July 29, 1969 M. P. GROTHEER ET AL 3,458,411

ELECTROLYTIC METHOD FOR ELECTROLYSIS OF HYDROCHLORIC ACID

Filed Jan. 30, 1967 3 Sheets-Sheet 1

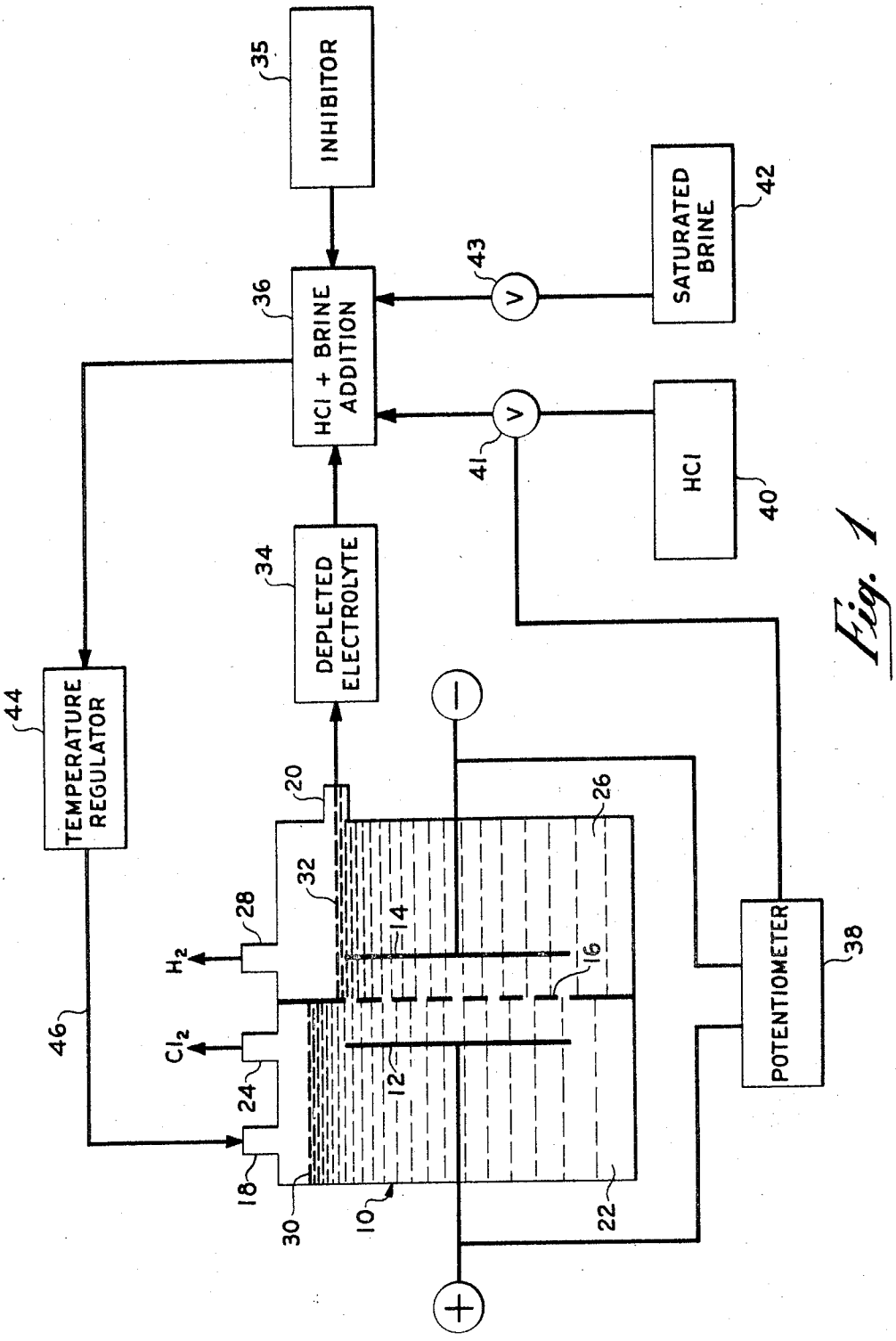


Fig. 1

ELECTROLYTIC METHOD FOR ELECTROLYSIS OF HYDROCHLORIC ACID

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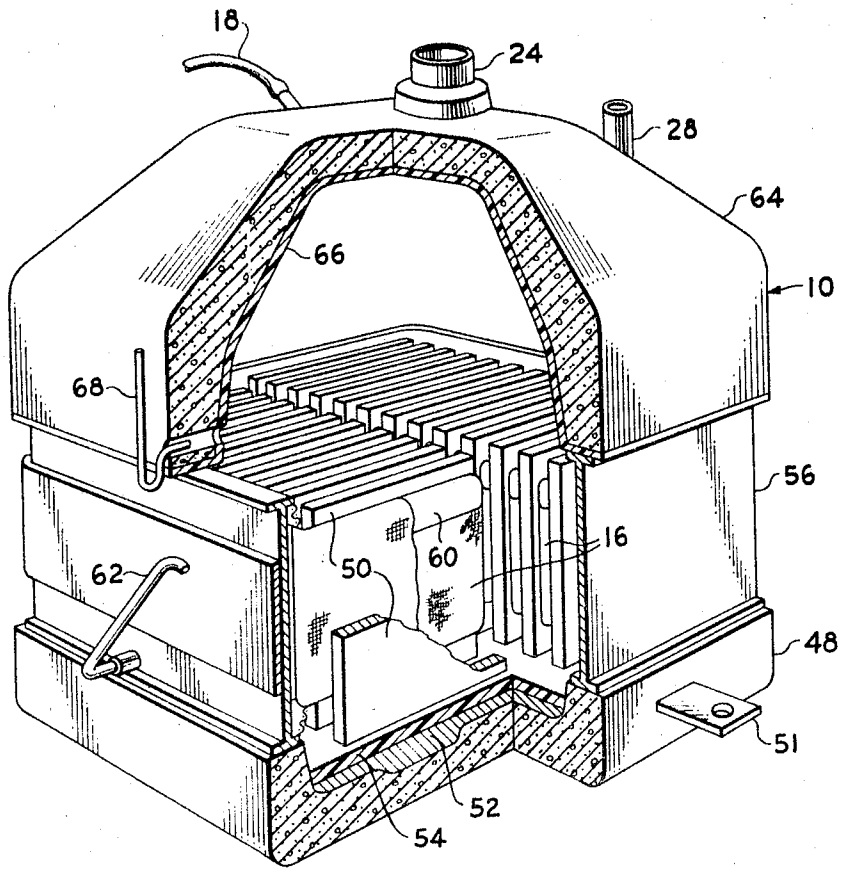


Fig. 2

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ELECTROLYTIC METHOD FOR ELECTROLYSIS OF HYDROCHLORIC ACID

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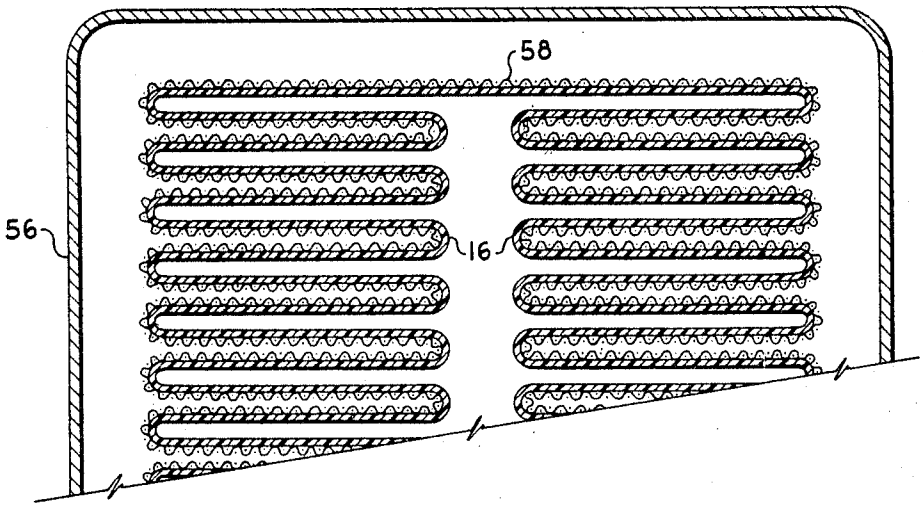


Fig. 3

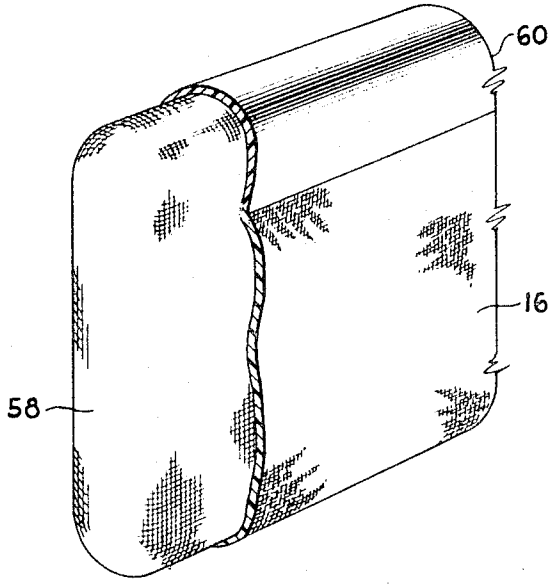


Fig. 4

United States Patent Office 3,458,411 Patented July 29, 1969

3,458,411

ELECTROLYTIC METHOD FOR ELECTROLYSIS OF HYDROCHLORIC ACID

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Continuation-in-part of application Ser. No. 393,171, Aug. 31, 1964. This application Jan. 30, 1967, Ser. No. 612,660

Int. Cl. B01k 3/10

U.S. Cl. 204—128 13 Claims

ABSTRACT OF THE DISCLOSURE

Hydrochloric acid is electrolyzed in a diaphragm type electrolytic cell in which the cell top is protected from the corrosive effect of the acidic cell contents by an acid resistant liner or coating. A porous plastic, acid resistant diaphragm separates the anode compartment from the cathode compartment. The electrolysis is performed at a relatively dilute hydrochloric acid concentration optionally in the presence of a support electrolyte. A corrosion inhibitor may be employed to further protect the cathode from attack by the acidic electrolyte. The primary, secondary and tertiary amines and hydroxyl amines are exemplary corrosion inhibitors and also function as depolarizers in the electrolytic cell.

