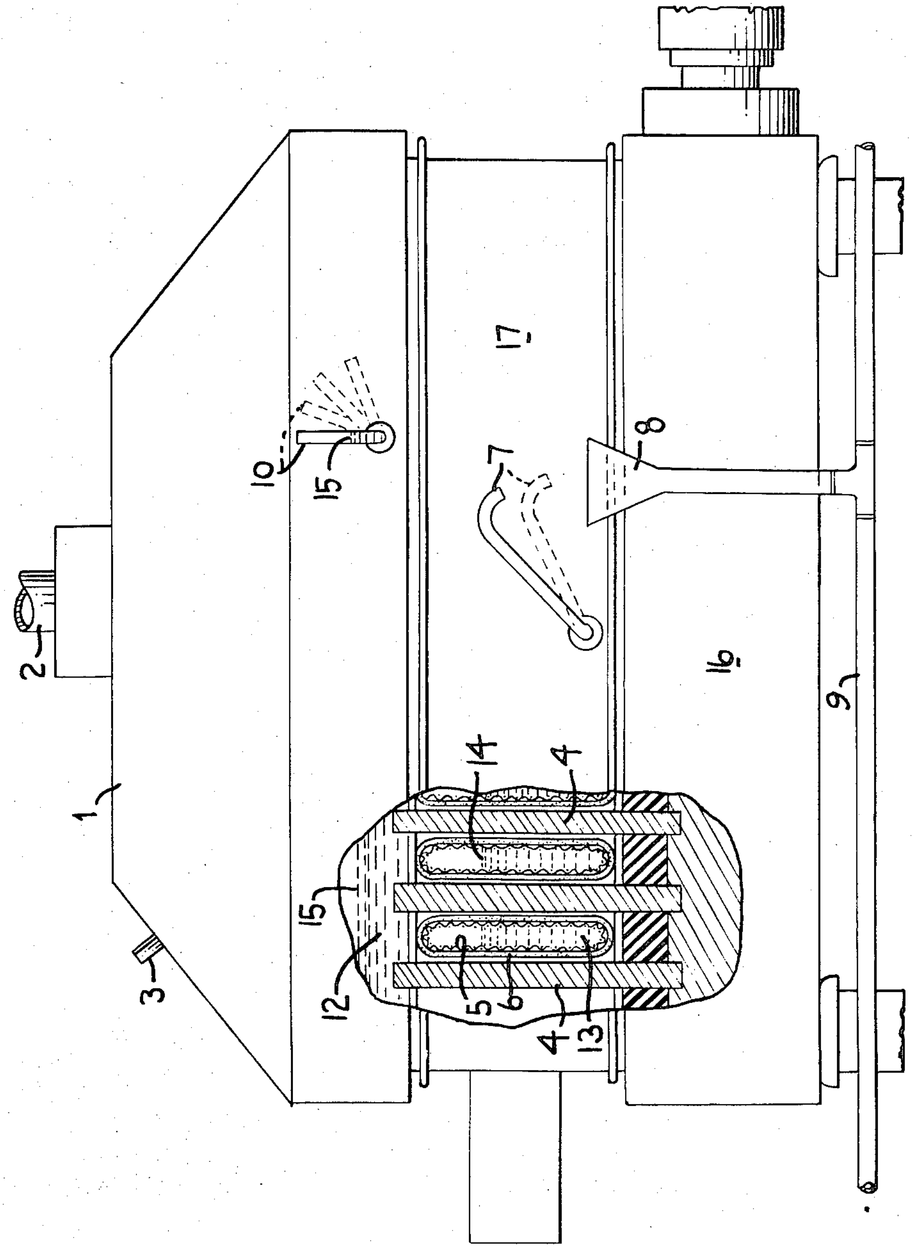
Dec. 28, 1971 T. C. JEFFERY ET AL 3,630,863

CELL DIAPHRAGM TREATMENT

Filed Nov. 13, 1968



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United States Patent Office 3,630,863
Patented Dec. 28, 1971

3,630,863

CELL DIAPHRAGM TREATMENT

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Filed Nov. 13, 1968, Ser. No. 775,426
Int. Cl. C01d *1/06*
U.S. Cl. 204—98 9 Claims

ABSTRACT OF THE DISCLOSURE

The effective life of electrolytic cell diaphragms is extended by treatment with hydroxy carboxylic compounds, e.g., hydroxy carboxylic acids such as gluconic acid or salts. This treatment removes substances which are known to restrict diaphragm porosity.

Commercial manufacture of chlorine and alkali metal hydroxide, notably, caustic soda (sodium hydroxide) involves electrolyzing an aqueous chloride solution in an electrolytic cell. One of the common types of chlorine-alkali cells used for this purpose is the "so-called" diaphragm cell. Such cells are characterized by having an iron mesh cathode, one side (the anolyte side) of which is covered with a porous diaphragm. Asbestos is the most common diaphragm material now used.

In operation, to produce chlorine and sodium hydroxide, the anolyte compartments of such diaphragm cells are charged continuously with brine establishing a brine level in that compartment. Chlorine liberated at the anode (made of graphite) is removed. Anolyte liquor flows through the porous diaphragm thereby establishing a difference in level between the anolyte and catholyte compartments. In the catholyte compartment within the iron mesh cathode (separated from the anolyte compartment by the diaphragm) hydrogen and caustic soda are formed, both of which are withdrawn from the cell. Caustic soda (catholyte liquor) flows from the cell through what the cell art refers to as the "perc" pipe.

As the cell continues in operation, the anolyte liquid level rises due among other things to the decrease in diaphragm porosity, and the "perc" pipe is adjusted to allow continued flow of caustic soda. Eventually, the anolyte level rises to the point where continuing cell operation is unrealistic, e.g., cannot be justified economically. At that time this problem can be alleviated by disassembling the cell and replacing the diaphragm. Diaphragm life (period normally elapsing between diaphragm changes) is a fraction (on the order of a fourth to one-half) of normal carbon anode life in these cells; ergo, the diaphragm's life becomes the controlling factor as to the frequency of cell shutdown and disassembly.

In order to replace diaphragms in such cells, the cell is electrically disconnected from the circuit and disassembled by removing its top and separating the cathode section. The aged diaphragm is removed and a new diaphragm deposited or placed on the cathode following which the cell is reassembled and returned to production. In practice spare cathode sections are used to minimize the time the cell is removed from the circuit. Nevertheless, labor and "down" time attributable to the diaphragm replacement is a significant cost element in the manufacture of chlorine and alkali metal hydroxide in diaphragm cells.

Plugging of asbestos diaphragms resulting in porosity loss apparently arises because of depositions in diaphragm pores. Primarily, these enter the cell as brine contaminents.

They may also come from materials of construction. Magnesium, calcium and iron compounds (probably in the form of their hydroxides) are believed to be the prevalent materials. Use of acids (such as mineral acids) strong enough to remove by acid-base reaction such materials has disadvantages. Often these strong acids are quite corrosive, especially with respect to the materials of construction found in the catholyte compartment which in cell operation are exposed to a base environment.

SUMMARY OF THE INVENTION

This invention provides a means for extending the effective life in an electrolytic cell of the cell diaphragm thereby prolonging the time the cell may be employed without the need for disassembly. Thus, pursuant to this invention diaphragms of electrolytic cells have their permeability (without the need for disassembling the cell) substantially improved permitting the cell to continue in service.

In accordance with this invention, cell diaphragms are treated with gluconic acid or like hydroxy carboxylic compounds. This treatment improves the porosity of the diaphragm to such an extent that continued use of the assembled electrolytic cell is economically justified. Such treatment also results advantageously in a drop in cell voltage. Yet another benefit is the significant lowering of the cell liquid level (the difference between anolyte brine level and catholyte liquor level).

