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ELECTROLYTIC APPARATUS FOR THE REGENERATION OF CHROMIUM SALT SOLUTIONS

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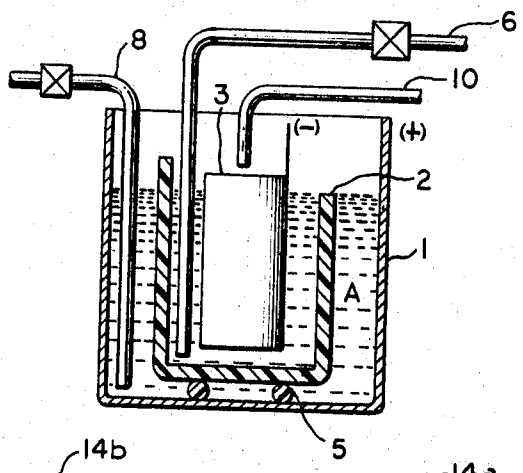


FIG. 1

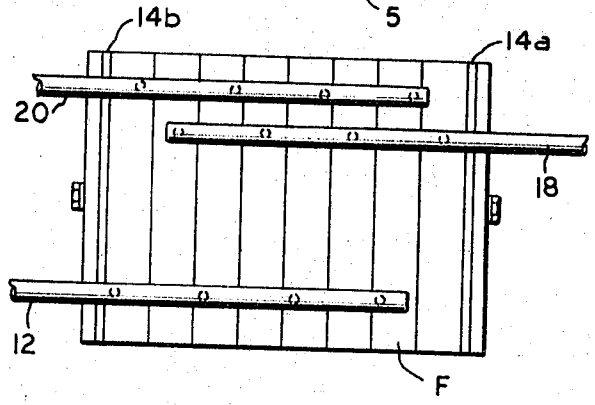


FIG. 2

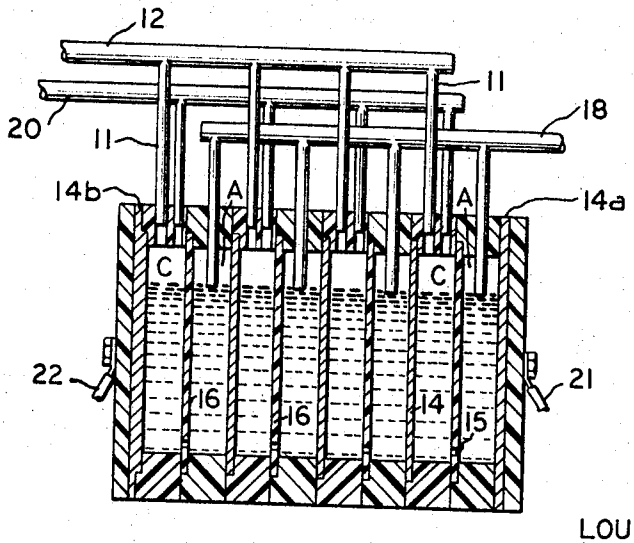


FIG. 3

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ELECTROLYTIC APPARATUS FOR THE REGENERATION OF CHROMIUM SALT SOLUTIONS

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U.S. Cl. 204—256
3 Claims

ABSTRACT OF THE DISCLOSURE

Electrolytic apparatus useful for regeneration of trivalent chromium salt solutions to form hexavalent chromium compounds comprises at least two electrodes separated by a polytetrahaloethylene diaphragm. The diaphragm has a pore diameter ranging from about 1 to about 300 microns, a void content of 40%, and is provided with at least one small orifice to allow solution flow through the catholyte and anolyte compartments without electrically short circuiting the cell.

This invention in one aspect pertains to the electrolytic regeneration of chromium salt solutions to form aqueous chromic acid oxidizing solutions. In another aspect the invention pertains to the provision of a cell of the diaphragm type for said regeneration.

As is well known, solutions of chromic acid in admixture with sulfuric acid are powerful oxidizing agents. Chromic acid or sodium or potassium dichromate oxidizing solutions are particularly effective for use in the oxidation of fused ring polynuclear hydrocarbons to form quinones. Quinones, such as anthraquinone and naphthoquinones are valuable intermediates and starting materials for the manufacture of dyes, drugs, and the like. Solutions containing available oxygen in the form of free chromic acid are also commonly employed for effecting the oxidation of relatively long chain unsaturated fatty acids and oils to produce a cleavage of the chain. The oxidation of fused ring hydrocarbons and the disruptive oxidation of double bonds is carried out by mixing the oxidizing solution with a batch of the hydrocarbon or fatty acid at an elevated temperature.

One of the advantages of chromic acid oxidation is that spent solutions can be electrolytically regenerated to form CrO_3 solutions, when chromic sulfate is present. The regenerative electrochemical reactions are effected in known electrolytic cells of the bipolar electrode type. The present invention relates to chromic acid regenerative processes of this type, one of the objects being to improve the electrolytic cell.

When an electrolytic cell is used, with attendant anodic oxidation of chromium salts, water is electrolytically decomposed to produce hydrogen ions at the cathode, which form molecular hydrogen, and nascent oxygen at the anode, which indirectly oxidizes trivalent chromium to hexavalent chromium the form in which it is present in chromic acid. This oxidation takes place at or near the active anode faces in the cell.

During regeneration the cell is supplied with a solution of a trivalent chromium salt in dilute sulfuric acid. Due to the application of a direct current (DC) voltage to the electrodes, a regeneration of the acid solution of the chromium sulfate to form a sulfuric acid solution of chromic acid occurs by oxidation at the anode, and hydrogen is formed at the cathode. A diaphragm is therefore required to separate the anode from the cathode to prevent the chromic acid from being reduced by nascent hydrogen which develops on the cathode.

Properly operated to prevent electrode corrosion, a chief source of wear and tear in chromium salt solution regeneration cells is the diaphragm. Because of required chemical resistance, cells generally contain ceramic diaphragms. However, ceramic diaphragms do not lend themselves to large scale industrial operation. In addition ceramic diaphragms tend to pulverize on continued use. In accordance with one aspect of this invention is has been found that polytetrahaloethylene can be adapted as a diaphragm for replacement of ceramic diaphragms.

This is especially significant since the diaphragms of this invention permit the operation of a filter press type bipolar cell. These electrolytic cells are composed of a plurality of unit cells in a filter press type arrangement, adjacent each other in a row, each unit cell being divided by a diaphragm into an anolyte compartment and a catholyte compartment. In other of its aspects the invention provides a bipolar electrolytic cell as well as a continuous process for the regeneration of chromium salt solutions, generally of trivalent chromium, to form hexavalent chromium compounds.

Two types of cells can be employed in regenerating a chromic acid solution according to this invention, and these can perhaps better be explained by reference to the accompanying drawing. Only sufficient equipment has been shown to illustrate the invention; pumps, valves and other equipment being omitted for simplicity.

FIG. 1 is a central vertical section of a tank type electrolytic cell.

FIG. 2 is a top view of an electrolytic cell comprising a filter press type assembly.

FIG. 3 is a transverse sectional elevation of the cell of FIG. 2.

While filter press type electrolytic cells are known in the art, it is believed that they have not been employed for chromic acid solutions. Ceramic diaphragms are difficult to use in filter press type electrolytic cells, due to their rigidity and brittleness. Consequently diaphragms disclosed in prior art for filter press type electrolytic cells are fabric, such as canvas, or plastic, for instance polyethylene. However these cannot withstand the chemical attack of chromic acid.

Referring now to the electrolytic cell of FIG. 1, this cell includes cylindrical anode **1** and cathode **3** concentrically arranged with the porous diaphragm **2** therebetween supported on rods **5**. However, according to this invention diaphragm **2** is not made of ceramic, but rather permeable polytetrahaloethylene. By "polytetrahaloethylene" is meant polymers of tetrafluoroethylene or trifluorochloroethylene. These known polymers, in a broader sense, are described in U.S. 2,393,967 and U.S. 2,600,202. Those contemplated herein are permeable and are of sufficiently high molecular weight to be solids. By "permeable" it is intended that the sheet or diaphragm of the polymer is so formed that, unlike "Teflon" cooking ware, the polymer sheet possesses a given porosity. As is known the porosity of the diaphragm should be such that it permits electron flow, inhibits flow of ions and prevents flow of hydrogen. In the case of the diaphragm of our invention this pore size is in the range of 1 to 300 microns in its largest dimension. Thus, the diaphragm should prevent or minimize nascent hydrogen developed on the cathode from reducing the chromic acid formed. The diaphragm should also inhibit ionic flow in order to minimize the kilowatt and anode area requirements. Preferably, then, pore sizes are in the range of 50 to 150 microns in the permeable, but essentially gas-tight diaphragm of the invention.

Referring again to FIG. 1, the unit is filled by means of conduit **6** leading into the cathode compartment. The solution then flows over the low or cutaway side of dia-

phragm **3** into the anode area A. A conduit **8** is provided in the anode compartment away from the cutaway portion for withdrawal of anolyte. When the unit is operated, the oxidation will take place in the anode compartment, and molecular hydrogen formed at the cathode will be removed through a conduit **10** provided therefor. It has been found that the long life and durability benefits of the diaphragm of the invention are realized and the system can be operated using either batch or continuous operation.

During continuous operation divalent and trivalent chromium salts and metallic chromium tend to accumulate in the catholyte. These form unwanted deposits on the various compartment surfaces. However according to an aspect of this invention a continuous chromium salt solution electrolytic regeneration process is provided which can be operated much longer than known continuous processes. In addition a long lasting electrolytic cell is provided therefor. It has been found that the problems encountered in continuous operation in electrolytically regenerating trivalent chromium salt solutions to form hexavalent chromium compounds can be overcome by effecting circulation of both the catholyte and the anolyte. By another practice of this aspect of the invention, a feed solution of the trivalent chromium salt solution to be regenerated is continuously introduced into the catholyte in an electrolytic cell having an anolyte and a catholyte separated by a permeable polytetrahaloethylene diaphragm. In this embodiment, shown in FIG. 3, the feed stream is passed through the cathode compartment C then through at least one orifice in the diaphragm into the anode compartment A to provide a circulation pattern in the catholyte as well as in the anolyte preventing salt deposition in said catholyte compartment.

Referring to FIG. 2 and FIG. 3, the continuous cell shown is composed of eight frames F, forming four unit cells A-C between plate electrodes **14***b* and **14***a*. In this particular cell the electrodes are so disposed that, with the exception of electrodes **14***a* and **14***b*, one side of each electrode **14** functions as an anode whereas the opposite side of the electrode serves as a cathode. This can be seen by referring to anode sections A and cathode sections C in the drawing.

Examining FIG. 2, it can be seen that the electrolytic cell shown therein has the advantage that it overcomes the need to step down the voltage. Unit cell voltage is usually between 4 and 8 volts D.C., requiring a transformer and a large number of electrical connections. These are eliminated by the series arrangement of FIG. 2. The current is applied at the two ends of the series of plates, and the cell voltage is determined by the number of cells connected in the series. Each electrode **14** preferably is lead. Nickel plated anodes and the iron cathodes have been used, but due to corrosion, use of these metals is not recommended.

As indicated the electrolytic cell of FIGS. 2 and 3 is particularly suited to continuous operation. To provide for the circulation of electrolyte the chromium salt feed solution is introduced into catholyte compartment C through inlet conduits connected to header **20**. Circulation of catholyte is accomplished by this introduction coupled with flow through the diaphragm and residence time in the anolyte compartment. To achieve this flow through the diaphragm, the polytetrafluoroethylene diaphragm **16** is provided with one or several smaller orifices **15** providing unrestricted flow at that point. It was first believed that with an orifice in the diaphragm the system would be conductive, forming a short circuit rendering the unit inoperable. Operation of the unit proved that the effect of the orifice was negligible. The orifice is positioned near the bottom of the catholyte compartment so that the feed must pass through the catholyte. Any compounds reduced in the catholyte compartment will be oxidized in the anolyte compartment. The orifice area is such that the transfer of catholyte to anolyte is no more rapid than the rate of anolyte withdrawal. Residence time in the anolyte is one unit cell volume per one to one and one-half hours. The regenerated chromium compound solution is withdrawn through manifold **18** controlled by vacuum. Hydrogen formed at cathode **14** is withdrawn through manifold **12**. During the continuous operation an electric current applied at **21** and **22** passes continuously through the catholyte, the diaphragm and the anolyte to bring about the anodic oxidation of ionic chromium.

The invention thus contemplates an electrolytic apparatus for the continuous regeneration of trivalent chromium salt solutions to form hexavalent chromium compounds which includes a plurality of electrode plates held by frames in a filter press type of arrangement forming a series of unit cells, the plates being series connected with one side of the plate acting as an anode, the other as a cathode. A permeable polytetrahaloethylene diaphragm is interposed between adjacent electrode plates dividing each unit cell into two compartments, an anolyte and a catholyte compartment. An orifice in said diaphragm connects the anolyte and catholyte compartments. Means are provided for introducing a liquid feed stream into the catholyte compartment, for withdrawing regenerated chromium compound solution from the anolyte compartment, and for withdrawing hydrogen from the catholyte compartment.

Some of the facets of this invention can be further illustrated by a study of results obtained using different polytetrafluoroethylene diaphragms. Thus, a preferred porosity of 50 to 150 microns was established. It was then deemed necessary to examine the void content of the polytetrafluoroethylene diaphragm. Diaphragms having a void content due to their porosity of thirty, forty and fifty per cent voids were investigated. For this investigation a batch electrolytic cell was employed with a static catholyte. The current was applied for one hour and the anolyte analyzed for chromium (VI) ion. The data obtained was as follows, kilowatts and anode area requirements being based on a calculated basis of one pound of sodium dichromate per hour.

TABLE I

[At 6.5 volts Cathode area—⅙ anode area]

Diaphragm:			
Void content (percent	30	40	50
Pore size (microns)	50–150	50–150	50–150
Thickness (inches)	0.01	0.12	0.01
Kw. required	1.42	1.41	1.73
Anode area required	2.72	2.56	2.36

Having determined that a pore size of 50–150 microns and a void content of forty percent were optimum for large scale regeneration, performances of this diaphragm at different voltages were compared, still in batch operation.

TABLE II

Voltages (volts)	Kw. required	Anode area required ($ft.^2$)
4.5	1.10	6.72
5.5	1.21	3.20
6.5	1.42	2.56

Table II shows that the optimum voltage for the system, a filter press type with static catholyte, is between 5.5 and 6.5 volts depending on power cost. (kw. required) or capital investment (anode area required).

The electrolytic cell used in obtaining the data of Tables I and II was built as shown in FIG. 3 and continuous operation was begun. The charge was fed to anode compartments via the cathode compartments. One such run was as follows. For clarity the data in this and all

of the following tables is reported on a calculated basis of various requirements per pound of sodium dichromate.

TABLE III

Cell potential	7 volts.
Diaphragm	⅛ in. polytetrafluoroethylene (40% voids).
Electrodes	Lead sheets.
Electrode separation	2⅛ inches.
Charge	4.89 g. Cr/100 g. solution.
Cell volume	500 ml.
Flow rate	1 cell volume (500 ml.)/hr./cell.

Length of run (hours)	Current density (amp./cm.²)	Kwh./lb. ($Na_2Cr_2O_7$)	Ft.² anode/lb. ($Na_2Cr_2O_7$/hr.)
10	0.0716	3.04	6.54
15	0.0647	3.15	7.48
20	0.0659	3.84	8.95
25	0.0592	3.50	9.08
30	0.0631	2.47	6.03
35	0.0651	2.56	6.04
40	0.0722	2.94	6.26
45	0.0795	2.53	4.88
50	0.0662	2.49	5.79
55	0.0593	2.17	5.63
60	0.0540	2.02	5.75
65	0.0584	2.23	5.63
70	0.0521	2.20	6.20
75	0.0573	3.18	8.54
80	0.0603	3.69	9.41
85	0.0638	2.83	6.83

Average current efficiency—72.7 percent.

The data in Table III shows a continuous regeneration period of extreme length. Even at the end of eighty-five hours it was not necessary to shut down the operation. The example shows not only the efficiency of the process but the value of the diaphragm of the invention.

Flow rates were varied in the cells by withdrawing less than the cell capacity of 500 ml. per hour per cell, resulting in a longer residence time in each full cell. Flow rate data is given in Table IV.

TABLE IV

Flow rate	Length of run (hours)	Current density (amp./cm.²)	Kwh./lb. ($Na_2Cr_2O_7$)	Ft.² anode/lb. ($Na_2Cr_2O_7$/hr.)
500 ml./hr./cell	10	0.0716	3.04	6.54
	15	0.0647	3.15	7.48
	20	0.0659	3.84	8.95
		Average current efficiency—59.4		
350 ml./hr./cell	5	0.0862	2.47	4.42
	10	0.0806	2.28	4.35
	15	0.0828	2.65	4.93
	20	0.0789	2.11	4.11
		Average current efficiency—82.6		
175 ml./hr./cell	5	0.0832	2.55	4.72
	10	0.0815	2.35	4.44
	15	0.0763	2.65	5.36
	20	0.0741	2.63	5.46
		Average current efficiency—76.7		

For this cell and under these conditions the slightly longer residence time afforded by a flow rate of 350 ml. is more desirable.

The feasibility of regenerating solutions not completely reduced (containing different amounts of chromium (VI) ions) was investigated in the following runs.

TABLE V

Percent Cr (VI) (In the feed)	Length of run (hours)	Current density (amp./cm.²)	Kwh./lb. ($Na_2Cr_2O_7$)	Ft.² anode/lb. ($Na_2Cr_2O_7$/hr.)
0	10	0.0716	3.04	6.54
	15	0.0647	3.15	7.48
	20	0.0659	3.84	8.95
		Average current efficiency—59.4		
10	5	0.0622	2.51	6.22
	10	0.0718	4.67	6.79
		Average current efficiency—69.5		
21.1	5	0.0588	4.93	12.88
	10	0.0616	3.57	8.90
	15	0.0627	4.76	11.66
	20	0.0634	4.00	9.69
		Average current efficiency—46.0		

Also with the idea of attenuating reduction in the catholyte the anode to cathode area ratio was increased. This was done by insulating a portion of the cathode. The result is an increase in current density. It was believed that an increase in current density on the cathode would increase the hydrogen ion content thereby forming

molecular hydrogen more rapidly which would leave the system. The charge contained 33.28 percent hexavalent chromium ion. A slight effect is shown by a ratio 2.6 to 1.

TABLE VI

Anode to cathode ratio	Length of run (hours)	Current density (amp./cm.²)	Kwh./lb. ($Na_2Cr_2O_7$)	Ft.² anode/lb. ($Na_2Cr_2O_7$/hr.)
1 to 1	5	0.0674	14.39	32.83
	10	0.0682	12.31	27.76
	15	0.0690	8.03	17.88
		Average current efficiency—17.9		
2.6 to 1	5	0.0825	5.30	9.87
	10	0.0756	8.37	16.98
	15	0.037→	10.90	22.75
		Average current efficiency—26.0		
8 to 1	5	0.0444	12.18	42.19
	10	0.0431	13.54	48.32
		Average current efficiency—15.2		

TABLE VII

Electrode separation	Length of run (hours)	Current density (amp./cm.²)	Kwh./lb. ($Na_2Cr_2O_7$/hr.)	Ft.² anode/lb. ($Na_2Cr_2O_7$/hr.)
2⅛ in. apart, ⅛ in diaphragm.	10	0.0716	3.04	6.54
	15	0.0647	3.15	7.48
	20	0.0659	3.84	8.95
		Average current efficiency—59.4		
1⅛	5	0.0593	2.98	7.73
	10	0.0573	2.83	7.58
	15	0.0538	2.57	7.12
	20	0.0539	2.75	7.85
		Average current efficiency—70.2		

The data in Table VII shows that bringing the electrodes closer together reduces operation cost, but more anode area is required.

The foregoing examples and descriptions illustrate that according to this invention a durable and efficient filter press type electrolytic cell is provided. Ceramic diaphragms crack under their own weight in such use. Diaphragms employed in other electrolytic processes are not generally considered for chromic acid regenerations because of the acidic and corrosive nature of the substances involved. The adaptation of the cell for commercial operation results in a long running continuous process. Modifications in sizes, voltages, the various chromium salts, electrolytic systems, and the like will of course be obvious. In addition the cells of this invention can be employed for producing electrolytic chromium from chromium ores, regeneration of chromic acid baths utilized in electrodeposition of chromium, and the electrolytic production of chromium hydride. Such ramifications and variations are deemed to be within the scope of this invention.

What is claimed is:

1. An electrolytic apparatus for the continuous regeneration of trivalent chromium salt solutions to form hexavalent chromium compounds comprising: a plurality of electrode plates held by frames in a filter press type of arrangement forming a series of unit cells, the plates being connected in series with one side of a plate acting as an anode and the other as a cathode; a permeable polytetrahaloethylene diaphragm interposed between adjacent electrode plates dividing each unit cell into an anolyte and a catholyte compartment, said polytetrahaloethylene diaphragm being a membrane having pores of a diameter within the range of about 1 to about 300 microns and a void content of about 40%; at least one orifice in said diaphragm connecting the anolyte and catholyte compartments at a location and of an area sufficient to allow controlled flow of the solution through both compartments of the cell consecutively without electrically short-circuiting the cell; means for introducing

a liquid feed stream into the catholyte compartment; means for withdrawing regenerated chromium compound solution from the anolyte compartment; and means for withdrawing hydrogen from the catholyte compartment.

2. The electrolyte apparatus of claim 1 wherein the diaphragm is polytetrafluoroethylene; wherein the orifice in the diaphragm is near the bottom thereof; wherein the means for introducing a liquid feed stream into the catholyte compartment comprises a feed stream conduit opening into the top of said compartment; wherein the means for withdrawing regenerated chromium compound solution from the anolyte compartment comprises a conduit system connected into the top of said compartment; and wherein the means for withdrawing hydrogen from the catholyte compartment comprises a gas vent opening into the top of said compartment.

3. The apparatus of claim 2 wherein the polytetrafluoroethylene diphragm has a pore size range of about 50 to 150 microns.

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U.S. Cl. X.R.

204—89, 266, 296

United States Patent Office

CERTIFICATE OF CORRECTION

Patent No. 3,450,623 Dated June 17, 196

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L. E. Hutchings

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

In column 6, line 15, in the third column of Table VI, delete "0.037→" and substitute instead -- 0.0737 --.

SIGNED AND
SEALED
JAN 27 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents