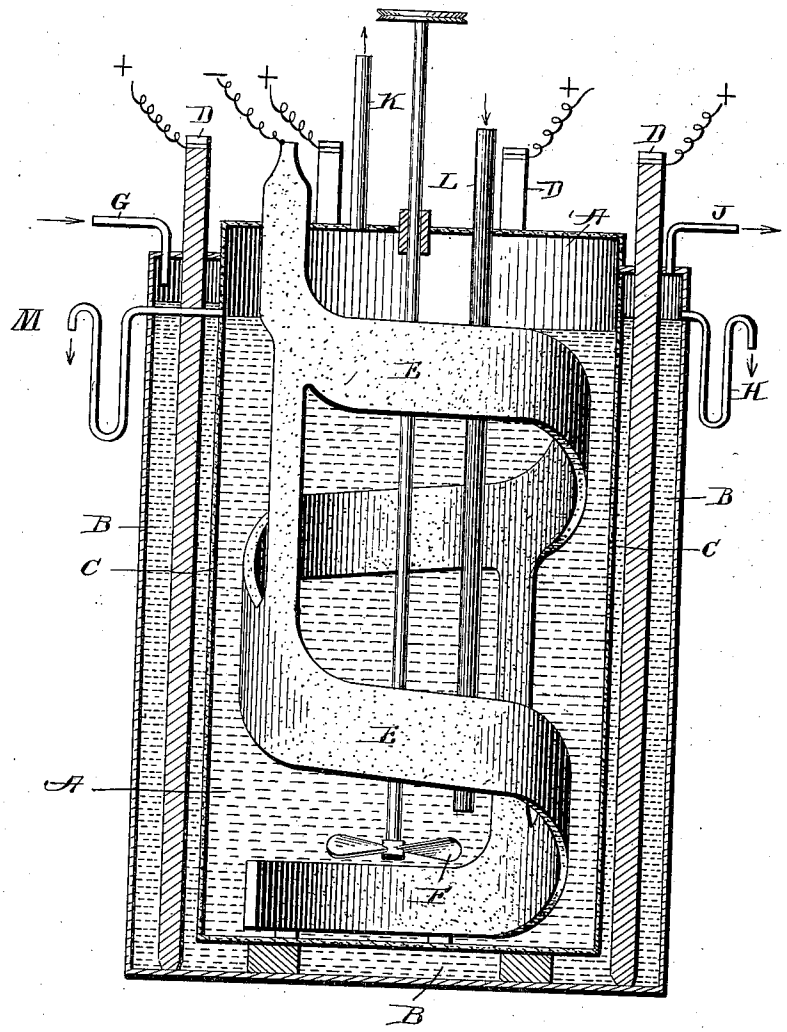


FIG 2.

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UNITED STATES PATENT OFFICE.

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PROCESS OF MAKING CHROMOUS CHLORID.

1,369,204. Specification of Letters Patent. Patented Feb. 22, 1921.

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To all whom it may concern:

Be it known that I, MAURICE C. TAYLOR, a citizen of the United States, stationed at Niagara Falls, New York, have invented an Improvement in Processes of Making Chromous Chlorid, of which the following is a specification.

The invention described herein may be used by the Government, or any of its officers or employees, in prosecution of work for the Government, or by any other person in the United States, without payment of any royalty thereon.

This invention relates to a process for the electrolytic reduction of chromic chlorid to the divalent salt in which process a high current efficiency is maintained, based upon the principle that the proper amount of current to employ for this electrolysis is a function of the chromic ion concentration.

Among the objects of this invention is the production of chromous chlorid from chromic chlorid by having proper concentration of electrolyte; conducting the electrolysis in a two compartment cell having a spongy lead cathode; automatically regulating the flow of chromic chlorid into the electrolytic cell by the pressure of the hydrogen evolved from the electrolysis; continuously drawing off the chromous chlorid produced, thus making the process a continuous one, if desired.

The current used in this electrolysis serves only as a means of producing nascent hydrogen which is the real reducing agent. If the current produces more hydrogen than is consumed in changing the chromium from the trivalent to the divalent salt, the excess hydrogen will be evolved in gaseous form and serve as a measure of the inefficiency of current used. The amount of current required at any particular time depends upon the velocity of the reduction reaction of the chromium chlorid to chromous chlorid.

When the amperage is such that gaseous hydrogen is being evolved, there is present in the reacting zone on or near the surface of the electrode, a constant and never failing excess of nascent hydrogen, which, not being used, is transformed into gaseous hydrogen and evolved. Under such conditions, the velocity of reduction, according to the law of mass action, depends, not on the amount of nascent hydrogen which varies with the current, but on the concentration of the chromic ion present in the system.

As long as there is a sufficient amperage to give an appreciable evolution of hydrogen (about 3 or 4% of that which would be evolved were none of the hydrogen used for reduction purposes) the speed of the reduction is not increased by increasing the amount of current. Also, if the amount of current is increased, the efficiency is decreased. In the reduction process of this invention, the amperage is so regulated that the evolution of hydrogen is not in excess of 3 or 4% of the amount which would be evolved if none of it were used for reduction purposes. Operating in this way, it is found that the current density usually varies from 3 amperes per square decimeter when little or no chromous ion is present down to one ampere per square decimeter when 80–90% of the chromium has been reduced.

In carrying out this reduction process the current should be regulated, as directed above, until the cathode solution has been sufficiently reduced to meet the particular requirements. Then the amperage should be maintained steady and, as the hydrogen flow increases, fresh chromic chlorid solution should be added to the cell. At the same time a corresponding amount of chromous chlorid should be removed as finished product. The addition of fresh chromic chlorid will increase the concentration of the trivalent chromium and therefore the velocity of reduction will be increased, thus using up the excess hydrogen previously evolved.

Referring to the drawings, Figure 1 is a device for automatically regulating the flow of chromic chlorid into the cell. Fig. 2 is a sectional view of one form of cell which may be used in carrying out the process. The flow regulating apparatus consists of the flow-meter (1) having mercury (2) at the bottom of the U-tube connected thereto. On one side of the U-tube there are a series of contact points A, B, C, D, and E, in which are sealed platinum wires having their other terminals in the contact points A^1, B^1, C^1, D^1 and E^1, of a switch (3). These platinum wires are connected singly in series with an electromagnet (4), a storage battery (5) and a contact (6) at the bottom of the U-tube containing the mercury

(2). A storage battery supplying 5–10 volts is usually sufficient. When the contact arm (7) of the switch is at B^1, as shown in the drawing, it will be necessary for the mercury in the manometer to reach the contact B, before the circuit is closed. When this occurs, the electromagnet will attract the arm (8) thereby throwing in a switch (9) which will start the motor (10), connected to a pump (11), which supplies chromic chlorid to the cell. As the chromic chlorid is fed to the cell the hydrogen evolved will be used in reducing the chromic chlorid to chromous chlorid and the pressure of the hydrogen will fall off, consequently, the mercury in the manometer will drop thus breaking the circuit containing the electromagnet, which in turn will throw out the switch (9) and stop the motor and, consequently, the flow of chromic chlorid into the cell.

By manipulating the arm (7) of the contact switch, the pressure which the evolved hydrogen should reach before the circuit containing the electromagnet is closed may be regulated, thus permitting a satisfactory control of the supply of chromic chlorid to the cell. It will be seen that this control of chromic chlorid inflow by the hydrogen evolved is automatic. While the chromic chlorid is being pumped into the cell as outlined above, the chromous chlorid may be allowed to flow off as a finished product, through a U-tube connected to the electrolytic cell in such a way as to maintain the solution being reduced in the cell at the desired level. If desired, the withdrawal of the chromous chlorid solution may be controlled and regulated by automatic means, for example, like that shown for controlling the inflow of the chromic chlorid solution. Operating in this way the reduction may be carried to any desired point up to and above 90% reduction while maintaining at all times a current efficiency from 95–97%, that is, 95–97% of the current used being effective in the production of divalent chromium.

In carrying out this process a two compartment cell is employed in order to prevent the chlorin produced at the anode from oxidizing the chromous salt formed at the cathode. The cell as illustrated in Fig. 2, consists of a cathode chamber A, surrounded by the anode compartment B from which it is separated by the porous wall C. A plurality of carbon anodes D surround the cathode chamber which contains the spongy lead cathode E, arranged in the form of a spiral in order to allow free circulation of the cathode solution. A stirrer F is provided in order that the solution may be agitated. The strong hydrochlorid acid solution necessary to maintain the acid content of the anode compartment enters by way of the pipe G; pipe H is arranged so as to allow for the overflow of a small amount of anode liquor while adding the strong hydrochloric acid. This overflow of liquor obtained at H can be strengthened and returned to the cell if desired. The chlorin escapes by way of the gas exit J. When the automatic device for regulating the flow is employed the hydrogen running to the flowmeter is obtained from the pipe K, and this regulates the chromic chlorid inflow to the cell at L. M is an overflow pipe for the chromous chlorid solution produced, which solution must, of course, be protected from the air. Both the anode and cathode chambers should be gas tight, the former in order to carry away the chlorin produced and the latter to make possible the measurement or regulation of the pressure of the hydrogen evolved, which pressure is necessary for the control of the supply of chromic chlorid to the cell by means shown above.

Although the preparation of the chromic chlorid solution used in this process is no part of this invention, it is recommended that the preparation be made by reducing chromic anhydrid (CrO_3) with hot concentrated HCl solution. When chlorin is no longer evolved, the liquid is cooled and HCl gas passed in, thus precipitating the chromic chlorid in crystaline form. The crystals are washed with dry acetone until nearly free from acid. The product is the green modification of chromic chlorid and is readily soluble in water, thus making possible the use of very concentrated solutions for electrolysis.

An alternative but less satisfactory method for obtaining suitable solutions of chromic chlorid is to heat carbon and chromic oxid (Cr_2O_3) in a current of chlorin. Chromic chlorid will be deposited as violet scales quite soluble in water containing a trace of chromous chlorid.

It is very important that the chromic chlorid solution be very strong as the best efficiencies are obtained from solutions containing 350–500 grams of chromic chlorid per liter. This strength can be easily obtained with crystals prepared from the anhydrid by the method recommended and outlined above. It is also important that the acid content of the chromic chlorid solution be not over 70–80 grams of HCl per liter and concentrations as low as 10–20 grams of HCl per liter or 1–2% acid are recommended. Of course, reduction will take place in more dilute or more acid solution but not with best efficiency.

The anode chamber is filled with HCl solution and is maintained at a gravity of 1.02 to 1.04 which is a solution containing 6–7% of HCl by weight.

The resistance of this cell should be such that a tension of 3 or 4 volts is sufficient to give the required current density. It is

recommended that the reductions be made as near room temperature and pressure as possible, although a rise to 50 or 60° C. due to resistance to current, etc., is not known to be detrimental to results.

By using a mechanical agitator in the cathode chamber and preparing the chromic chlorid solution, as recommended, no trace of a deposit of insoluble oxysalt on the electrode is obtained. When these precautions are not followed, a deposit of insoluble oxysalt on the electrode will occur and will prevent the proper reduction of the chromic chlorid.

Chromous chlorid solution prepared by this process is especially applicable in converting acetylene to ethylene without the production of any ethane. It may also be used for reducing other organic compounds such as the reduction of maleic or fumaric acids to succinic acid.

The present invention is not limited to the specific details set forth in the foregoing examples which should be construed as illustrative and not by way of limitation, and in view of the numerous modifications which may be effected therein without departing from the spirit and scope of this invention, it is desired that only such limitations be imposed as are indicated in the appended claims.

I claim as my invention:

1. A process comprising passing an electric current through a solution of chromic chlorid containing from 1–2% free hydrochloric acid in a cell having separate anode and cathode compartments until the chromic chlorid is reduced to chromous chlorid.

2. A process comprising passing an electric current through a solution of chromic chlorid in a two compartment cell until the chromic chlorid is changed to chromous chlorid.

3. A process comprising passing an electric current through a solution of chromic chlorid in a two compartment cell using a spongy lead cathode until the chromic chlorid is changed to chromous chlorid.

4. A process comprising passing an electric current through a solution of chromic chlorid containing free hydrochloric acid in a two compartment cell using a cathode of spongy lead until the chromic chlorid is changed to chromous chlorid.

5. A process comprising electrolytically reducing a solution of chromic chlorid in a two compartment cell having a cathode of spongy lead and agitating the solution during the electrolysis.

6. A process comprising electrolytically reducing a solution of chromic chlorid containing 1–2% of free hydrochloric acid in a two compartment cell having a cathode of spongy lead and agitating the solution during the electrolysis.

7. A process comprising passing an electric current through a concentrated solution of chromic chlorid in a cell having separate anode and cathode compartments until the chromic chlorid is reduced to chromous chlorid.

8. A process comprising passing an electric current through a solution containing 350–500 grams of chromic chlorid per liter and a small amount of free hydrochloric acid in a cell having separate anode and cathode compartments until the chromic chlorid is reduced to chromous chlorid.

9. A process comprising passing an electric current through a solution containing 350–500 grams of chromic chlorid per liter and a small amount of free hydrochloric acid in a two compartment cell using a spongy lead cathode until the chromic chlorid is reduced to chromous chlorid.

10. A continuous process for making chromous chlorid comprising electrolyzing a solution of chromic chlorid in a cell having separate anode and cathode compartments and regulating the flow of chromic chlorid into the electrolytic cell by means of the hydrogen evolved.

11. A continuous process for making chromous chlorid comprising electrolyzing a concentrated solution of chromic chlorid containing a small amount of free hydrochloric acid, in a two compartment cell, using a spongy lead cathode, stirring the solution during electrolysis and automatically regulating the flow of chromic chlorid into the electrolytic cell by the hydrogen evolved.

12. A process of reducing chromic chlorid to chromous chlorid consisting in passing an electric current through a chromic chlorid solution in a cell having separate anode and cathode compartments, the amperage of said current being such as will give an evolution of hydrogen equal to 3–4% of the total hydrogen which would be evolved by said current if none of the hydrogen were used for reduction.

MAURICE C. TAYLOR.