As the diaphragm continues in use it becomes plugged, or at least its porosity decreases. If brine continues to be fed at the same rate, the brine level in the anolyte compartment rises. The "perc" pipe must be lowered thus reducing the catholyte level. The difference between these two levels is herein referred to as cell liquid level. In a typical chlorine-alkali electrolytic cell, this liquid level is the difference (vertical) between the uppermost portion of the "perc" pipe and brine level as shown in the sight glass. Not only is there a limit to how high this cell liquid level may be, but cell power efficiency is adversely affected as cell porosity decreases.

In preferred practice of this invention, a cell in which the diaphragms have become plugged (i.e., diaphragm porosity has been materially reduced) is electrically disconnected from the circuit and its brine feed discontinued. Thereafter, gluconic acid or like hydroxy carboxylic compound (usually as an aqueous solution) is introduced into the cell, conveniently via the brine feed inlet to the anolyte compartment and into contact with and through the diaphragm thence out of the cell. Thereafter, the cell is returned to the circuit, brine feed resumed and chlorine alkali hydroxide manufacture recommenced.

Gluconic acid is a water soluble hydroxy carboxylic acid found to work admirably. It typically and conveniently is fed to the cell as an aqueous solution containing between 25 and 75 weight percent gluconic acid. It is effective either in its acid form or as a salt therefor. For example, aqueous solutions of sodium gluconate have been used with good results. Other water soluble salts of gluconic acid, notably alkali salts include alkali metal salts such as potassium and lithium are useful. Sodium salts enjoy a preferred status in treating chlorine-caustic cells since they do not introduce foreign ions. When potassium chloride is being electrolyzed (chlorine-caustic potash), the potassium salts would be particularly attractive on this basis.

Water soluble hydroxy carboxylic compounds, notably the acids and their salts other than gluconic acid are effective. Suitable acids include aliphatic as well as aromatic hydroxy carboxylic acids having one or more hydroxyl and one or more and usually up to 5 (usually no more than 10, having only frequently up to 6) carboxyl groups. Useful monohydroxy monocarboxy acids include glycolic, lactic, hydracrylic, 3-hydroxybutyric, 2-hydroxybutyric and 1-hydroxybutyric while glyoxylic, erythric, aralitic, mannitic and glyceric are exemplary polyhydroxy monocarboxylic acids. Tartronic, malic, tartaric, trihydroxyglutaric, saccharic, citric and isocitric are illustrative hydroxy polycarboxylic acids. Mandelic, phenyl-lactic and tropic acids are typical aromatic hydroxy carboxylic acids.

Steric isomers of most, if not all, of these acids exist. Either the individual steric isomer (e.g., the dextro or levo form) or a mixture of the steric isomers (dl form may be used.

In addition to the hydroxy carboxylic acids and salts hereof, useful compounds of hydroxy carboxylic acids include esters, ethers and lactones of the acids. For example, ascorbic acid (a lactone corresponding to gluconic acid) as well as other lactones of hydroxy carboxylic acids are of use. Hydroxy carboxylic compounds include the esters of the mono as well as polycarboxylic acids in which at least one of the carboxylic acid groups (where there are more than one, e.g., the hydroxy polycarboxylic acids) is esterified with alcohols such as methanol, ethanol, n-propanol, isopropanol, 1-chloro-propanol-2, 2-chloro-propanol-1, all four butanols, the amyl alcohols, n-hexyl alcohol, n-octyl alcohol, n-decyl alcohol, ethylene glycol, diethylene glycol, and glycerine. Likewise, the ethers resulting from the etherification of one or more hydroxyl groups of the hydroxycarboxylic acids with these alcohols are included. Also those esters resulting from esterification of one or more of the hydroxyl groups of the acid with acids such as acetic, mono, di, and trichloroacetic, formic, propionic, butyric, etc. can be of use.

In effecting treatment of the diaphragm, the treating agent is used conveniently as a water solution. Essentially any concentration of treating agent is operative; but unduly dilute solutions offer practical deterrents. Solutions containing upwards of 5 to 10 weight percent to as high as 90 percent carboxylic agent thus are most aptly employed.

Expeditious performance of this invention in connection with chlorine-alkali diaphragm cells will be understood with particular facility by reference to the drawing which illustrates schematically (with cross sectional cut out) the pertinent cell elements. Such cells typically include concrete cover **1** having a chlorine outlet means **2** and a brine feed inlet **3**. They contain a plurality (three shown in the cut out) of thin vertical carbon anodes 4 which traverse the central area of the cell and are embedded in the cell base **16**. A plurality of iron mesh cathodes **5**, each of which is covered with an asbestos diaphragm **6** are located between anode pairs in an intermediate removable cell section **17**. Other parts of the cell include "perc" pipe **7** movable (as shown by dotted lines) in a vertical plane parallel to the cell side in which it is mounted, collecting funnel **8** and caustic product collection pipe **9**. Sight glass **10** is movably mounted in the face of cover **1** for movement parallel to the cell face.

In the operation of such a cell, brine is fed via inlet **3** providing anolyte liquor **12**. Chlorine is evolved and removed through outlet **2** provided in the cell top from the anolyte compartment. Catholyte liquor **13** (caustic soda) forms the catholyte liquor in the compartment within the asbestos covered ion mesh cathode **5**. Each of the individual catholyte compartments are connected to a common hydrogen gas withdrawal means (not shown) and the common caustic soda withdrawal means, "perc" pipe **7**. When first placed in operation and fed with brine, certain anolyte and catholyte liquor levels **15** and **14** are established. To the cell operator, these levels are indicated by liquid level in sight glass **10** (which is connected at its bottom to the anolyte compartment) and the highest level "perc" pipe **7** may be set and still have caustic soda product flow therefrom.

"Perc" pipe **7** is set so as to allow caustic soda to flow from the catholyte into collecting funnel **8** and then into

pipe **9** where it joins product (collected in like manner) from other cells. As the cell continues in operation its diaphragms **6** become less porous and the anolyte level rises. To prevent this level from exceeding practical limits, the "perc" pipe **7** is rotated clockwise (as shown in the dotted lines) about a lower horizontal axis as needed until it can be lowered no further. At such time, the cell would heretofore be electrically disconnected and disassembled by removing the cell cover and its intermediate section in which the cathodes are mounted so that the old diaphragms can be replaced with new ones.

However, the present invention obviates the need to replace the diaphragms. Thus, in accordance with this invention, operation of electrolysis in the cell is temporarily halted, e.g., the cell is electrically disconnected, brine feed is stopped, the "perc" pipe raised and the sight glass turned down so that the brine in the cell flows out. When this brine flow stops, the sight glass is returned to its upright position and treating agent (ideally, for example, an aqueous solution of gluconic acid containing 50 weight percent of the acid) is added through the brine inlet. Sufficient water is then added via the brine inlet to fill about ½ the sight glass. The "perc" pipe is pushed down and the cell contents allowed to drain therethrough. When draining ceases, the "perc" pipe is raised, brine feed is recommenced and electrolysis resumed in the cell by electrically connecting the cell. A notable drop in the liquid level difference (indicating the porosity of the asbestos diaphragm has been improved) and cell voltages lower than those prevailing prior to the treatment result from the treatment.

The following examples illustrate the manner in which this invention may be practiced.

EXAMPLE 1

Following the procedure described immediately hereinbefore, commercial chlorine-caustic electrolytic cells of the type described having a cathode area of about 205 square feet were treated with 10 gallons of D-gluconic acid solution (50 weight percent gluconic acid). Results of the treatment on specific cells which results were typical of those attained with a large number of cells are tabulated in the following Table 1:

TABLE 1

Cell	Liquid level difference, inches [1]		Cell voltage (volts)	
	Before	After [2]	Before	After
A	29	16½	3.85	3.80
B	31	16	3.80	3.65
C	33	14	3.90	3.85
D	33	17	3.85	3.75
E	32	15	3.90	3.60
F	30	15	3.80	3.60
G	31½	13	3.90	3.80
H	30	18	3.75	3.65

[1] Difference between sight glass reading of brine level and "perc" pipe level for caustic flow.

[2] Obtained at least 7 days after returning the treated cell to service

Product quality continued high after the treatment. In lieu of the gluconic acid, its salts may be used effectively with results as illustrated by Example 2.

EXAMPLE 2

Duplicating the described procedure in cells of the described type, cells were treated with (A) 10 gallons of an aqueous solution provided by mixing 1 part of 50 weight percent NaOH with 9 parts of 50 weight percent gluconic acid and (B) the same solution as in (A) except that 2 parts of the 50 percent NaOH per 9 parts of acid was used (providing about 3 percent excess caustic over that stoichiometrically to neutralize fully the gluconic acid). Table 2 lists typical significant data including information relative to the effluent during treatment.

TABLE 2

	Cell treatment								
	A			A			B		
Liquid level change (inches)	14			13			16		
	Effluent analysis								
Minutes	pH	CaO, g.p.l.[1]	Fe, g.p.l.	pH	CaO, g.p.l.[1]	Fe, g.p.l.	pH	CaO, g.p.l.[1]	Fe, g.p.l.
0	12.8	0.073		12.8	0.140		12.1	0.347	
10	12.1	1.742	0.0349	11.1	0.414	0.045	11.9	0.272	0.082
20	7.9	2.184	0.059	8.5	1.389	0.037	11.0	0.207	
30	6.0	1.960		7.8	1.366		11.9	0.204	0.072
40	6.2	1.848		7.3	1.344		11.9	0.210	
50	6.5	1.848		7.1	1.291		11.9	0.252	
60	7.0	1.837		8.7	1.204				
70	7.4	1.826		8.5	1.218				

Calcium and magnesium reported as CaO in grams perliter (g.p.l.).

The effectiveness of the treatment using excess NaOH (treating solution B) emphasizes by hydroxy carboxylic compound treatment of this invention is not dependent upon any mere acid-base relationship.

Usefulness of hydroxy carboxylic compounds besides gluconic acid and its salts is illustrated by Example 3.

EXAMPLE 3

Using as the treating solution, a citric acid solution provided by dissolving 25 pounds of citric acid in enough water to provide 5 gallons of treating solution, cells of the described type were treated by the procedure followed in Examples 1 and 2. In one such cell, the treatment reduced the level from 30 to 16 inches while the cell voltage dropped from 3.90 to 3.80 volts. Another cell so treated had its level dropped from 31½ to 17½ inches and its voltage reduced from 3.75 to 3.65 volts.

Analysis of the treating solution effluent from the cell during the treatment was as follows:

TABLE 3

Time treating after effluent commenced (minutes)	CaO (g.p.l.)[1]	pH
15	3.84	8.7
25	7.22	8.3
35	6.69	8.1
45	6.90	8.1

[1] Calcium and magnesium reported as CaO in grams per liter (g.p.l.).

Asbestos is the most common diaphragm material in commercial use. Electrolytic cell diaphragm of other materials may be similarly treated to improve its porosity and effect a rejuvenation of the diaphragm's usefulness. Perminonic membrane cell members which lose their porosity are treatable too.

Best overall results stem from flowing the treating agent (usually as an aqueous solution) through the cell from the anolyte to catholyte compartments. Reverse flow will also improve diaphragm porosity but offers the possibility of loosening the diaphragm. It is also preferred to disconnect electrically the cell before commencing the treatment; however, improvement is attained by treating while electrolysis is proceeding in the cell. Temperatures of treatment are variable. One advantage of the process is its operability while the cell is at or near its normal operating temperatures, e.g., 150 to 200° F. Its utility is however not limited to any particular temperature.

Repeated treatment of the same diaphragm as it becomes clogged again and again will rejuvenate the diaphragm or like porous electrolytic cell member. With cells having carbon anodes, carbon anode life becomes the limiting factor in the number of treatments. Carbon anodes have a normal life of between twice and four times the period of time in which the diaphragm requires treatment. Economics favor replacing the diaphragm at the time it is necessary to disassemble the cell for carbon anode replacement.

This invention is especially useful, however, in connection with electrolytic cells having anodes made of materials other than carbon which have a longer life. Thus, a preferred embodiment of this invention treats diaphragms (or other porous membrane members) of electrolytic cells having anodes of titanium, tantalum, zirconium and/or tungsten either as such or as a substrate or base containing an electrically conductive coating of the elements or compound (e.g., oxide and/or sulfide) ruthenium, rhodium, irridium, palladium, platinum, zirconium and rhenium. Such coatings can also include oxides of indium, silicon, tantalum and tin. Specific anodes which may be mentioned by way of illustration include anodes of titanium metal, titanium coated with platinum or other noble metal, titanium coated with ruthenium oxide alone or in combination with platinum and titanium base coated with a ruthenium oxide-titanium dioxide mixture. When this invention is applied to cells with long life anodes of this nature, the period of time between cell disassemblies may be extended for years.

Many of these anodes such as those of platinum coated titanium and titanium coated with ruthenium oxide are dimensionally stable. Electrolytic cells with such dimensionally stable anodes may be fabricated so that spacing between anode and cathode is constant and at a minimum. Such cells offer advantageous power savings. Coupled with this invention, it is possible to operate diaphragm cells with dimensionally stable anodes for extended periods without the necessity of disassembling the cell.

While this invention has been described by reference to certain details of specific embodiments it is not intended the invention be limited thereto.

What is claimed is:

1. A method of operating a diaphragm chlorine-alkali electrolytic cell which comprises electrically disconnecting the cell and halting brine feed to the cell whereby to temporarily halt electrolysis, contacting the diaphragm with a water soluble compound selected from the group consisting of gluconic acid, citric acid, and their water soluble salts and thereafter resuming electrolysis within the cell.

2. The method of claim 1 wherein the compound is introduced into the anolyte compartment of the cell and the resulting liquid in the anolyte is passed through the diaphragm.

3. The method of claim 2 wherein the diaphragm is an asbestos diaphragm.

4. The method of claim 2 wherein the compound is gluconic acid and it is introduced as an aqueous solution containing 25 to 75 weight percent gluconic acid.

5. The method of claim 1 wherein the compound is an alkali salt of gluconic acid.

6. The method of claim 1 wherein the compound is sodium gluconate.

7. In the method of electrolyzing a brine to produce chlorine and alkali metal hydroxide in a diaphragm chlorine alkali electrolytic cell, the improvement which comprises electrically disconnecting the cell when the

liquid level becomes excessive and halting brine flow to the cell whereby to halt temporarily electrolysis, flowing a water soluble compound selected from the group consisting of gluconic acid, citric acid and salts of said acids from the anolyte compartment of the cell through the diaphragm to the catholyte compartment and thereafter recommencing electrolysis.

8. The method of claim **7** wherein the diaphragm is asbestos, the compound is an alkali metal salt of gluconic acid and wherein upon recommencing electrolysis the liquid level is improved.

9. A method of operating a diaphragm chlorine-alkali electrolytic cell containing dimensionally stable anodes wherein as a result of using said dimensionally stable anodes spacing between anode and cathode remain substantially constant during extended periods of operation comprising a plurality of occasions during said period of operation electrically disconnecting the cell and halting brine feed thereto when the liqid level becomes excessive contacting the diaphragm with a water soluble compound selected from the group consisting of gluconic acid, citric acid, and their water soluble salts and thereafter recommencing electrolysis whereby to extend the period of time between cell disassemblies for replacement of anodes or diaphragms.

References Cited

UNITED STATES PATENTS

3,250,691	5/1966	Broun et al.	204—98
1,309,214	7/1919	Moore	204—100
3,454,501	7/1969	Ziffer et al.	134—3
3,467,586	9/1969	Grotheer et al.	204—98

FOREIGN PATENTS

594,888	3/1960	Canada	204—98

TA-HSUNG TUNG, Primary Examiner

U.S. Cl. X.R.

204—295, 296

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,630,863 Dated December 28, 1971

Inventor(s) Thomas C. Jeffery and Waylon L. White

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

In Claim 9, column 7, line 17, after "comprising", insert --on--, which is missing.

Signed and sealed this 6th day of June 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents