July 27, 1971 L. A. JOO 3,595,765

PPOCESS FOR THE ELECTROLYTIC REGENERATION
OF REDUCED CHROMIUM COMPOUNDS
Original Filed Oct. 8, 1965

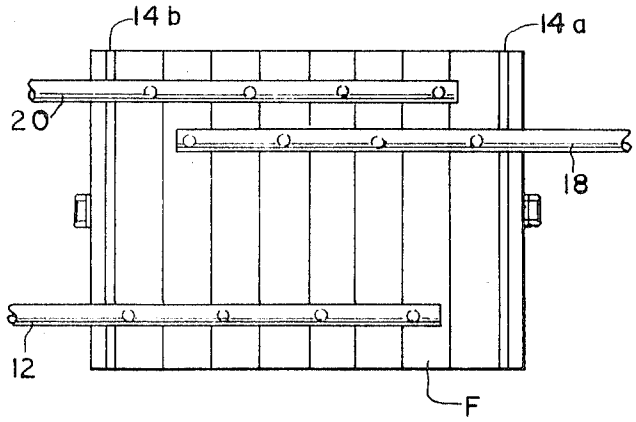


FIG. 1

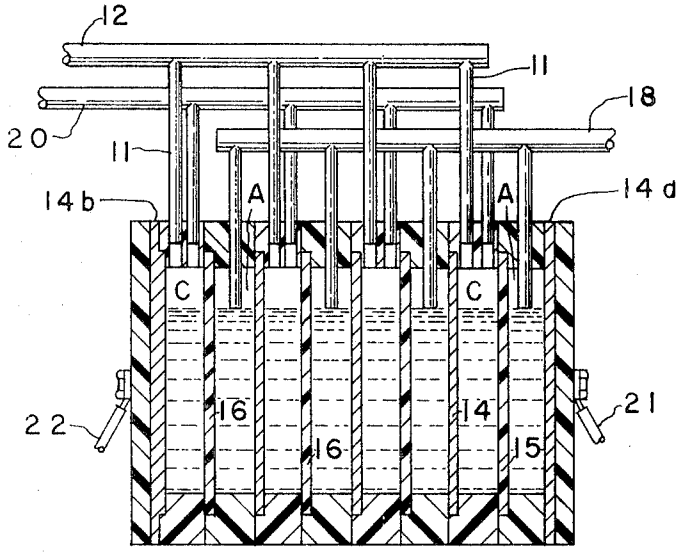


FIG. 2

INVENTOR.
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3,595,765

PROCESS FOR THE ELECTROLYTIC REGENERATION OF REDUCED CHROMIUM COMPOUNDS

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Original application Oct. 8, 1965, Ser. No. 493,995, now Patent No. 3,450,623, dated June 17, 1969. Divided and this application Aug. 7, 1968, Ser. No. 750,967
The portion of the term of the patent subsequent to Jan. 21, 1986, has been disclaimed
Int. Cl. B01k *1/00*; C01g *37/00*
U.S. Cl. 204—89 6 Claims

ABSTRACT OF THE DISCLOSURE

An electrolytic process for the continuous conversion of reduced chromium values to the hexavalent form, which consists in subjecting an aqueous sulfuric acid solution of reduced chromium to the action of direct current voltage applied in series to a multi-unit filter press type cell assembled from chromic acid resistant material, lead electrodes and polytetrahaloethylene diaphragms having a porosity of about 40% and a pore diameter preferably within the range of 50 to 150 microns.

The chromium solution follows a prescribed path through the cathode compartment, through one or more special orifices in the diaphragm and through the anode compartment. The residence time in the cathode compartment is approximately one hour.

The process is characterized by continuity, high current density, low energy requirements, low anode plate requirements and a high level of one-pass regeneration.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a division of an earlier co-pending application Ser. No. 493,995, filed on Oct. 8, 1965, now U.S. Pat. 3,450,623, issued June 17, 1969.

This application is particularly concerned with the process aspects of this invention. The apparatus features described therein have already been claimed in copending application Ser. No. 493,995 filed on Oct. 8, 1965 and are described here strictly for the purpose of rendering the process disclosure more intelligible.

