United States Patent

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[54] **ABSORPTION OF GASEOUS CELL PRODUCT IN CELL LIQUOR APPARATUS**
3 Claims, 1 Drawing Fig.

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[51] **Int. Cl.** **B01k 3/00,** C01b 11/26
[50] **Field of Search** 204/81, 96, 98, 257, 258, 264, 266, 278

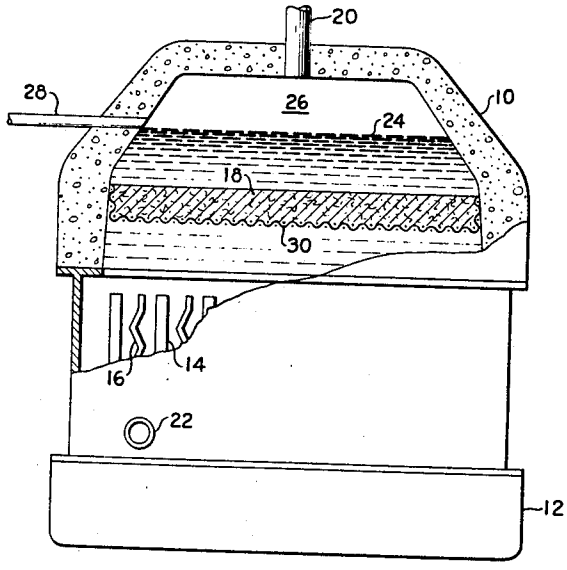
[56] **References Cited**

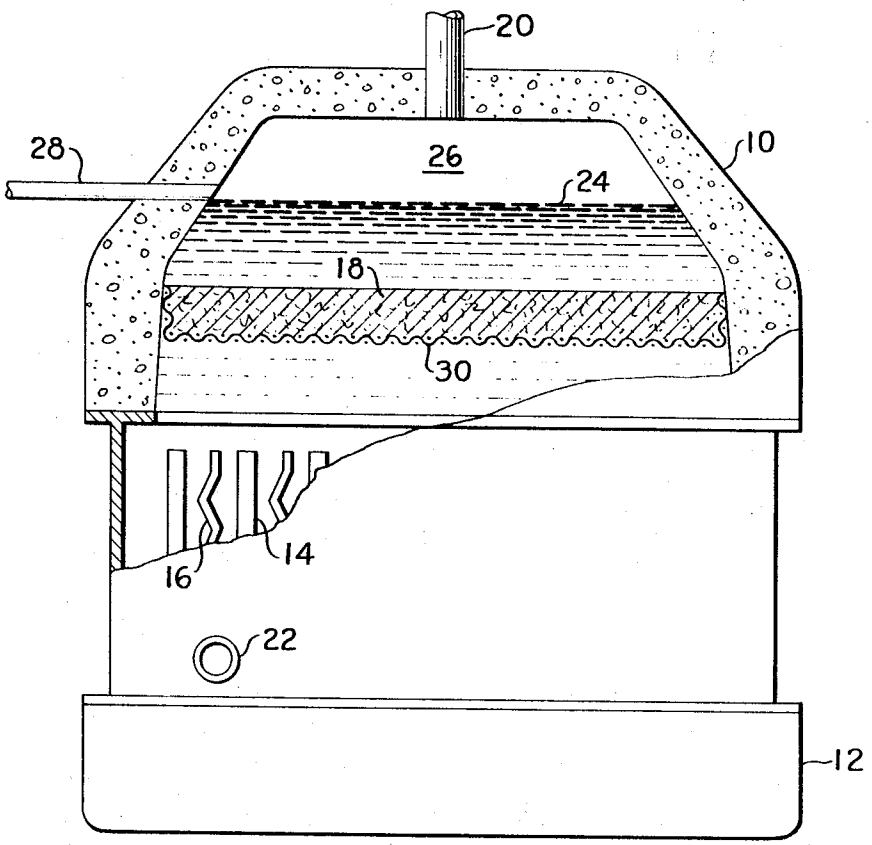
UNITED STATES PATENTS

583,718	6/1897	Teter	204/264
1,582,398	4/1926	Hausmeister	204/278
2,763,607	9/1956	Staverman	204/257 X
3,214,362	10/1965	Juda	204/254 X
3,403,083	9/1968	Currey et al.	204/98
3,471,382	10/1969	Grother	204/98

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ABSTRACT: The efficiency of electrolytic cells in which a gaseous cell product reacts with a component of the cell liquor or a reagent added to the electrolytic cell, may be substantially improved by the insertion of gas-dispersing means above the electrodes of the electrolytic cell and below the surface of the cell liquors. The dispersing means serves to mechanically diffuse the gaseous cell product into the cell liquor containing the reactant to provide intimate mixing and increased contact of reactants. The gas-dispersing means may be any inert conventional absorption packing or distillation column packing such as, Berl saddles, Raschig rings, bubble trays, glass beads, and the like.




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ABSORPTION OF GASEOUS CELL PRODUCT IN CELL LIQUOR APPARATUS

Diaphragmless electrolytic cells for the production of alkali metal chlorates are effectively equipped with gas dispersing means to remove residual chlorine values form the hydrogen gas evolved at the cathode. The packing serves to disperse and break up gas bubbles which contain small amounts of chlorine. This dispersion results in intimate mixing with the near neutral cell liquor or hydroxyl ion produced at the cathode. The packing also effectively increases the retention time within the cell causing more of the hypochloride to be converted to chlorate within the cell. This increased conversion within the cell decreases the amount of hypochlorate available for subsequent decay to produce oxygen and sodium chloride. This decay is one of the major inefficiencies in chlorate cells.

BACKGROUND FOR THE INVENTION

Chemical reactions are frequently conducted within the confines of electrolytic cells. Generally a component product of electrolysis is caused to react with another reagent chemically within the electrolytic cell. Such reactions may be broadly grouped into electrolytic oxidations and addition-type reaction. The reactant which is caused to undergo chemical reaction with the product of the electrolytic cell may in itself be part of the electrolyte within the cell or may be an added foreign reagent, such as, an olefin, acetylenic compound, an aliphatic hydrocarbon or halogenated hydrocarbon. For example, in a cell producing chlorine at an anode, chlorination reaction can occur within the electrolytic cell. Such reactions include chlorination of olefin, acetylene, aliphatic hydrocarbon; a partially chlorinated hydrocarbon or any chemical compound normally considered to undergo chlorine substitution or chlorine addition. In addition, oxidation reaction where the sole function of the chlorine is to act as an oxidant.

Various methods have been used in the past to optimize the reaction between an electrolytic cell product and another reactant. Conventionally, the cell product is removed from the cell and caused to react in a specially designed reactor where the conditions for reaction may be closely controlled. It is generally considered to be advantageous to avoid the necessity for complex costly chemical apparatus and to perform the reactions of electrolytic cell products, especially the gaseous products, as soon as possible so as to initiate the reaction while the gaseous reaction is still in a nascent or near nascent state.

BRIEF DESCRIPTION OF THE INVENTION

In accordance with the instant invention, there is provided an electrolytic cell wherein a compound is produced by chemical interaction between a gaseous electrolytic product and a reactant which is dissolved in the electrolyte of said cell or introduced into a reaction zone within the electrolyte. electrolyte. The electrolytic cell of the instant invention comprises a cell top, a cell bottom and sidewalls, electrodes comprising an anode and a cathode, means for conducting current to said cell, electrolyte feed means and withdrawal means, in which there is disposed above the cell electrodes but at least partially immersed beneath the top of the cell liquor a dispersing means which serves to break up and diffuse, large gas bubbles within the liquid phase of the cell contents.

The gas dispersion means may be completely submerged below the upper level of the cell liquors, in which case it serves as packing to completely mix a gaseous cell product with the cell liquor or foreign reactant. In certain operations, it is desirable to only partially submerge the gas dispersion means below the upper level of the cell liquors. This manner of operation produces a twofold advantage. First, the gaseous cell product is intimately mixed with the cell liquors. Second, the portion of the dispersion means which extend above the top or upper level of the cell liquors acts as an antimisting shield. An additional advantage attributable to the electrolytic cell packing of the instant invention resides in an overall increase in the yield of the desired product within the cell itself.

By increasing the in-cell production, the necessity for special retention tanks or external reaction vessels is diminished as is the additional reaction time normally lost in completing reactions in extra-cell reactors.

The dispersing means disposed within the electrolytic may consist of packing material conventionally employed in absorption towers or distillation columns. For example, a packing of Berl saddles Raschig rings, glass bead bubble trays or any known device for dispersing gases and liquids by mechanical diffusion which is inert toward the contents of the electrolytic cell, may constitute the dispersing means of the instant invention.

Electrolytic cells, either of the diaphragm or diaphragmless type may be provided with internal dispersing means in accordance with this invention. The electrolytic cells may be of the monopolar or bipolar type.

DETAILED DESCRIPTION OF THE INVENTION

For a complete understanding of the present invention, reference may be made to the accompanying drawing in which:

The FIGURE represents a side elevation partly in section of the electrolytic cell of this invention.

The electrolytic cell depicted in the FIGURE represents the conventional monopolar cell provided with a cell top **10** cell bottom **12** and internally a disposed anodes **14** cathodes **16**. Cell feed inlet **22** provides for the introduction of electrolyte while gas vent **20** allows for the discharge of the gaseous electrolysis products and overflow outlet **28** provides liquid removal means. The dispersing means or absorption packing **18** which represents one aspect of this invention is disposed within the cell top **10** on tray **30**. The normal operating liquid and suspended gas level **24** exemplifies operation with absorption packing **18** completely submerged in the electrolyte. The gas-disengaging region within the electrolytic cell is shown **26**.

In operation a suitable electrolyte is introduced into the electrolytic cell through cell feed line **22**. Current is introduced into the cell via current-conducting means (not shown) and the electrolyte within the cell is decomposed between anodes **14** and cathodes **16**. The gaseous product of the electrolysis, whether produced at the anode or cathode, rises in the electrolytic cell, enters the region of the dispersing means or absorption packing **18** at which point large gas bubbles are finely dispersed and intimately mixed with a reactant within the cell, either foreign or inherent to the electrolyte, to produce a desired product. The product is withdrawn from the cell by overflow withdrawal means **28**. Nonreactive gases continue to rise in the liquid electrolyte and form a relatively less dense liquid filled with suspended gas at **24**, within cell top **10**. The nonreactive gas disengages itself from liquid **24** filling space **26** and exiting cell top through gas vent **20**.

When employing gas dispersion means in a conventional diaphragm-type electrolytic cell, where the chlorine generated at the anode is to react with an added reactant such as ethylene, propylene or butylene, the cell packing is placed above the anodes in the anolyte. The olefin may be introduced into the cell via the cell feed inlet **22** or by way of a manifold injection system which inserts the gaseous olefin at a point below the packing in the cell. The gaseous olefin reacts with hypochlorous acid to form the corresponding halohydrin which in gaseous form exits the cell via vent **20**. The halohydrin may be recovered from the other gaseous cell products by procedures known to the art.

The following examples are directed toward exemplification of the instant invention through illustration of the operation of an alkali metal chlorate cell. The conventional alkali metal chlorate cells are diaphragmless mono-/or bipolar cells. In operation, an alkali metal chloride brine is fed to the electrolytic cell. The application of a decomposition voltage, between the anode and cathode across the electrolyte, results in the production of chlorine at the anode and hydrogen plus hydroxy ions at the cathode. Chlorine within the aqueous elec-

trolyte reacts with water to form hypochlorous acid and the chloride ion. Hypochlorous acid is in equilibrium with hypochlorite ions in the substantially neutral electrolyte. The hypochlorous acid will react with a hypochlorite ion to produce chlorate ions and chloride ions. The hydrogen gas evolved at the cathode intermingles with some of the gaseous anode product within the electrolyte and serves to entrain chlorine, which is carried with the hydrogen and vented from the conventional chlorate cell. By means of the instant invention, this conventionally lost chlorine value is recovered directly within the cell through reaction with water in the cell to produce more hypochlorous acid. This recovery occurs as a result of the disposition of absorption-packing or gas-dispersing means above the electrodes of the cell.

EXAMPLE 1

An electrolytic cell capable of operating on approximately 55,000 amperes, equipped with graphite anodes and sheet steel cathodes was operated under conventional sodium chlorate producing conditions. The cell top was modified to provide a perforated shelf extending entirely over the surface area of the electrolyte. One-quarter-inch Berl saddles (3 inches deep) were placed on top of the perforated shelf to serve as gas-dispersing means. Under overwise equivalent conditions except for the perforated shelf and Berl saddles inside the cell top, the cell was operated to determine the relative amount of chlorine recovered in the gas-dispersing region of the cell. The results of this operation are presented in table I.

TABLE I

CURRENT DENSITY	% Cl_2 IN VENT GAS Without Saddles	With Saddles
0.6 Amperes per square inch	4.10	0.75
	5.10	0.34
	3.36	0.60
	2.92	1.04
	3.36	1.00
	4.03	1.84
	4.11	
	3.49	
	2.49	
	3.12	
	3.29	
Average	3.58	0.93
0.8 Amperes per square inch	5.85	1.39
		4.40
		3.93
Average	5.85	3.24
0.9 Amperes per square inch	11.2	2.56
	7.7	2.47
	5.35	
Average	8.08	2.51

The height of the absorption-packing or dispersing means within the electrolytic cell serves to increase the efficiency of chlorine absorption within the cell.

EXAMPLE 1-6

An electrolytic cell comparable to that described in example 1 containing no diaphragm, equipped with graphite anodes and sheet steel cathodes, was employed in the production of sodium chlorate. The solution containing approximately 260 grams per liter sodium chloride, 100 grams per liter sodium chlorate and 2 grams per liter sodium dichromate was continuously electrolyzed in each of the following examples until the desired amount of sodium chlorate was produced. Sodium chloride brine was added as makeup during the course of the electrolysis. The cell operating temperature was between 40° C. and 45° C. The results of these experiments are tabulated in table II. The current efficiencies shown in the table are based on chemical assay over the life of the experiment.

TABLE II

Experiment Number	Current amperes	Current density, per square inch	Current volume ratio	Temperature range, degrees centigrade	Ph range	Flow rate, liters per minute	Cell head, inches	Final NaCl, grams per liter	Final $NaClO_3$, grams per liter	Hypochlorite, grams per liter	Batch assay current efficiency, percent	Remarks
1	260	0.6	3.25	41–45	7.0–7.5	1–1.5	20	101	483	1.4–3.3	79.0	No packing.
2	340	0.8	4.25	42–50	6.8–7.2	1	25	107	503	1.2–3.7	86.4	Three inches packing above cell.
3	260	0.6	3.25	40–44	6.9–7.3	1,4	25	162	344	1.8–3.1	87.6	
	390	0.9	4.87									
	340	0.8	4.25	40–48	6.8–7.1	4	25	128	437	2.1–2.9	84.7	Three inches packing.
4	340	0.8	4.25	40–41	6.8–7.0	4	25	160	340	1.5–2.7	90.2	Ten inches packing—second part of run insufficient because flow through cell stopped on weekend.
	340	0.8	4.25	44–47	6.6–7.0	1–4	25	106	498	1.7–2.2	83.7	
5	340	0.8	8.5	42–52	6.7–7.0	1.4–2.1	25	87	559	2.1–2.9	89.4	Ten inches packing.
6	340	0.8	16.2	43–49	6.7–7.1	1.1–1.6	21	92	520	1.9–3.7	89.3	Ten inches packing lowered cell head.

Although chlorine losses during operation of the chlorate cells involved in the preceding experiments could be substantially eliminated by maintaining the electrolyte pH between 7 and 7.5, in this pH range more oxygen is produced at the anode and the overall current efficiency is only 79 percent (experiment 1). Therefore, for efficient operation of this chlorate cell a lower pH range must be maintained in the electrolyte to avoid oxygen production of the anode.

In comparison with experiment 1, operating the electrolytic cell with a 3-inch layer of ¼-inch Berl saddles placed in the electrolyte above the electrodes it was possible to operate the cell at a lower pH range (6.8 to 7.2) with lower chlorine losses than if absorption packing is absent. The height of the electrolyte was 25 inches while operating the cell with gas-dispersing means. The combination of lower pH and the 3-inch packing above the electrodes resulted in increased current efficiency from 79 percent to between 85 and 87 percent (experiments 2 and 3). Increasing the absorption packing height to 10 inches further increased the current efficiency to 90 percent over most of experiment 4. However, during the last days of experiment 4, the flow of brine to the cell was interrupted, causing a stagnant situation to develop. One night's operation at very low efficiency caused the overall batch efficiency to drop to 84 percent. Approximately 94 percent of the

sodium chlorate produced in experiments 2 through 4 was produced inside the cell, as opposed to lower in-cell production followed by production in a conventional retention tank. Continuing with a 10-inch level of absorption packing, the current concentration of 340 amperes (0.8 amperes per square inch) was raised from 4.25 amperes per liter to 8.5 amperes per liter by decreasing the size of the retention tank. This resulted in an overall current efficiency of 89.4 percent (experiment 5) from electrolysis of the solution low in sodium chloride (87 grams per liter) with a high sodium chlorate (559 grams per liter) concentration.

In experiment 6, the current-volume ratio was further increased to 16.2 amperes per liter at the same current density. An overall efficiency of 89.3 percent was observed at a final sodium chloride concentration of 92 grams per liter and a final sodium chlorate concentration of 520 grams per liter.

With a 3-inch layer of packing, increasing current density from 0.6 to 0.8 amperes per square inch increased chlorine losses in the vent gases by about 1 percent. However, these losses were eliminated by increasing the absorption packing height to 10 inches. In the absence of the packing, chlorine losses varied from 1 to 12 percent. With 3 inches of packing, chlorine losses varied from 0.7 to 4 percent; and with 10 inches of packing the chlorine losses were below 2 percent at chlorate concentrations below 400 grams per liter. Higher chlorine losses were usually observed at chlorate concentrations above 400 grams per liter.

EXAMPLE 7

An electrolytic cell capable of operation on approximately 55,000 amperes and equipped with graphite anodes and steel cathode separated by an asbestos diaphragm was provided with 6 inches of packing in the cell top above the anodes in the anode compartment. The packing was below the surface of the anolyte within the anode compartment.

The cell was operated under normal conditions for the electrolysis of sodium chloride brine. Sodium chloride brine containing 300 grams per liter NaCl was introduced into the anode compartment and a decomposition voltage was applied between the electrodes. Ethylene was continuously introduced into the anolyte below the lower level of the packing in stoichiometric excess.

The gaseous product recovered contained predominately ethylene chlorohydrin and small amounts of unreacted ethylene and ethylene dichloride.

What is claimed is:

1. an electrolytic cell comprising a cell housing, anodes and cathodes disposed within said cell housing, means for introducing a liquid electrolyte into said cell housing, so as to form and maintain a body of electrolyte within said housing in contact with said anodes and cathodes but having an upper surface which is above said anodes and cathodes, means for applying an electrical potential between said anodes and cathodes to decompose said electrolyte and form decomposition products, at least one of which is gaseous, means for conducting reaction products from said cell housing, and means for dispersing said gaseous decomposition products within said liquid electrolyte, said dispersion means comprising a layer of inert packing material, which layer is pervious to gas and disposed within said cell housing so as to be at least partially below the upper surface of the body of electrolyte formed within said cell housing but completely above all said anodes and cathodes.

2. The electrolytic cell as claimed in claim 1 wherein the layer of inert packing material which forms the gas dispersion means is selected from Berl saddles, Raschig rings, bubble trays, and glass beads.

3. The electrolytic cell as claimed in claim 2 wherein the gas-dispersing means is disposed within the cell housing so as to be completely below the upper surface of the body of electrolyte formed within the cell housing.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,616,443 Dated October 26, 1971

Inventor(s) Edward H. Cook, Jr. 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 1, lines 54 and 55, "electrolyte.electrolyte." should be ---electrolyte.---
Column 6, after line 9, the following should be inserted as a new paragraph, ---Having disclosed the invention, it will be apparent to those given the art that it is applicable to any electrolytic process in which a gaseous product of the electrolysis is intentionally caused to react with another reactant within the electrolytic cell. Thus, although the specific examples presented in this application are directed toward alkali metal chlorate production these examples are presented as representative embodiments of the invention rather than limitations on the scope of the invention.---; line 11, "an" should be ---An---.

Signed and sealed this 25th day of April 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents