United States Patent Office 3,756,930 Patented Sept. 4, 1973

3,756,930

ELECTROLYTIC RECOVERY OF CHLORINE AND HYDROGEN FROM AQUEOUS HYDROCHLORIC ACID

Guenther Weiss, Wachenheim, and Heinz Weller and Ewald Wygasch, Ludwigshafen, Germany, assignors to Badische Anilin- & Soda-Fabrik Aktiengesellschaft, Ludwigshafen (Rhine), Germany

No Drawing. Filed June 28, 1971, Ser. No. 157,766
Claims priority, application Germany, July 28, 1970, P 20 33 802.7
Int. Cl. C01b 7/06, 13/02
U.S. Cl. 204—129 3 Claims

ABSTRACT OF THE DISCLOSURE

Aqueous hydrochloric acid is electrolyzed in a diaphragm cell to recover chlorine and hydrogen therefrom. The acid to be electrolyzed should have a concentration of from 18 to 28% by weight of HCl and should be degraded by not more than 2% by weight during its passage through the cell. The mean temperature in the cell is kept at from 75° to 90° C.

In the chlorinating substitution of organic compounds, half of the chlorine originally used is obtained as hydrogen chloride. Since this cannot always be used and nowadays disposal thereof with effluents is often out of the question, the need for recovery of the chlorine from hydrogen chloride gains continually in importance. Two methods have been adopted: hydrogen chloride is oxidized with air or oxygen in the presence of catalysts, or hydrochloric acid is first formed from the gaseous hydrogen chloride by absorption and the resultant acid is subjected to electrolytic decomposition to recover chlorine and hydrogen. These methods of recovering chlorine differ from the widely used chlor-alkali method in that it is possible to produce chlorine without the simultaneous production of alkali and therefore the alkali-chlorine balance is not affected.

In the electrolytic recovery of chlorine from aqueous hydrochloric acid, which is preferably carried out in diaphragm cells, the energy consumption plays a significant part as in all electrochemical processes. There has therefore been no lack of attempts in the course of the years to decrease the consumption of energy as far as possible by decreasing the achievable cell potential.

This object may be achieved for example by appropriate choice of the diaphragm which prevents mixing of the gases formed on the cathode and anode sides but does not impede the flow of current. Another possibility is to decrease the resistance in the electrolyte by carrying out the electrolysis in the region of maximum conductivity of hydrochloric acid, or to decrease the hydrogen overvoltage at the graphite cathodes generally used. The hydrogen overvoltage may be lowered for example in known manner by adding certain metals to the electrolyte, the added metal cations being deposited in the course of the electrolysis on the cathodes and the electrolytic decomposition takes place at the layers of the electrodes thus activated with a decrease in the overvoltage. Metals of the platinum group, copper, nickel, antimony, silver, molybdenum and cobalt are preferred as metals and they may be added to the electrolytes either batchwise or continuously.

In carrying out the hydrochloric acid electrolysis, acids having an HCl concentration of more than 20% up to about 26% by weight are used. The rate of flow of the acid is controlled so that a concentration gradient between the acid introduced into the electrolyzer and the acid withdrawn of more than 3% by weight, for example of 5% by weight, is maintained. Since there is no freedom as regards the temperature of the acid leaving the cell because of its HCl partial pressure (generally a temperature of the effluent acid of 80° C. should not be exceeded) it is necessary to cool the acid strongly before it enters the cell. In this way the mean temperature in the cell is kept fairly low. The temperature range used is therefore one in which the hydrochloric acid has a low conductivity so that an increased amount of energy has to be used.

We have now found that the electrolysis of hydrochloric acid can be carried out with economically favorable current consumption and low potential and without adding substances to decrease the overvoltage when the acid to be electrolyzed has a concentration of from 18 to 28% by weight of HCl, the acid electrolyzed is degraded to the extent of not more than 2% by weight of HCl and the mean temperature of the acid in the cell is kept at from 75° to 90° C.

The acid being electrolyzed is preferably degraded by from 0.5 to 1.6% by weight.

The low degradation of the hydrochloric acid is achieved by passing the acid to be electrolyzed at an increased rate of flow through the cathode and anode chambers at the known and conventional current densities of from 2000 to 5000 amperes per square meter. In this way it is possible to eliminate the resistance produced by the gas bubbles forming at the electrodes, as the bubbles are rapidly detached from the cathode and anode and entrained. A considerable decrease in the cell potential is thus achieved by simple means.

Another advantage of the method in accordance with the invention is that it is possible to use a higher mean cell temperature. Because of the increased throughput of acid it is possible to allow the acid to enter at a relatively high temperature and a further gain of potential is achieved because of the higher conductivity of hydrochloric acid at increasing temperatures.

The following example illustrates the invention.

EXAMPLE

(A) A 25% by weight hydrochloric acid is passed through a diaphragm cell (having an anode area of 2.32 $m.^2$ and consisting of thirty successive individual cells) at such a rate that the concentration of the degraded acid leaving the cell is 21.5%. At a current of 9400 amperes a cell potentail of 2.25 volts is measured. The mean temperature of the acid is 65° C.

(B) If the acid being electrolyzed is degraded from 25% by weight to only 23.5% by weight, the cell potential is 2.03 volts at a mean temperature of the acid in the cell of 77° C.

We claim:

1. In a process for the electrolytic recovery of chlorine and hydrogen by continuous flow of aqueous hydrochloric acid through a diaphragm cell having anode and cathode chambers maintained at a current density of from 2000 to 5000 amperes per square meter, the improvement which comprises introducing into said cell said aqueous hydrochloric acid to be electrolyzed at a concentration

of 18 to 28% by weight of HCl, conducting said acid through said cell at a flow rate which is sufficiently high to degrade the acid by not more than 2% by weight and maintaaining the mean temperature of the acid in the cell at from 75° C. to 90° C.

2. A process as claimed in claim 1 wherein said flow rate of the acid is maintained sufficiently high so as to degrade the acid by from 0.5 to 1.6% by weight.

3. A process as claimed in claim 1 wherein said aqueous hydrochloric acid being electrolyzed is substantially free of metal additives which lower the hydrogen overvoltage at the cathodes of the cell.

References Cited

UNITED STATES PATENTS

1,746,542	2/1930	Low	204—128
3,236,760	2/1966	Messner	204—128

JOHN H. MACK, Primary Examiner

R. L. ANDREWS, Assistant Examiner

U.S. Cl. X.R.

204—128

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,756,930 Dated September 4, 1973

Inventor(s) Guenther Weiss, Heinz Weller and Ewald Wygasch

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

Column 1, tenth line, "July 28, 1970" should read -- July 8, 1970 --.

Column 2, line 53, "potentail" should read -- potential --.

Column 3, line 4, "maintaaining" should read -- maintaining --.

Signed and sealed this 1st day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334.