The prior art

As is well known, hexavalent chromium solutions such as chromic acid in admixture with sulfuric acid, are powerful oxidizing agents. These solutions are particularly effective in the oxidation of fused ring polynuclear hydrocarbons to quinones, the latter quinones being of course valuable starting materials and intermediates in the manufacture of dyes, drugs, and the like. Solutions containing available oxygen in the form of chromic acid are also commonly employed to effect the oxidation of relatively long chain unsaturated fatty acids and oils by producing a cleavage of the chain. The oxidation of fused ring hydrocarbons and the disruptive oxidation of double bonds are 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 chromic sulfate solutions can be electrolytically regenerated to form CrO_3 solutions. The regenerative electrochemical reactions are effected in an electrolytic cell of the bipolar electrode type. The present invention deals with chromic acid regenerative processes of this type, one of its objects being the improvement of the electrolytic cell.

In a typical cell used for the oxidation of trivalent chromium salts, a direct current (DC) voltage is applied to the electrodes to cause the electrolytic decomposition of water. The hydrogen atoms produced form molecular hydrogen, which is allowed to escape from the cell, while the oxygen is involved in the formation of lead dioxide which in turn is believed to oxidize the trivalent chromium to the hexavalent form that is present in chromic acid. Obviously, under such circumstances, means must be employed to prevent the migration within the cell of the freshly oxidized chromic acid to the cathode area where it would merely be reduced again. Porous ceramic diaphragms have therefore been used as barriers between the anode and cathode compartments of the cells.

The diaphragms constitute a chief source of wear and tear in the cells. While other potential difficulties such as electrode corrosion may be prevented by proper operation, ceramic diaphragms, although selected because of their chemical resistance, tend to pulverize on continued use. Furthermore, they do not lend themselves to large scale industrial operations.

In accordance with one aspect of this invention it has been found that polytetrahaloethylenes 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 filter press type bipolar cells. These electrolytic cells are composed of a plurality of unit cells in a filter press type arrangement, adjacent to each other in a row, each unit cell being divided by a diaphragm into an anolyte compartment and a catholyte compartment. In another 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.

Filter press type electrolytic cells are of course known in the art, but it is believed that they had not previously been employed for the oxidation of chromic acid solutions. Ceramic diaphragms are difficult to use in this type of cell due to their rigidity and brittleness. Consequently, the diaphragms disclosed in the prior art for filter press type electrolytic cells are either fabric, such as canvas, or plastic, such as polyethylene. None of these can withstand the chemical attack of chromic acid.

SUMMARY OF THE INVENTION

The invention thus consists of a continuous process for the regeneration of trivalent chromium salt solutions to form hexavalent chromium compounds, which comprises continuously introducing into the catholyte compartment of an electrolytic cell containing a permeable polytetrahaloethylene diaphragm, a feed solution of a trivalent chromium salt, passing the solution through the compartment and then through at least one orifice in the diaphragm into the anolyte compartment of the cell, thereby preventing salt deposition in the catholytic compartment. A continuous electric current is passed through the catholyte, the diaphragm and the anolyte to bring about anodic oxidation of the chromium salt and the regenerated solution is removed from the anolyte compartment.

The invention contemplates the carrying out of this process in an apparatus which includes a plurality of electrode plates held by inert tubular frames in a filter press type of arrangement forming a series of unit cells, the plates being placed in series with one side of each plate serving as anode and the other as cathode. A permeable polytetrahaloethylene diaphragm is interposed between adjacent electrode plates, dividing each unit cell into two compartments, an anolyte and a catholyte compartment. These compartments are connected by an orifice in the

diaphragm. Means are provided for introducing a liquid feed stream into the catholyte compartment, for withdrawing regenerated chromium compound from the anolyte compartment, and for withdrawing hydrogen from the catholyte compartment. Details of the apparatus are given in the drawing and in the text which describes the figures therein.

DESCRIPTION OF THE DRAWING

The cell that can be employed in the regeneration of chromic acid solution according to the present invention can be better visualized by reference to the accompanying drawing which is that found in Ser. No. 493,995. It must be noted that only equipment sufficient to illustrate the invention has been shown, pumps, valves and other secondary features being omitted for simplicity.

FIG. 1 gives a top view of an electrolytic cell comprising a filter press type assembly.

FIG. 2 is a transverse sectional elevation of the cell of FIG. 1.

During continuous operation, reduced chromium salts and metallic chromium tend to accumulate in the catholyte and cause unwanted deposits on the various compartment surfaces. However, a continuous chromium salt solution electrolytic regeneration process has been provided which can be operated much longer than any heretofore known continuous process. 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. According to this practice, a feed solution of the trivalent chromium salt solution to be regenerated is continuously introduced into the catholyte compartment of an electrolytic cell having an anolyte compartment and a catholyte compartment separated by a permeable polytetrahaloethylene diaphragm. In this embodiment, shown in FIG. 2, 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 compartment preventing salt deposition in said catholyte compartment.

Referring to FIG. 1 and FIG. 2, 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. 1, 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 DC, requiring a transformer and a large number of electrical connections. These are eliminated by the series arrangement of FIG. 1. 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 iron cathodes have been used, but due to corrosion, these metals are not recommended.

As indicated, the electrolytic cell of FIGS. 1 and 2 is particularly suited to continuous operation. To effect 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 flow through the diaphragm, the polytetrafluoroethylene membrane **16** is provided with one or several smaller orifices **15** allowing unrestricted flow at that point. Although it was first believed that an orifice in the diaphragm woulud render the system conductive by short circuiting the unit, actual operation of the unit has demonstrated that the effect of the orifice is negligible. The orifice is positioned near the bottom of the catholyte compartment so that the feed must pass through that compartment. Any compound reduced in the catholyte compartment will be oxidized in the anolyte compartment. The orifice area is such that passage from the catholyte compartment to the anolyte compartment is no more rapid than the rate of anolyte withdrawal. Residence time in the anolyte is one unit cell volume per 1 to 1.5 hours. The regenerated chromium compound solution may be 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 polytetrahaloethylene of which the diaphragm of the invention is made may be a polymer of tetrafluoroethylene or trifluorochloroethylene. These known polymers are described broadly in U.S. Pats. 2,393,967 and 2,600,202, the ones usable here being permeable and having a sufficiently high molecular weight to be solids. A permeable sheet means a porous sheet, with a porosity such that electron flow is permitted while the flow of ions and hydrogen is inhibited. For this invention, the pore size should be in the range of 1 to 300 microns at its largest. Thus the reduction of regenerated chromic acid at the cathode will be minimized and the energy and anode area requirements will be at their lowest due to inhibited ionic flow. The preferred pore sizes are in the range of 50 to 150 microns for a permeable membrane. It should be noted also that successful use has been made of nonporous Teflon® polytetrafluoroethylene fibers woven or matted into a cloth. In such instances, the only voids present in the resulting structure were the spaces between the filaments. Yet, the cloth has been made to the proper specifications so that its resistance to current is minimal and its barrier properties are satisfactory. Fibrous membranes of this nature are available to industry under the trade name of Zitex®.

Some of the facets of this invention can be further illustrated by a study of results obtained using different polytetrafluoroethylene diaphragms. In this manner, the preferred pore size 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 percent voids were investigated. For this purpose, 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 the 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
Kilowatts 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

	Kilowatts required	Anode area required (ft.²)
Voltage (volts):		
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 shall now be described. For clarity, the data in this and all of the following tables are reported on a calculated basis of various requirements per pound of sodium dichromate.

TABLE III

Cell potential: 7 volts
Diaphragm: 1/8 inch polytetrafluoroethylene
Electrodes: Lead sheets (40% voids)
Electrode separation: 2 1/8 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	Current density (amp./cm.²)	Kwh./lbs. ($Na_2Cr_2O_7$)	Ft.² anode/lbs. ($Na_2Cr_2O_7$/hr.)
Hours:			
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

NOTE.—Average current efficiency=72.7%.

The data in Table III illustrates 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 demonstrates not only the efficiency of the process but also 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 are given in Table IV.

TABLE IV

Flow rate	Length of run (hours)	Current density (amp./cm.²)	Kwh./lbs. ($Na_2Cr_2O_7$)	Ft.² anode/lbs. ($Na_2Cr_2O_7$/hr.)
500 ml./hr/cell [1]	10	0.0716	3.04	6.54
	15	0.0647	3.15	7.48
	20	0.0659	3.84	8.95
350 ml./hr./cell [2]	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
175 ml./hr./cell [3]	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

[1] Average current efficiency=59.4%.
[2] Average current efficiency=82.6%.
[3] 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./lbs. ($Na_2Cr_2O_7$)	Ft.² anode/lbs. ($Na_2Cr_2O_7$/hr.)
0 [1]	10	0.0716	3.04	6.54
	15	0.0647	3.15	7.48
	20	0.0659	3.84	8.95
10 [2]	5	0.0622	2.51	6.22
	10	0.0718	4.67	6.79
21.1 [3]	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

[1] Average current efficiency=59.4%.
[2] Average current efficiency=69.5%.
[3] 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 more rapidly forming molecular hydrogen 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./lbs. ($Na_2Cr_2O_7$)	Ft.² anode/lbs. ($Na_2Cr_2O_7$/hr.)
1 to 1 [1]	5	0.0674	14.39	32.83
	10	0.0683	12.31	27.76
	15	0.0690	8.03	17.88
2.6 to 1 [2]	5	0.0825	5.30	9.87
	10	0.0756	8.37	16.98
	15	0.0737	10.90	22.75
8 to 1 [3]	5	0.0444	12.18	42.19
	10	0.0431	13.54	48.32

[1] Average current efficiency=17.9%.
[2] Average current efficiency=26.0%.
[3] Average current efficiency=15.2%

TABLE VII

Electrode separation	Length of run (hours)	Current density (amp./cm.²)	Kwh./lbs. ($Na_2Cr_2O_7$/hr.)	Ft.² anode/lbs) ($Na_2Cr_2O_7$/hr..
2 .125" apart, 0.125" diaphragm [1]	10	0.0716	3.04	6.54
	15	0.0647	3.15	7.48
	20	0.0659	3.84	8.95
1.125 [2]	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

[1] Average current efficiency=59.4%.
[2] Average current efficiency=70.2%.

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

The foregoing examples and descriptions illustrate an efficient continuous process for the electrolytic regeneration of trivalent chromium solutions. This process is car-

ried out in a specially designed filter press type electrolytic cell fitted with polytetrahaloethylene membranes which allow the passage of electricity while acting as a barrier to ions and molecules. It is of course obvious that modifications can be made in procedures, sizes, voltages, nature of chromium salt, electrolytic system and so on, without departing from the concept and the scope of the invention. For example, the process of the invention can be carried out on several types of trivalent chromium solutions including solutions for producing electrolytic chromium from ores, chromic acid baths for electrodeposition, solutions from the electrolytic production of chromium hydride, spent oxidizing solutions from organic oxidation processes such as the aromatic hydrocarbon-quinone process, and so on. Such variations and ramifications are deemed to be within the scope of the following claims.

What is claimed is:

1. A continuous process for the electrolytic oxidation regeneration of reduced chromium compounds including trivalent chromium to the hexavalent state, which comprises:

(a) introducing continuously into the catholyte compartment of a filter press type bipolar electrolytic cell, a feed solution consisting essentially of a sulfuric acid solution of the chromium compound to be regenerated, said cell having interposed between adjacent electrode plates thereof a porous polytetrahaloethylene membrane having a pore diameter of 1 to 300 microns and which permits flow of electrons therethrough while inhibiting flow of ions and hydrogen;

(b) passing the feed solution into the upper part of the catholyte compartment and then through at least one orifice in the diaphragm into the anolyte compartment, thereby providing a circulation pattern in said catholyte compartment and preventing salt deposition therein, while

(c) subjecting the apparatus to direct current unit cell voltage of about 4 to 8 volts so that the current, in

passing through the catholyte, the diaphragm and the anolyte, brings about the anodic oxidation of the chromium compound, and

(d) withdrawing the regenerated solution from the anolyte compartment of the cell.

2. The process of claim **1** wherein the solution also contains sodium sulfate.

3. The process of claim **1** wherein the orifice area is of a magnitude such that the residence time of the feed solution in the catholyte compartment is one to one and one half hour.

4. The process of claim **1** wherein the reduced chromium compound solution contains the Cr(III) species obtained from the oxidations of an organic compound by hexavalent chromium.

5. The process of claim **1** wherein the reduced chromium compound solution is a chromite ore sulfuric acid extract.

6. The process of claim **1** wherein the diaphragm used has a void content of about 30 to 50%.

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