This is a continuation-in-part of copending application S.N. 393,171, filed Aug. 31, 1964, now abandoned.

This invention relates to an apparatus and a method for the electrolysis of hydrochloric acid. More particularly, this invention relates to a diaphragm cell and a method for the electrolysis of hydrochloric acid possessing advantages over previously known cells and methods.

Hydrochloric acid is a by-product of numerous chlorination procedures, and as such it must be disposed of by sale or further chemical reaction. It is often desirable to form more useful and salable products from hydrogen chloride by converting it to hydrogen and chlorine. The demand for chlorine is such that it is readily disposed of by sale or used in further chlorination reactions.

Various electrolytic cells for the electrolysis of hydrochloric acid are known, but they have only achieved limited commercial acceptance. This is most likely due to the slow development of a good commercial cell, the fluctuating demand for such a cell due to varying market conditions, the limited use thereof, and the high investment cost for such cells. The electrolysis of hydrochloric acid presents many unique problems because of the highly corrosive electrolyte used and the environment existing in an operating cell, and therefore the hydrochloric acid cell has been specially constructed for this purpose.

It is an object of this invention to provide an electrolytic cell for the decomposition of hydrochloric acid to hydrogen and chlorine. Another object of this invention is to provide a method for the electrolysis of hydrochloric acid in an electrolytic cell having a graphite anode and a cathode of metal. A further object of this invention is to provide a diaphragm for the described electrolytic cell useful with metal cathodes and resistant to the acidic environment without shrinkage, tightening, or plugging. Yet another object is to provide a method of inhibiting corrosion of the cathode by means in addition to the normal cathodic protection provided by the negative charge. Yet a further object is to provide a method for depolarizing the electrolytic cell of this invention. Still another object is to provide a method of converting a cell normally used for the electrolysis of brine to a cell useful

for the electrolysis of hydrochloric acid. These and other objects will become apparent to those skilled in the art from a description of the invention.

In accordance with the invention, a method for producing hydrogen and chlorine from hydrochloric acid is accomplished in an electrolytic cell having a metal cathode and a graphite anode by feeding an aqueous solution of hydrochloric acid and alkali metal chloride into the cell, passing the aqueous solution through a porous plastic diaphragm means separating the anode and the cathode, imposing a decomposition voltage across the cell to yield chlorine at the anode and hydrogen at the cathode and withdrawing a depleted catholyte from the cell.

The present invention has distinct advantages over prior hydrochloric acid cells. It is readily converted to a cell for the electrolysis of brine and the production of caustic in accordance with raw material demands. In addition, this particular cell does not require a large additional investment where chlor-alkali cells are already used since a conversion of brine-caustic cell to a hydrochloric acid cell can be made. Thus, chlor-alkali cells can be modified by the methods of this invention to electrolyze either brine or hydrochloric acid as the demand warrants. In addition, the efficiency of the present hydrochloric acid cell is extremely high, ranging from 95% to 99%, based on current input.

The electrolytic cell in the present invention is constructed of a base plate normally of concrete to which the anodes are secured, a center portion to which the cathode is secured and a cover for sealing the cell. It is preferred to secure the anodes to the base plate, using a conductive metal such as lead, copper, bronze, and the like, to hold the anodes in position. The conductive metal is in electrical communication with the exterior of the cell, but is sealed from the interior of the cell by an inert non-conductive material so as to eliminate leakage of electrolyte to the base plate during cell operation. Sealants such as asphalt, polyester resins, polyvinyl chloride, polytetrafluoroethylene, and like compositions inert to hydrochloric acid, chlorine gas and temperatures up to one hundred degrees centigrade are used. The seal is complete with respect to the concrete and conductive metal such that in an assembled condition neither concrete nor metal is exposed to electrolyte.

The center portion of the cell is a part of the cathode, and is preferably constructed of a metal or a metal alloy, as is the rest of the cathode. The cathode may be constructed of any metal conductor which is commonly used by those skilled in the art for this purpose. Some of the materials which may be used include the metals of Group I–B of the periodic table—copper, silver, and gold; cadmium; the metals of Group VI–B of the Periodic Table—chromium, molybdenum, and tungsten; the metals of Group VII–B of the Periodic Table—manganese, technetium, and rhenium; iron; ruthenium; cobalt; rhodium; iridium; nickel; palladium; and alloys of the aforementioned metals such as Stellite alloys (which are comprised of cobalt, chromium, carbon, and iron); gold alloys; wrought iron (which is comprised of 98.5% iron); steel (which is comprised of 99% iron and 1% carbon); stainless steel alloys (which are comprised of iron, chromium, carbon, and manganese; Enduro alloys (which are comprised of iron, chromium, silicon, and carbon, and may additionally contain nickel and/or manganese); Duraloy alloys (which are comprised of iron, chromium, and manganese); Ascoloy alloys (which are comprised of iron, chromium, manganese, nickel, silicon, and carbon); Sweetaloy alloys (which are comprised of iron, chromium, manganese, and nickel); Durimet alloys (which are comprised of iron, nickel, silicon, and carbon); Invar al-

loys (which are comprised of iron, nickel and carbon); tungsten steel (which is comprised of iron, tungsten, and carbon); Duriron (which is comprised of iron, silicon, carbon, and manganese); Chromel alloys (which are comprised of nickel and chromium); Nichrome alloys (which are comprised of nickel and chromium); Monel metals (which are comprised of nickel, copper, and iron); Hastelloy alloys (comprised of nickel); Incaloy alloys; and the like. It is to be understood that this list is merely exemplary, and a detailed description of the compositions and properties of the aforementioned alloys as well as a description of other alloys which are operative may be found on pages 830–838 of the Eighth Edition of Lange's Handbook of Chemistry. On pages 56–57 of said Handbook may be found the periodic chart to which the inventors have referred in describing the classes of metals which are operative.

It is preferred to have the cathode constructed of a metal selected from the group consisting or iron, nickel, copper, gold, platinum, silver, steel, nickel plated steel, nickel alloy, stainless steels, Monel metals and Hastelloy alloys, and it is even more preferred to have the cathode constructed of a metal selected from the group consisting of iron, nickel, copper, steel, stainless steels, Monel metals, Hastelloy alloys, nickel plated steel, and nickel alloy.

Attached to the cathode or center portion of the electrolytic cell is an overflow pipe, often referred to as a perc pipe, through which depleted electrolyte exits from the cell. The overflow pipe also regulates the liquid level in the cathode portion of the cell. The overflow pipe is normally not cathodically protected and, therefore, it is preferable to use an inert plastic or other non-conductive, chemically resistant material. Plastics similar to those used in the cell cover are preferably used in the construction of the overflow pipe, especially polyesters, phenolic resins and epoxy resins, used with or without reinforcing.

The top portion of the cell is constructed of concrete or metal such as iron, steel, and similar materials. The internal portion of the cell cover is coated with a plastic resistant to the environment, chlorine gas and hydrogen chloride. The plastic coating is applied so as to adhere permanently to the cover or is used as a preformed removable insert for the cover, or a combination of both methods may be employed.

Several acid and chlorine resistant plastic materials have been found to be suitable protective liners for the cell cover. Reinforced, non-reinforced or filled polyesters, phenolic resins, Teflon (polytetrafluoroethylene), polypropylene, polyethylene, polyvinyl chloride, and the like, have been found to be suited for this application. Polyesters manufactured under the trade name of Hetron® are particularly suitable.

In addition to lining or coating the concrete or steel cell cover with plastic material inert to the environment existing in the cell, a cover constructed entirely of reinforced polyester, reinforced epoxy resin, or the like inert materials can be used. When using a cell cover constructed entirely of polyester or the like material, it is preferred to provide a means of securing the cell cover to the cell. The light weight construction such as that provided by a polyester is often insufficient to provide a secure seal to prevent electrolyte leakage without a fastening means or additional weight to hold the cover in place.

The electrodes of the present invention comprise an anode constructed of graphite and a cathode constructed of one or more of the materials hereinbefore described as being suitable for this purpose.

The mesh construction is preferred because mesh provides a ready exit for the hydrogen gas evolved.

Interposed between the anode and the cathode is an electrolyte-permeable plastic diaphragm. The diaphragm is preferably a woven synthetic fabric prefabricated or tailored to fit the cathode like a glove. The porous diaphragm is further defined in terms of water porosity. The weave, fiber size and other characteristics are such so as to provide a fabric having a water porosity of 0.01 to 2.0 gallons per minute per square foot, using a constant liquid pressure equal to ten inches of water.

The diaphragm itself is constructed of woven synthetic fabric which is acid and chlorine resistant at temperatures up to one hundred degrees centigrade. Materials such as polytetrafluoroethylene, polypropylene, polyvinyl chloride, polyvinylidene chloride, rechlorinated polyvinyl chloride, and similar halogenated polymers, mixed halogenated polymers and non-halogenated polymers, resistant to the environment are preferred. The portion of the diaphragm covering the uppermost portion of the cathode need not be porous, and it is even preferred that it be non-porous to prevent hydrogen gas produced at the cathode from rising through the diaphragm.

The cell is operated in a continuous manner by the addition of hydrochloric acid solution and replenishing amounts of sodium chloride. The start-up procedure for the cell is somewhat modified from normal operation in that the normal feed stream is not used. During start-up, the cathode must be protected from contacting excess hydrogen chloride and therefore the electrolysis commences with an alkali metal chloride solution. Hydrochloric acid is then added so as to reduce the anolyte pH to less than one. The addition rapidly neutralizes the caustic produced in the catholyte during the initial start-up and reduces the pH of the catholyte to an acidic condition. Having commenced electrolysis by imposing a decomposition voltage across the cell, chlorine is liberated at the anode and hydrogen is liberated at the cathode. The feed mixture is then regulated so as to comprise a saturated solution of sodium chloride and about a 1 to 20 percent hydrochloric acid solution. The hydrochloric acid addition is regulated so as to maintain an acidic catholyte containing up to about 20 grams per liter hydrochloric acid or a pH of less than 7.

During the operation of the cell, hydrochloric acid and recycled sodium chloride solution are fed into the cell so that they flow from the anode to the cathode and, subsequently, are withdrawn through the overflow as depleted electrolyte. The concentration of hydrochloric acid fed to the cell is regulated so as to maintain hydrochloric acid concentration of less than about 20 grams per liter in the catholyte. Regulation of the hydrogen chloride content in the catholyte is readily effected by observation of the cell voltage from which the hydrochloric acid content of the catholyte can be determined and changed when desired. The cell voltage is directly related to the pH of the catholyte. At low pH's, the reaction voltage is lower than at higher pH's. Thus, by using a potentiometer to control the flow of hydrochloric acid in the feed liquor, the amount of hydrochloric acid in the catholyte is readily maintained at a preferred level. This flexibility in the supply of feed liquor permits the use of a wide range of hydrochloric acid concentrations which can be automatically regulated in the feed stream according to the reaction voltage.

It has been found that the presence of small amounts of hydrochloric acid in the catholyte as described has several distinctive advantages in the present electrolysis procedure. The more important advantages are the lack of chlorate formation, a higher anode efficiency resulting in lower graphite consumption and a lower cell voltage than that obtained in chlorine-caustic cells.

The cell voltage varies as a function of the acidity of the catholyte. A low pH results in lower voltages while increasing pH values result in higher voltages. It is therefore preferred to operate the present cell with a low catholyte pH. Under such conditions the cell efficiency is extremely high, being capable of producing chlorine at a lower kilowatt-hour rate per pound of chlorine than the most efficient chlor-alkali cells.

Highly efficient operation of the present cell is effected over a wide range of current densities. Amperage in the

range of 0.5 to 3.0 and more amps per square inch have been found to be particularly useful and are preferred.

The alkali metal chloride present in the feed solution serves to maintain the electrolyte highly conductive, and this permits a reduction of the hydrogen chloride concentration to a low level in passing through the cell. Efficient operation of the cell is therefore aided by the presence of the highly ionized alkali metal chloride.

As a means of further protecting the cathode so as to provide for the use of more concentrated hydrochloric acid solutions, a corrosion inhibitor can be used. It has been found that amines are suitable corrosion inhibitors which do not interfere with the electrolysis. The amines particularly useful as corrosion inhibitors under electrolysis conditions are of the formulae

$$R\text{—}NHA,\ R_1\text{—}\underset{\displaystyle R_2}{\underset{|}{N}}A,\ \text{and}\ R_3\text{—}\underset{\displaystyle R_4}{\underset{|}{N}}\text{—}R_5$$

wherein:

(a) A is selected from the group consisting of hydrogen and hydroxy;

(b) R is selected from the group consisting of alkyl of 2 to 12 carbon atoms and alkylol of 2 to 12 carbon atoms;

(c) R_1 and R_2 are selected from the group consisting of alkyl of 2 to 6 carbon atoms and alkylol of 2 to 6 carbon atoms; and

(d) R_3, R_4, and R_5 are selected from the group consisting of alkyl of 1 to 4 carbon atoms and alkylol of 1 to 4 carbon atoms.

Some of the primary amines which are within the scope of this invention include, e.g., butylamine, propanolamine, hexylhydroxylamine, nonylamine; and the like. When a primary amine is used, it is preferred that it have from about 2 to about 12 carbon atoms, and it is even more preferred that it have from about 3 to about 9 carbon atoms.

Some of the secondary amines which are within the scope of this invention include, e.g., dipropylamine, dihexylamine; propylbutanolamine; dipropylhydroxylamine, propylbutylhydroxylamine, propylhexylamine; pentanolpropylamine, dihexylamine; butylhexylamine, diethylamine, butylpentylhydroxylamine; and the like. When a secondary amine is used, it is preferred that each chain thereof contain from about 2 to about 6 carbon atoms.

Some of the tertiary amines which are within the scope of this invention include trimethylamine, triethylamine, tributylamine; tripropylamine; triethanolamine; ethyldiethanolamine; dipropanolethylamine; tributanolamine, butanoldiethylamine; and the like. When a tertiary amine is used, it is preferred that each chain thereof have from about 1 to about 4 carbon atoms. It is preferred to use tertiary amines, especially trimethylamine, triethylamine, tripropylamine, trimethanolamine, triethanolamine, and tripropanolamine.

Said amines may be used at a concentration of from about 0.1 gram per liter of feed liquor to about 25 grams per liter of feed liquor, though it is preferred to use from about 1 gram per liter to about 15 grams per liter. Thus, when the preferred concentration of amine is employed, the combined feed liquor for the hydrochloric acid cell hereinbefore described will be comprised of from about 5 to about 20 percent of hydrochloric acid, from about 1 to about 20 percent of alkali metal chloride, from about 0.5 to about 1.5 percent of corrosion inhibitor, most of the remainder of said feed liquor is comprised of water.

The inventors have discovered that, when the aforementioned corrosion inhibitors are used in the aforementioned hydrochloric acid cell, they surprisingly exert a depolarizing effect, and the cell voltages needed to decompose the electrolyte are significantly lower than those in systems wherein said corrosion inhibitors are not present. For example, in the case of a cell with an uninhibited electrolyte, a cell voltage of 3.9 to 4.0 volts was needed to decompose a 1 gram/liter hydrochloric acid solution at a current density of 3 amperes/square inch; but when an inhibitor was used, under essentially the same conditions, a cell voltage of only 3.2 volts was required.

The inventors are not sure how said amines exert a depolarizing effect. It is apparent, however, that said depolarizing effect will occur whenever said corrosion inhibitors are added to a cell wherein the electrolyte is aqueous. This effect is especially pronounced in aqueous electrolyte systems wherein the catholyte is acidic.

The method and apparatus of this invention will be further described with reference to the drawings in which:

FIG. 1 is a partial schematic and flow sheet illustrating the method of this invention;

FIG. 2 is a partially cutaway elevated view of an electrolytic cell of this invention;

FIG. 3 is a partial sectional view of the cathode of the electrolytic cell; and

FIG. 4 is an elevated and partial view of a cathode section of this invention.

The combination schematic and flow sheet illustrating the method of this invention shows a schematic view of the electrolytic cell **10**, comprising a graphite anode **12**, and a steel cathode **14**, separated by a porous, woven plastic diaphragm **16**. The cell **10** has an inlet **18** for acidic electrolyte, an outlet **20** for depleted electrolyte, an anolyte chamber **22**, having an outlet **24** for chlorine gas and a catholyte chamber **26** having an outlet **28** for hydrogen gas produced in the catholyte chamber **26**. The anolyte level **30** is slightly higher than the catholyte level **32**, thereby producing a slightly forced flow of electrolyte through the diaphragm **16** from the anolyte chamber **22** to the catholyte chamber **26**. Chlorine gas is produced at the anode **12** and hydrogen gas is produced at the cathode **14** by imposing a decomposition voltage across the electrodes.

Depleted electrolyte **34** flows from the catholyte chamber **26** to replenishing zone **36** where it is replenished with hydrochloric acid and resaturated with alkali metal chloride. Potentiometer **38** measures the cell voltage and thereby regulates the flow of concentrated hydrochloric acid **40** to replenishing zone **36** by controlling valve **41** in response to a cell voltage signal. The replenishment of brine is nominal and is controlled by constant or periodic additions of saturated brine **42** through valve **43**. Properly replenished electrolyte from replenishing zone **36**, into which a corrosion inhibitor is added from zone **35**, flows through temperature regulator **44** wherein the acidic electrolyte is heated or cooled as may be required so as to result in the desired electrolyte temperature within cell **10** of fifty degrees centigrade to about one hundred degrees centigrade. Lower temperatures can be used being limited only by practical operating rates. The electrolyte then flows via line **46** to re-enter cell **10** at inlet **18**.

It will be noted that the present process is a continuous cyclic process wherein all the products are gaseous, e.g., chlorine and hydrogen. The replenishment of brine or alkali metal chloride within the system is relatively small because caustic is not produced and alkali metals are not removed from the system.

The apparatus of this invention is more fully described by reference to FIGS. 2, 3 and 4. The electrolytic cell of this invention comprises a base plate or bottom **48** to which are secured anodes **50** by means of a conductive metallic material **52** such as lead, copper, brass, and the like. The conductive metal is preferably poured in molten form about the base of the anodes **50**, thereby securing them in position while also forming a low resistance connection to an external bus bar **51**. A sealant **54** is placed over the conductor so as to completely seal the conductor **52** and cell bottom **48** from electrolyte.

The center section **56** of cell **10** houses a cathode having internal finger-like projections **58** covered with a diaphragm **16** which fit between anode **50**. The internal portion of the finger-like projections **58** is hollow, permitting the passage of gas and electrolyte therethrough. Fitting securely about and around the finger-like projections **58** is a porous plastic diaphragm **16**, the upper portion of which is preferably a non-porous plastic material **60** such as woven plastic fabric that has been fused to a non-porous state. This provides a sealed channel for the flow of hydrogen gas and prevents leakage to the anolyte chamber.

Projecting from the center section **56** is the overflow pipe **62** which regulates the level of catholyte **32** in the catholyte chamber **26**. The overflow pipe **62** is constructed of a corrosion resistant material as previously described. Also projecting from center section **56** is hydrogen gas outlet **28**.

The top of the cell **10** is covered by cell top **64** having a plastic liner **66** which covers the internal surface of the cell top and prevents gaseous chlorine and anolyte from contacting parts of cell top **64** which are not inert to chemical attack. Projecting from cell top **64** is the chlorine gas outlet **24**, electrolyte inlet **18** and the sight glass **68**. Sight glass **68** permits observation of the anolyte level **30** in the anolyte chamber **22**.

The following example illustrates certain preferred embodiments in the present invention. Unless otherwise indicated all parts and percentages are by weight and all temperatures are in degrees centigrade.

Example 1

Using the electrolytic cell illustrated in FIG. 2 comprising graphite anodes and steel mesh cathodes, a woven polypropylene diaphragm having a water porosity of 0.9 gallon per minute per square foot at 10 inches of water pressure was fitted securely about the cathode. A reinforced polyester cell top liner constructed of Hetron 72®, was molded into the concrete cell top. The cell was so constructed as to prevent exposure of the concrete cell bottom to electrolyte and the concrete cell top to chlorine gas and electrolyte.

Cell operation was commenced by charging an 8 percent sodium chloride solution to the cell and applying a current density of 0.8 ampere per square inch, equal to 30,000 amperes, to the electrodes. Having commenced electrolysis, an acidic feed solution comprising 12 percent hydrogen chloride, 8 percent sodium chloride and 0.5 percent triethanolamine was fed into the anolyte chamber at a rate of 1.4 gallons per minute. The alkaline condition which developed in the cathode chamber on start-up was rapidly reduced to an acidic condition having a pH of about 1 and a hydrogen chloride content of 3.0 grams per liter. The cell voltage was 2.1 volts, the pH of the feed solution was less than 1. Chlorine was produced at the anode at a rate of 85.7 pounds per hour while hydrogen was produced at the cathode.

Depleted catholyte withdrawn from the catholye chamber was replenished with hydrochloric acid to a 12 percent concentration using 24 percent hydrochloric acid solution and was resaturated with sodium chloride, using a 16 percent sodium chloride solution. Additional amine was added to retain a 0.5 percent level. The replenishing feed solution was then recycled to the cell for further decomposition of hydrochloric acid.

Examples 2 through 13

Changes in operating current density and the effect of hydrogen chloride concentration in the catholyte were studied to determine the effect on the cell voltage and to establish the preferred operating conditions. The experiments were conducted using a laboratory cell constructed as illustrated in FIG. 1, operating with a feed solution of 12 percent hydrogen chloride and 8 percent sodium chloride at a temperature of 98.5 degrees centigrade ±0.5 degrees centigrade. Nickel plated steel mesh cathodes and graphite anodes were used, spaced so as to provide a one-fourth inch electrode gap. A polypropylene diaphragm having a porosity of 1.0 gallon of water per minute per square foot at 10 inches of water pressure, was inserted between the electrodes so as to restrict the flow of electrolyte from the anode to the cathode. The results for a series of experiments under the stated conditions are tabulated in Table I.

TABLE I

Example No.	Current density (amps per in.²)	HCl catholyte concentration (g./l.)	Cell voltage (volts)
2	3	0.40	3.87
3	3	1.46	3.28
4	3	2.94	2.74
5	2	0.73	2.93
6	2	2.70	2.64
7	2	3.67	2.25
8	1	0.73	2.51
9	1	2.70	2.00
10	1	3.85	1.90
11	0.87	1.04	3.42
12	0.87	3.31	1.92
13	0.87	5.00	1.83

From Examples 2 through 13 it is readily seen that highly efficient cell operation is achieved over a wide range of current densities. It is also seen that lower cell voltages are obtained under the more acidic catholyte conditions as indicated by the concentration of HCl in the catholyte.

The method of the Example 1 was repeated varying the feed concentrations of hydrochloric acid between 5 percent and 20 percent, and varying the temperature between about 50 degrees centigrade and 100 degrees centigrade. Various amine inhibitors, including trimethylamine, triethylamine, trimethanolamine and triethanolamine, were used in amounts ranging from 1 gram per liter to 15 grams per liter feed solution. In all processes, the feed rate of the electrolyte to the anolyte chamber was controlled so that the amount of hydrochloric acid in the catholyte did not exceed about 20 grams per liter. The examples were also repeated using woven Teflon (polytetrafluoroethylene) and rechlorinated polyvinyl chloride as the diaphragm fabric. Nickel plated steel mesh and nickel alloy mesh were also used as the cathode. It was found that the care in start-up and shut-down of the electrolytic cell to prevent acid attack on the cathode did not have to be as great when using nickel plated steel mesh or nickel alloy as the cathode material. Similarly good results are obtainable when, in place of nickel plated steel mesh or nickel alloy, the cathode material is constructed of a metal selected from the group comprising iron, nickel, copper, steel, stainless steels, Monel metals, and Hastelloy alloys.

In Examples 14–18, the depolarizing effect of the corrosion inhibitors of this invention was determined. The experiments were conducted with two laboratory cells constructed as illustrated in FIG. 1, each cell being operated with a nickel plated 6″ x 6″ mesh steel cathode. The electrolyte of one cell was comprised of 1.32 grams of hydrochloric acid per liter and 5 grams per liter of triethanolamine corrosion inhibitor. The electrolyte of the second control cell was comprised of 1.8 grams of hydrochloric acid per liter and no inhibitor. The current density per square inch of cathode was varied, and the cathode potential was noted. A summary of the results noted follows:

Example	Amperes/square inch	Cathode potential vs. saturated calomel electrode with 1.32 g./l. of HCl and 5 g./l. inhibitor	Cathode potential vs. saturated calomel electrode with 1.8 g./l. of HCl and no inhibitor
14	1.0	−0.8	−0.8
15	1.5	−0.98	−1.30
16	2.0	−1.14	−1.40
17	2.5	−1.28	−1.46
18	3.0	−1.36	−1.50

Similar results are obtainable when amines such as trimethylamine, ethyldiethanolamine, butanoldiethylamine, tripropanolamine, tributylamine, triethylamine, diethanolmethylamine, and the like are used instead of triethanolamine, and when said amines are used with other aqueous electrolytes.

Example 19

The cell used in Examples 14–18 was operated at a current density of 125 amperes per square foot with a nickel-plated cathode. 5 grams/liter of triethanolamine inhibitor were added to the catholyte. When the catholyte was comprised of 2 grams per liter of hydrogen chloride, the cell voltage was 1.9 volts. When the catholyte was comprised of 1 gram per liter of hydrogen chloride, the cell voltage was 2.4 volts.

In all of the tests conducted, using the variables and within the ranges described, the hydrochloric acid cell of this invention functioned extremely efficiently.

While there have been described various embodiments of the invention, the apparatus and methods 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 further 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 producing hydrogen and chlorine in an electrolytic cell having a graphite anode and a metal cathode wherein the metal on said cathode is selected from the group consisting of the metals of Groups I–B, VI–B, VII–B, and VIII of the Periodic Table and the alloys thereof, and having a porous plastic diaphragm separating said anode from said cathode, comprising:
   (a) feeding an aqueous solution of hydrochloric acid and alkali metal chloride into an electrolytic cell;
   (b) passing the feed solution through the porous plastic diaphragm;
   (c) maintaining an anolyte pH of less than one;
   (d) imposing a decomposition voltage across the electrodes to yield chlorine at the anode and hydrogen at the cathode; and
   (e) withdrawing a depleted caustic-free catholyte from the cell.

2. The method of claim 1, wherein the aqueous solution comprises from about 1 to about 20 percent hydrochloric acid, and from about 1 to about 20 percent of alkali metal chloride.

3. The method of claim 2, wherein:
   (a) the feed solution has a pH of less than 1;
   (b) the depleted catholyte has a pH of less than 7 and contains less than 20 grams per liter of hydrogen chloride;
   (c) the cathode is foraminous;
   (d) the plastic diaphragm is constructed of a plastic material selected from the group consisting of polypropylene, polytetrafluoroethylene, polyvinylidene chloride, and rechlorinated polyvinyl chloride, and said diaphragm is designed to fit securely about the cathode.

4. The method of claim 3, wherein the metal of said cathode is selected from the group consisting of iron, nickel, copper, steel, stainless steels, Monel metals, Hastelloys, nickel plated steel, and nickel alloy.

5. The method of claim 4, wherein the metal of said cathode is selected from the group consisting of steel, nickel plated steel, and nickel alloy.

6. The method of claim 1, wherein the aqueous feed solution is comprised of hydrochloric acid, an alkali metal chloride, and a compound selected from the group consisting of



wherein:
   (a) A is selected from the group consisting of hydrogen and hydroxy;
   (b) R is selected from the group consisting of alkyl of 2 to 12 carbon atoms and alkylol of 2 to 12 carbon atoms;
   (c) R_1 and R_2 are selected from the group consisting of alkyl of 2 to 6 carbon atoms and alkylol of 2 to 6 carbon atoms; and
   (d) R_3, R_4, and R_5 are selected from the group consisting of alkyl of 1 to 4 carbon atoms and alkylol of 1 to 4 carbon atoms.

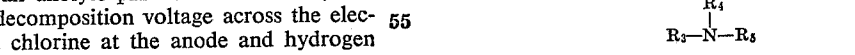
7. The method of claim 3, wherein the aqueous feed solution is comprised of hydrochloric acid, alkali metal chloride, and a compound selected from the group consisting of trimethylamine, triethylamine, tripropylamine, trimethanolamine, triethanolamine, and tripropanolamine.

8. A method of depolarizing electrolytic cells, comprising adding to the aqueous electrolyte of said cells an effective amount of a compound selected from the group consisting of



wherein:
   (a) A is selected from the group consisting of hydrogen and hydroxy;
   (b) R is selected from the group consisting of alkyl of 2 to 12 carbon atoms and alkylol of 2 to 12 carbon atoms;
   (c) R_1 and R_2 are selected from the group consisting of alkyl of 2 to 6 carbon atoms and alkylol of 2 to 6 carbon atoms; and
   (d) R_3, R_4, and R_5 are selected from the group consisting of alkyl of 1 to 4 carbon atoms and alkylol of 1 to 4 carbon atoms.

9. The method of claim 8, wherein said compound is of the formula



wherein R, R, and R are as hereinbefore described.

10. The method of claim 8, wherein from about 1 to about 15 grams of said compound is added per liter of electrolyte.

11. The method of claim 8, wherein R is selected from the group consisting of alkyl of 3 to 9 carbon atoms and alkylol of 3 to 9 carbon atoms and from about 0.1 to about 25 grams of said compound is added per liter of aqueous electrolyte.

12. The method of claim 11, wherein said compound is selected from the group consisting of trimethylamine, triethylamine, tripropylamine, trimethanolamine, triethanolamine, and tripropanolamine.

13. The method of claim 12, wherein the electrolyte to which said compound is added is comprised of hydrogen chloride.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,458,411 Dated July 29, 1969

Inventor(s) M. P. Grotheer et al.

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

Column 8, Table I, Example No. 11, under "Cell voltage" delete "3.42" and insert--"2.42"--;

Column 10, Claim 8, lines 36 to 39, correct the structural formula in the third amine depicted to insert a valence bond between "N" and "R_5".

SIGNED AND
SEALED
MAR 10 1970

(SEAL)
Attest:

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Commissioner of Patents