Aug. 2, 1949. P. C. CONDIT 2,477,579

ELECTROLYTIC PROCESS FOR THE PRODUCTION OF CYCLOHEXADIENE DICARBOXYLIC ACIDS

Filed Dec. 1, 1945 3 Sheets-Sheet 1

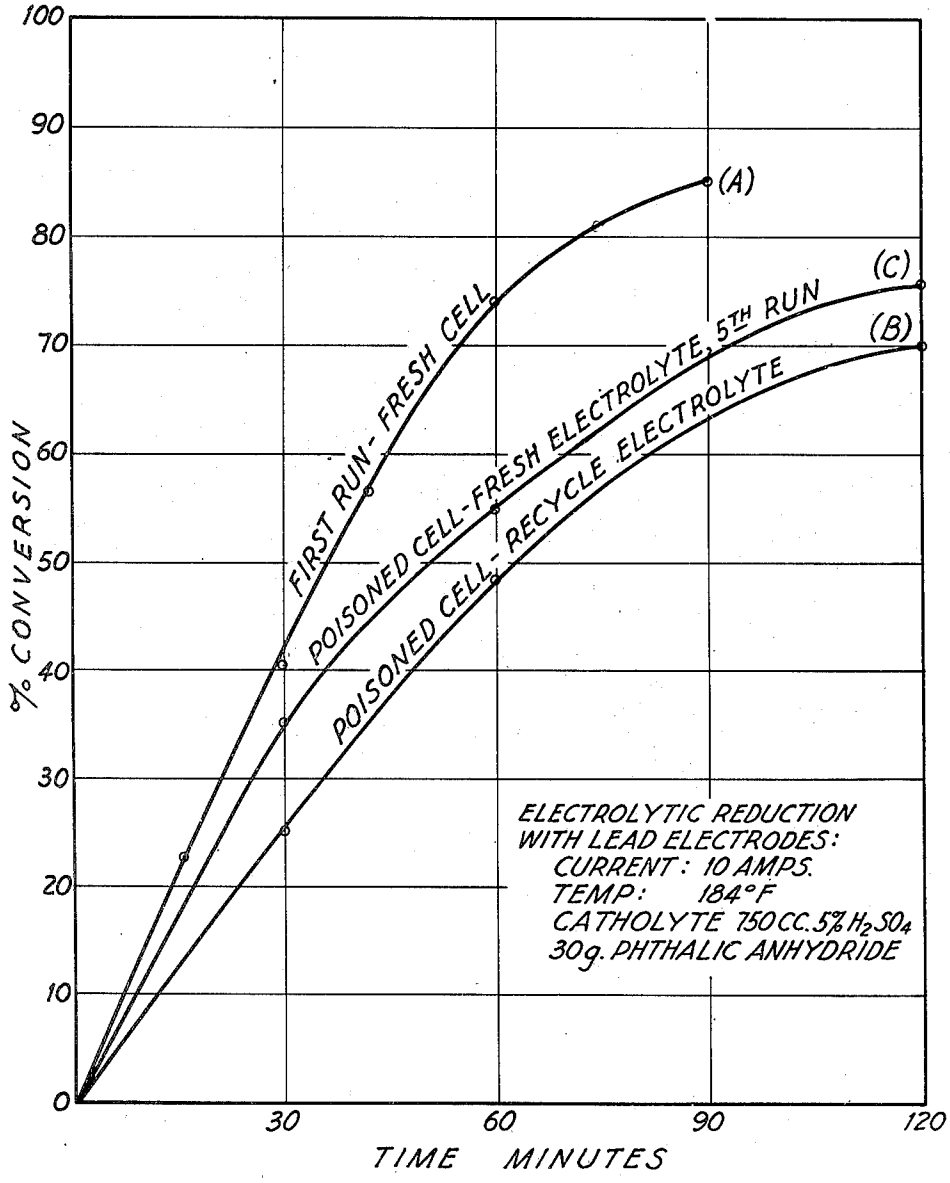


Fig. 1

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Filed Dec. 1, 1945 3 Sheets-Sheet 2

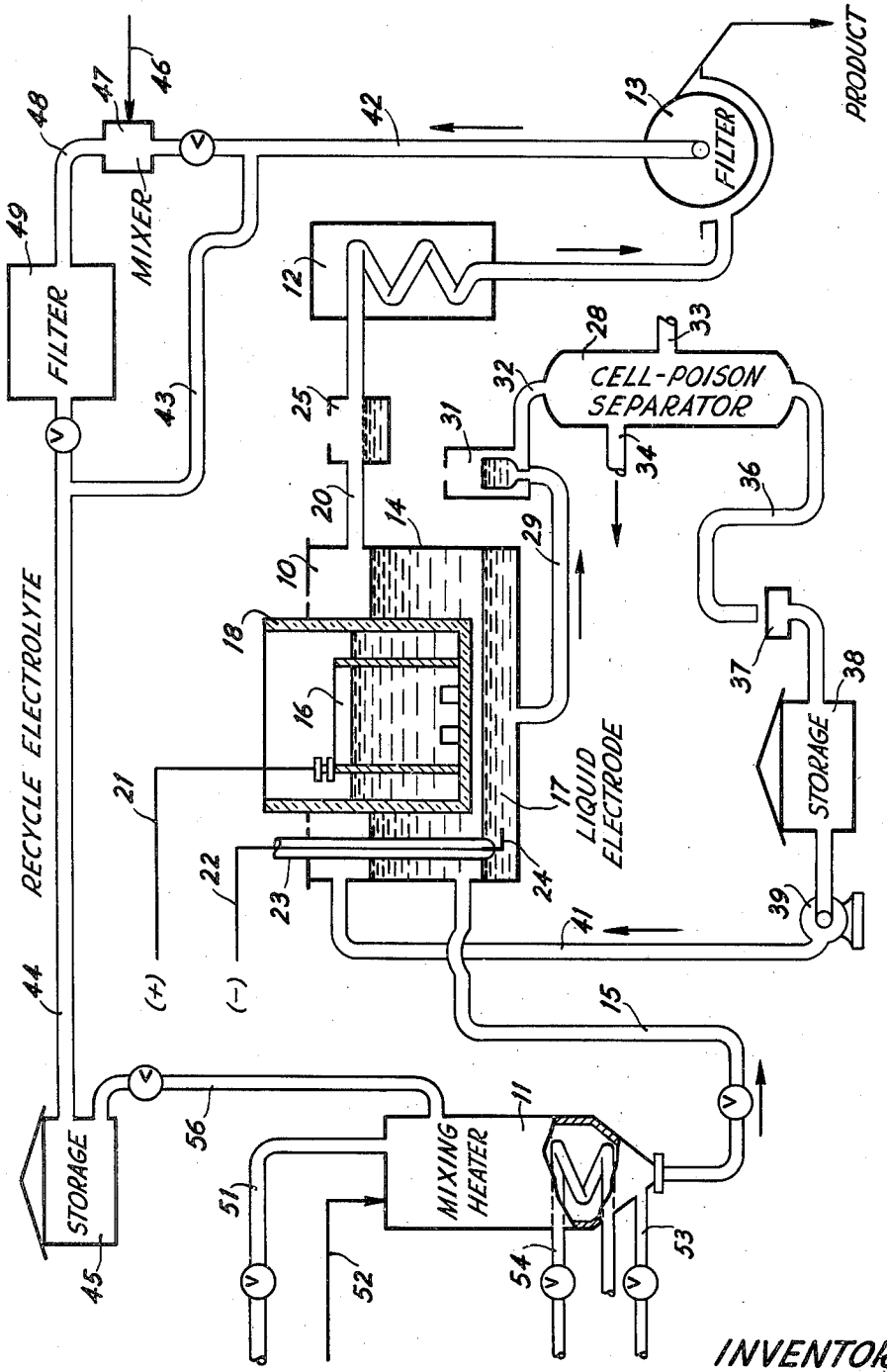


Fig. 2

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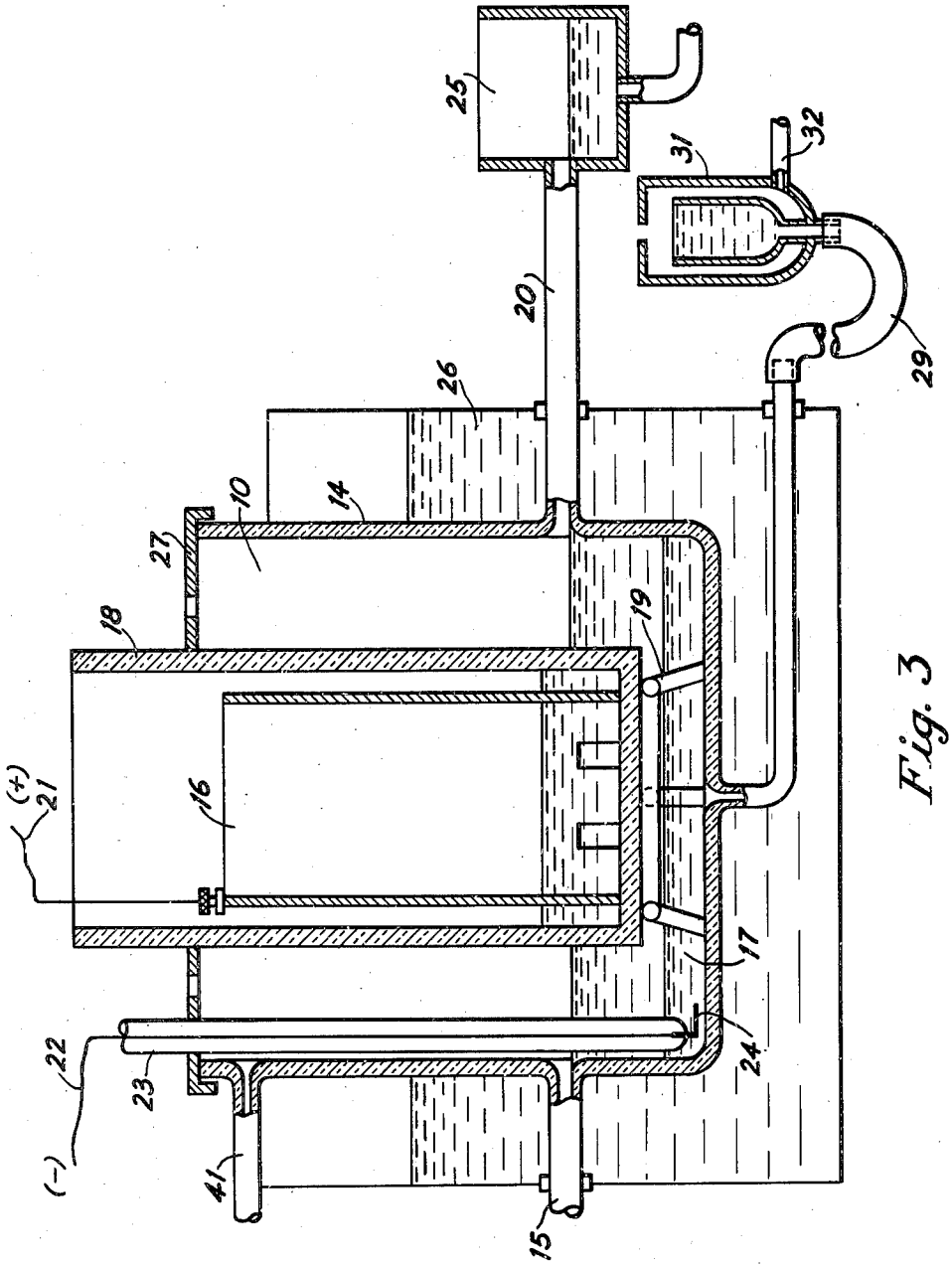


Fig. 3

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UNITED STATES PATENT OFFICE

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ELECTROLYTIC PROCESS FOR THE PRODUCTION OF CYCLOHEXADIENE DICARBOXYLIC ACIDS

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Application December 1, 1945, Serial No. 632,170

5 Claims. (Cl. 204—75)

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This invention relates to the electrolytic treatment of organic compounds, and, more particularly, to an improved process and apparatus for electrolytically inducing organic reactions such as the reduction of organic compounds.

One of the preeminent problems which has been encountered in electrolytically inducing reactions with organic compounds has been the accumulation or formation of cell poisons during cell operation. Little is known concerning the nature of these cell poisons, nor is the mechanism of their poisoning action adequately understood. But their effect is unequivocally deleterious, and the unsolved cell-poisoning problem in many instances has been largely responsible for the total rejection or, at the most, limited acceptance of proposed commercial electrolytic syntheses of organic compounds. The deleterious action of cell poisons is a greater problem in cathodic reductions exemplified by the electrolytic reduction of a carbon-to-carbon double bond of an organic compound in an aqueous electrolyte where two primary competing reactions are involved:

(1) $-C=C- + H_2O + 2(F) \longrightarrow -\underset{H}{\overset{|}{C}}-\underset{H}{\overset{|}{C}}- + \tfrac{1}{2}O_2$

(2) $H_2O + 2(F) \longrightarrow H_2 + \tfrac{1}{2}O_2$

In the above, "(F)" represents a Faraday of electricity and the remaining symbols have their usual chemical significance. The effect of cell poisons in this reaction is to increase the extent of reaction "(2)" or other reactions, and hence decrease either the desired conversion "(1)" or the electrical efficiency of the cell or both. Cell efficiency, and in many instances the practical feasibility of the entire process, depends upon the extent to which reaction (1) can be effected to the exclusion of reaction (2) above, and, in turn, therefore, on the extent to which cell poisoning can be controlled or avoided.

The solution of this problem has not been facilitated by the fact that neither the composition of cell poisons nor the mechanism of cell poisoning is adequately understood.

An object of the invention is to provide an apparatus and process for eliminating cell poisoning or reducing the deleterious action thereof in the electrolytic treatment of organic compounds.

Another object of the invention is to furnish an apparatus and process for effecting electrolytic treatment of organic compounds and for selectively removing cell poisons without the necessity of interrupting cell operation.

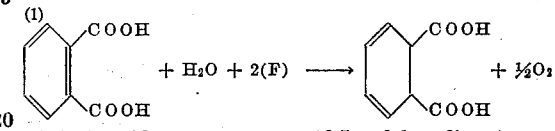
A further object is to provide an apparatus and

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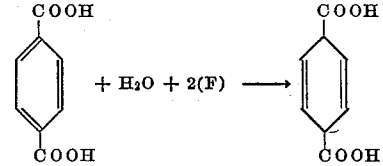
process for recycling electrolyte in an electrolytic treatment of organic compounds, and for preventing or minimizing accumulation of cell poisons which are formed in said recycling operation.

The invention is here illustrated by an apparatus and process particularly adapted to the electrolytic selective reduction of only one carbon-carbon double bond in the benzene ring of a phthalic acid to produce a cyclohexadiene dicarboxylic acid. The production of cyclohexadiene dicarboxylic acids by the process of this invention is believed new and is exemplified by production of two alternative compounds in accordance with the following chemical reactions:

(1)



Phthalic acid — Δ3,5-cyclohexadiene trans-dicarboxylic acid-1,2



Terephthalic acid — Δ2,5-cyclohexadiene dicarboxylic acid-1,4

However, the invention in its broader aspects, particularly the utility of the apparatus, is not limited to the foregoing specific reactions but includes the electrolytic treatment of other organic compounds where the same or similar cell poisoning problems are encountered. In general, it will be found that other electrolytic reductions of organic compounds may be effected with advantage according to the present invention. Such other reductions are exemplified by the conversion of unsaturated carboxylic acids to saturated acids, the reduction of organic carbonyl compounds such as carboxyl, keto or aldehyde groups in aromatic and aliphatic compounds, and the nuclear reduction of pyridine to piperidine compounds.

In the drawing, Figure 1 is a graph illustrating the effects of cell poisoning in the electrolytic partial reduction of the benzene ring in phthalic acid. Figure 2 is a flow sheet, partly diagrammatic, of an apparatus and process for electrolytically reducing organic compounds according to this invention. Figure 3 is a vertical section through an electrolytic cell of the type used in

Figure 2, which is provided with a mercury carrier for cell poisons and adapted for electrolytic reductions, such as the reduction of a phthalic acid to a cyclohexadiene dicarboxylic acid.

The deleterious effects of cell poisoning in an electrolytic reduction are illustrated by a recycle type operation in which (*a*) phthalic anhydride is added to a sulfuric acid catholyte, (*b*) electrolytic reduction is effected for a suitable contact time, (*c*) catholyte is removed from the cell, (*d*) cyclohexadiene dicarboxylic acid is crystallized out and separated from the catholyte, (*e*) more phthalic anhydride is added to the catholyte, and (*f*) the resulting solution is returned to the cell for an additional reduction treatment. This recycle type operation was thought highly desirable to avoid loss of uncrystallized product as well as to allow recovery of electrolyte. But cell poisoning seemed incurable. The extent of cell poisoning in such an operation is shown by curves A and B of Figure 1 and by the corresponding data given in Table I.

Table I

Time, Minutes	Percent of Acid Reduced	
	(A) Fresh Cell	(B) Recycle; Poisoned Cell
15	23	
30	41.5	25
42	57	
60	74	48
75	81	
90	85	
120		70

As may be seen from the data and from the curves of Figure 1, the efficiency of the cell was very much lower after poisoning and in the recycle operation. This is particularly apparent when the time required to effect a given conversion of phthalic acid to cyclohexadiene dicarboxylic acid is tabulated and compared for the foregoing two runs, as in Table II below:

Table II

Percent of Acid Reduced	Time, Minutes		Delay in Minutes
	Fresh Cell	Poisoned Cell	
30	20	35	15
40	28	50	22
50	35	60	25
60	45	80	35
70	55	120	65
80	70	(1)	
85	90	(1)	

[1] Not reached.

It should be noted that the data of Table II are qualitatively correct but are not to be taken as exact experimental determination, since they represent values read from curves plotted from the data of Table I. But the curves and these data do definitely show that at 70% conversion, for example, more than 100% increase in reaction time was required with a poisoned cell. This increase in reaction time corresponds directly to decreased current efficiency, since current through the cell was held substantially constant. Such an increase in time also means an increase in cost of electrical current and a corresponding loss in cell capacity.

The details of procedure in the foregoing runs are as follows: An electrolytic cell comprising an anode and cathode, both of chemical sheet lead, a porous porcelain cup as a diaphragm for separating the cell into anode and cathode compartments, and an aqueous sulfuric acid catholyte and anolyte were utilized. The specific conditions for the run were as indicated on Figure 1 of the drawing. Samples were pipetted from the cathode compartment at definite intervals and analyzed for cyclohexadiene dicarboxylic acid by calculation from the amount of bromine added to the double bonds of this acid (i. e., bromine number). After the specified time of reduction, the catholyte was removed from the cell and chilled to a temperature just above its freezing point. The major portion of the cyclohexadiene dicarboxylic acid crystallized out and was filtered off and dried. This product was weighed and analyzed for its content of the desired acid. The filtered electrolyte was analyzed for its content of dissolved acid, and material balances calculated from these figures.

After run A of Figure 1 of the drawing was made by the foregoing procedure, a second run, substantially identical thereto, was carried out and the filtered catholytes from these two runs combined for recycle to run B. 30 grams of phthalic anhydride was added to 750 cc. of the combined recycle catholyte and the volume of the catholyte as well as other process conditions maintained the same in run B as in run A. In all runs the cell was heated and catholyte temperature controlled by a liquid jacketing bath surrounding the cell. The cathode compartment of the cell was outside the porous cup diaphragm and the anode compartment inside the same.

From the foregoing it should be apparent that the extent of cell poisoning is sufficient in a recycle operation to inordinately increase the cost of synthesis by this method. One possible way of avoiding cell poisoning involved the suggestion that poisons were being returned to the cell by the recycle electrolyte, and that the cell should be operated on single passes or successive batches of fresh electrolyte. Results of this method of operation under the same conditions as in runs A and B, are illustrated in curve C of Figure 1 from which it will be observed that, although cell efficiency was improved as compared with recycle operation, cell poisoning still occurred and had produced a very substantial deleterious effect at the end of the previous four runs (8 hours total) with fresh electrolyte. The data thus showed that recycle of electrolyte accelerated poisoning, but that cell poisons also accumulated at a deleterious rate even in a single pass operation.

In run C, as in all runs, 5% sulfuric acid was used as an electrolyte and the initial concentration of phthalic anhydride together with other process conditions was the same as in previous runs.

In attacking the cell poisoning problem from a different angle, it was discovered that a liquid mercury cathode gave unpredictable advantages in the reduction of phthalic acid to cyclohexadiene dicarboxylic acid. These discoveries included the fact that tar formation and discoloration of the conversion product obtained with a lead cathode were reduced by the use of mercury, and also that substantially increased rates of reduction, enhanced current efficiency, and superior conversion to the desired product could be obtained. Further, a mercury cathode was found to be more resistant to cell poisoning in that it occurs at a lower rate. (My copending applica-

tion "Process of preparing cyclohexadiene dicarboxylic acids, Serial No. 632,171, filed of even date herewith.) Nevertheless, the poisoning problem still was not solved but only mitigated, since cell efficiency for recycle or prolonged single pass operations could still be greatly increased if cell poisoning were eliminated or inhibited.

Agitation of the liquid body of the mercury electrode to displace the electrode surface with fresh metallic mercury did not avoid poisoning, even though prior theories have indicated that the mechanism of cell poisoning may involve alteration of the cathode surface only. It was found that even complete removal of mercury from the cell, agitation with distilled water, settling to remove suspended bodies, followed by a final filtration of the mercury, all of which most certainly might be expected to furnish a fresh mercury surface upon re-use, did not eliminate the poisoning effect. Thus, an impasse was apparently presented which would prevent efficient operation of such a cell on a continuous or prolonged basis, since neither presenting a new surface in the liquid mercury electrode nor supplying a new electrolyte, as by single pass operation, prevented cell poisoning sufficiently to avoid very substantial reduction in cell efficiency after only a few hours (for example, 4 to 6 hours) operation.

The foregoing detailed review of the cell poisoning problem and of various proposed solutions has been given to illustrate the many difficulties and complexities involved before describing what might otherwise, in retrospect, seem to be a simple answer to the problem.

It has been discovered that cell poisons may be removed without interrupting the reduction reaction and that efficient cell operation may be vastly prolonged, even in an electrolyte-recycle type operation, by providing an apparatus and process in which a liquid carrier is utilized for selectively conveying poisons out of the cell and the poisons are separated from the carrier.

More particularly, a liquid electrode body, preferably metallic mercury, is provided in an electrolytic cell and the liquid of the electrode body desirably is utilized as the carrier for the cell poisons. Further, it has been discovered that when the electrode body is a cathode of metallic mercury and the reaction is a reduction of phthalic acid to a cyclohexadiene dicarboxylic acid at the mercury cathode, the mercury appears to act as a selective solvent for extracting and carrying the poisons out of the cell. In any event the metallic mercury is utilized as a carrier which conveys poisons out of the cell and leaves the electrolyte, together with its dissolved phthalic acid and cyclohexadiene dicarboxylic acids, in the cell. As evidence that the carrier action of the mercury is a selective solvent action by the liquid mercury, it has been found that the poisons are not separated from the mercury by mere gravity separation, by water washing, or by filtration. On the contrary, more stringent treatment is required for removing from the mercury those poisons which are formed in the electrolytic reduction of phthalic acid to cyclohexadiene dicarboxylic acids.

Suitable poison-separation treatments for removing cell-poison from the carrier are (1) chemical removal of the poisons with strong chemical reagents, such as strong acids or strong bases, oxidizing agents and the like, (2) separation of the poisons by distillation, or, (3) thermal decomposition and separation of the poisons in suitable cases. After separation of poisons by one of the foregoing methods, preferably chemical treatment as with caustic alkali, the liquid mercury carrier desirably is recycled to the liquid electrode body where it may again extract cell poisons as well as function as an electrode. By continuous or intermittent circulation of liquid mercury carrier from a liquid electrode body through a cell poison separator back to a liquid electrode body, it has been found that high cell efficiency may be maintained. The carrying capacity of the liquid mercury for the poison is sufficiently great to maintain such a high efficiency even when electrolyte is recycled and this is a preferred type operation.

Reference is made to Figures 2 and 3 of the accompanying drawing which shows one type of apparatus and process utilizing the principles of this invention. The apparatus comprises an electrolytic cell **10** for inducing the desired organic reactions, a mixing heater **11** for preparing an electrolyte solution of chemicals and feeding the solution to the cell by way of cell inlet pipe **15**. As here shown, the electrolyte solution is a catholyte which flows from the cell through discharge conduit **20** and level controller **25** to any suitable means for effecting product separation such as a chiller **12** for crystallizing the conversion product from its dissolved state in the electrolyte and a filter **13** for recovering the crystals from the electrolyte.

In the form here illustrated, electrolytic conversion cell **10** comprises a container **14** of material capable of resisting the action of the electrolytes (e. g., glass), an electrode **16**, preferably serving as an anode, and a liquid electrode body **17**, preferably of metallic mercury, and as here indicated, comprising the cathode of cell **10**. The anode **16** desirably is made of roll sheet chemical lead and may be in the form of a cylinder or spiral provided with openings at its lower end to permit circulation of anolyte therethrough. The mercury of the liquid cathode body should be a product of high purity, preferably doubly distilled metallic mercury. Inspection of the drawing will reveal a porous diaphragm **18** in the form of a porous cup, preferably of unglazed porcelain, surrounding the anode **16** and serving to divide the cell into an anode compartment and a cathode compartment. This diaphragm, together with its enclosed anode, is supported above but in proximity to mercury cathode body **17** by an insulating glass ring tripod **19**. A suitable source of direct current (not shown) is provided and is connected with anode **16** by means of a positive electrical lead **21**. A negative direct current lead **22** passes through a glass tube **23** to a tungsten wire or other suitable conductor **24** which is in electrical contact with the liquid mercury cathode and is sealed in the glass tube to exclude cell fluids. Suitable means for adjusting and controlling the flow of electric current through the cell may be provided in the usual manner. The electrolytic cell, as here shown, is jacketed by a water bath **26** (see Figure 3) for the control of cell temperature, and particularly to control catholyte temperature. Desirably, thermostatically controlled heaters (not shown) are provided in the water bath to maintain cell temperature at preferred levels. A chemical lead sheet **27** may be provided, as shown in Figure 3, for covering the cathode compartment, and in some instances, cooling coils may be immersed in the anolyte to

furnish auxiliary temperature control and avoid overheating in the anode compartment.

The electrolyte used in the cell will depend upon the particular electrolytic treatment to be effected and upon the organic compound selected for the reaction. Many suitable electrolytes, usually aqueous, are known for various electrolytic oxidation or reduction reactions and may be utilized within the broader aspects of this invention. In the electrolytic reduction of phthalic acid to a cyclohexadiene dicarboxylic acid, the invention embraces an anolyte and a catholyte comprising a dilute aqueous acid solution, preferably sulfuric acid in water. A phthalic acid dispersion in the catholyte is formed by dissolving or dispersing phthalic anhydride or phthalic acid in the aqueous sulfuric acid. The reduction of this acid to the desired product is effected as described in more detail hereinafter.

In order to prevent or reduce cell poisoning, a liquid carrier is provided to extract and convey poisons out of the cell without the necessity of interrupting its operation. As here shown, the liquid carrier comprises mercury in the liquid electrode body which appears to extract poisons as formed, together with mercury in the conveying system of conduits, vessels and pumps, for transporting the cell-poisons from the liquid cathode body to a cell-poison separator **28**. More particularly, the liquid carrier flows from cathode body **17** through conduit **29** to a level controller **31** (non-siphoning) for maintaining the fluid level of the liquid electrode at a constant or predetermined height. The mercury carrier then passes from level controller **31** by way of conduit **32** to cell-poison separator **28**. As previously indicated, separator **28** may take one of several forms, such as: (1) a chemical treater for scrubbing the poisons out of the carrier or decomposing the same by chemical action; (2) a still or fractionating column for removing the cell poisons from the liquid carrier by distillation; or (3) a thermal treater for decomposing the poisons by the action of heat, when of the thermally unstable type, and removing of decomposition products.

The presently preferred form of cell-poison separator comprises a chemical treater, such as a caustic alkali scrubber, for removing the poisons. In this treater, an aqueous caustic alkali solution may be fed to separator **28** by way of line **33** and removed through conduit **34**. Preferably, the chemical treating agent fills at least a substantial portion of separator **28** to provide a relatively deep liquid body through which the mercury carrier is caused to fall in discrete droplets. As the mercury carrier droplets pass through the body of chemical treating agent (aqueous caustic alkali), cell poisons are removed by chemical scrubbing or decomposition. The substantially poison-free mercury then is collected in the bottom of separator **28** to form a mercury seal which prevents reverse flow and assures discharge of the chemical treating agent upwardly through the separator countercurrently to the flow of mercury. Mercury from the seal is then passed through outlet conduit **36** to open inlet **37** of the mercury storage vessel **38** which furnishes a constant supply of mercury for recirculation to the cell.

As will be apparent from the drawing, mercury outlet conduit **36** and open inlet **37** are constructed and arranged to operate as a level controller for the mercury seal. The open end of conduit **36** is placed at the limiting lower level desired for the mercury seal and the upper extremity of the inverted U formed by conduit **36** serves to limit the maximum upper level for the mercury seal. Thus, an automatic siphoning level controller is provided which also has the advantage that it may be used to displace chemical treating agent in separator **28** and force the same upwardly to overflow through outlet **34**. As the mercury seal approaches the upper level (of the inverted U in conduit **36**), the siphon begins to discharge mercury from the seal and "pumps in" treating chemical through caustic inlet **33**. This "pumping" action continues until the mercury falls to a lower level corresponding to that of the open end of conduit **36**. (Note that the hydraulic head from the aqueous treating agent has little effect on the siphon level, due to the high density of mercury.) The automatic siphon thereby serves not only as a level controller for the mercuy seal, but also may fix the ratio of treating chemical to mercury carrier flowing through the system. As indicated in the drawing, the inlet **33** for treating chemical should be above the maximum upper level of the mercury seal.

The foregoing or other forms of level controller may be utilized for fixing the level of the cell electrolyte or of the liquid electrode body **17**. However, the constant level types illustrated by **25** and **31** are preferred for control of fluid levels in cell **10**. Likewise, these constant level types may be utilized for maintaining the mercury seal in separator **28**.

Suitable means, such as a mercury recirculation pump **39** and conduit **41**, are provided for continuously or intermittently returning the mercury carrier from storage **38** to liquid electrode body **17**. As the liquid electrode level is raised by return of the liquid carrier thereto, a portion of the electrode liquid is forced through outlet pipe **29** to level controller **31** and again serves as a liquid carrier for cell poisons formed during interim operation of the electrolytic cell.

Despite the fact that recycle of electrolyte in processes such as those here involved has been found to accelerate cell poisoning, the foregoing system for removing cell poisons and maintaining cell efficiency is capable of overcoming such accelerating effects. In an electrolyte-recycle type of operation, the cell and process of this invention continue to function at an efficient level, which may be maintained for prolonged periods with striking economy in both electrolyte and electric current consumption as well as in product recovery. This recycle type of operation is illustrated in Figure 2, wherein the electrolyte may be returned from product filter **13** by way of conduit **42**, by-pass **43** and storage return conduit **44** to electrolyte storage tank **45**. The stored electrolyte is returned to cell **10** by way of mixer **11** either continuously or intermittently as desired.

In some instances it will be found advantageous to reduce the color-body content of the recycle electrolyte or diminish its tendency to accelerate poisoning by treatment with a solid adsorbent, such as active carbon, acid treated decolorizing clay, or the like. Provision is made for this mode of operation in Figure 2, where active carbon is introduced at **46** into mixer **47** and thoroughly contacted with the electrolyte to adsorb organic color bodies, cell poisons and the like contained therein. The resulting slurry then flows through conduit **48** to filter **49** for removal of the active carbon with its adsorbed materials and the filtrate is passed to storage through recycle line **44**. Al-

ternatively, this treatment with solid adsorbents may be effected before product separation as by inserting mixer 47 and filter 49 in line 20 adjacent level controller 25 where the electrolyte solution is above crystallization temperature.

The presently preferred process carried out in the foregoing apparatus involves cathodic reduction of an organic compound, desirably an unsaturated carbon-to-carbon bond in an organic carboxylic acid, such as maleic acid, fumaric acid, or preferably, nuclear partial reduction of an aromatic dicarboxylic acid selected from the group consisting of terephthalic acid and orthophthalic acid. Specific process conditions will vary among the reactants utilized, and even in the case of one type of reactant, preferred conditions may change with different cell structures, with ratio of volume of catholyte to surface area of cathode, as well as with other variables, such as temperature, electrolyte, and concentration in the catholyte of the compound to be reduced. However, to illustrate suitable conditions for operating the apparatus shown in the drawing, for the production of Δ3,5-cyclohexadiene trans-dicarboxylic acid-1,2 from orthophthalic acid, the following data are given:

Preferred operating temperatures for the catholyte are from about 80° C. to about 90° C., although temperatures as low as about 60° C. and as high as about 100° C. may be utilized. The concentration of sulfuric acid in the catholyte may vary from about 3% to about 20% by weight of concentrated sulfuric acid (specific gravity about 1.84) in water, and the anolyte is preferably approximately the same concentration. From about 2% to about 10%, preferably about 4%, by weight of phthalic anhydride is dissolved or dispersed in the aqueous sulfuric acid catholyte solution. Current densities may vary widely from about 2 amperes per square decimeter to about 40 amperes per square decimeter of cathode area, it having been found that about 10 amperes per square decimeter is desirable where the catholyte contains approximately 5% by weight sulfuric acid and about 4.5% by weight phthalic acid. Flow of poison carrier through the cell should be sufficiently great to remove cell poisons at the desired rate. On the average, the amount of mercury carrier passed through the cell should be sufficiently great to provide a poison carrying capacity at least equal to the poison accumulation rate. It has been found that an hourly rate of addition and removal of one volume of mercury for each volume of mercury in the cathode (150 cc.) is adequate.

In operating the process, a catholyte mixture is made up in mixing heater 11 by introducing fresh aqueous sulfuric acid by way of line 51 and phthalic anhydride, as indicated at 52, in the ratio, for example, of 40 parts by weight of phthalic anhydride per liter of 5% aqueous sulfuric acid. The mixture may be agitated by any suitable means, such as by introduction of air through line 53 and heated by steam in closed heating coil 54 to insure solution and bring the catholyte up to temperature. The cathode compartment of cell 10 is then filled with the catholyte mixture and 5% aqueous sulfuric acid added to the anode compartment by any suitable means. Cell poison separator 28 is sealed by addition of mercury, filled with 20% by weight of sodium hydroxide in water, and circulation of the mercury from storage and through the cell is begun, as previously indicated. Operation of the cell with an electric current density of 10 amperes per square decimeter is started and allowed to continue until a desired minimum amount of the phthalic acid has been reduced to cyclohexadiene dicarboxylic acid, as revealed by suitable tests such as measurement of bromine absorption (bromine number). Usually, at least 50% conversion is desired before circulation of the electrolyte through the cell is begun. After the minimum conversion point is reached, electrolyte, together with dissolved phthalic acid is passed from mixing heater 11 through conduit 15 to the cathode compartment at a rate corresponding to the capacity of the cell for conversion. Catholyte overflows through conduit 20 and constant level controller 25, and is then treated for separation of product by chilling to cause crystallization. In order to obtain maximum recovery of product, it is desirable that 90% or more conversion be effected in cell 10 and that the electrolyte be chilled to just above its freezing point, whereby most of the cyclohexadiene dicarboxylic acid is crystallized out and removed by filter 13, as indicated. Filtrate, which may contain some dissolved cyclohexadiene dicarboxylic acid or phthalic acid, or both, is recycled either by way of by-pass 43 or, alternatively, with an intermediate adsorption of organic color bodies and cell poisons in mixer 47 and filter 49 as previously disclosed. The recycle-electrolyte flows to storage tank 45 and is returned to mixing heater 11 by way of conduit 56. Make-up sulfuric acid may be added and additional phthalic anhydride is incorporated in the catholyte before recirculation to the cell.

It has been found that even when the recycle electrolyte contains residual uncrystallized Δ3,5-cyclohexadiene dicarboxylic acid-1,2, this residual acid may be recycled through the cell without substantial further reduction or loss thereof despite its high degree of cycloolefinic unsaturation. However, some isomerization of the Δ3,5 acid may occur to form Δ2,6-cyclohexadiene dicarboxylic acid-1,2.

Attention is directed to Table III, which gives data illustrating the effectiveness of the present invention in preventing cell poisoning. In this series of runs, the catholyte and anolyte were 5% sulfuric acid in water and an amount of phthalic anhydride equivalent to 40 grams of phthalic acid per liter of catholyte was added for each recycle operation. To facilitate separation of process variables recycle-electrolyte and product therefrom were handled as distinct batches in a semi-continuous operation. Current density was 10 amperes per square decimeter throughout all runs, and the volume of catholyte in the cell was 1500 cc., as indicated. Mercury poison carrier was passed through the cell at 150 cc. per hour and mercury cathode volume was 150 cc.

Examination of the data will reveal that cell poisoning difficulties were eliminated for a period of 20 hours, during which time the catholyte was recycled 10 times. After this period of 20 hours running, fresh catholyte was supplied and a 2-hour run showed that the conversion, as indicated by percent cyclohexadiene dicarboxylic acid in the recovered product, was substantially the same as in the initial run. This establishes that substantially all cell poisoning had been prevented. It should be noted that indicated percent conversion (last column Table III) is the important factor in measuring cell poisoning since amount of product recovered also is a function of proficiency in crystallization and separation from the electrolyte solution.

Table III

Recycle No.	Catholyte		Temp., ° C.	Amp.	Time, Hrs.	g. Recovered	Total Recovered Per Cent Theory	Per Cent Dihydro Acid in Recovered Product
	cc.	Source						
0	1,500	Fresh	85	20	2.0	51.0	[1] 75	95
1	1,500	0+Makeup	85	20	2.0	62.0	91	96
2	1,500	1+Makeup	85	20	2.0	62.7	92	95
3	1,500	2+Makeup	85	20	2.0	64.3	95	92
4	1,500	3+Makeup	85	20	2.0	61.4	90	97
5	1,500	4+Makeup	85	20	2.0	66.3	98	95
6	1,500	5+Makeup	85	20	2.0	61.6	91	97
7	1,500	6+Makeup	85	20	2.0	58.8	87	97
8	1,500	7+Makeup	85	20	2.0	54.0	[2] 79	92
9	1,500	8+Makeup	85	20	2.0	54.4	[2] 80	91
	1,500	Fresh	85	20	2.0	48.6	[1] 71	94

[1] Recovery was low in the first and last runs because fresh catholyte was used and it retained a substantial proportion of the product.
[2] Unusually large handling losses incurred in transferring electrolyte from the cell to the recovery equipment.

This series of runs should be contrasted with that of Table IV below, in which substantially the same operation conditions were utilized but without elimination of cell poisons by the process of this invention. Note that in this last series of runs the conversion dropped from 98 to 87% of cyclohexadiene dicarboxylic acid in the recovered product for the first recycle and after only 4 hours total operation, then to 84% in the second recycle, and that substitution of fresh catholyte did not avoid the difficulty but resulted only in additional cell poisoning.

Table IV

Recycle No.	Catholyte		Temp., ° C.	Amp.	Time, Hrs.	g. Recovered	Total Recovered Per Cent Theory	Per Cent Dihydro Acid in Recovered Product
	cc.	Source						
0	1,500	Fresh	85	20	2.0	48.9	72	98
1	1,500	0+Makeup	85	20	2.0	56.8	84	87
2	1,500	1+Makeup	85	20	2.0	58.2	86	84
	1,500	Fresh	85	20	2.0	49.8	73	66

As an example of conditions for the electrolyte reduction of fumaric or maleic acids to succinic acid with a circulating mercury poison carrier according to the process of this invention, the following data are given:

Catholyte temperature: 60 to 100° C., preferably 70 to 90° C.
Catholyte composition:
60 grams of fumaric acid
1000 cc. water
15 cc. H_2SO (specific gravity 1.84)

Any fumaric acid precipitated by the sulfuric acid may be kept in suspension by suitable agitation. A current density of 6.5 amperes per square decimeter is satisfactory, which may be reduced to 2.5 amperes per square decimeter of cathode area after 85% of the current theoretically necessary for conversion has been passed through the cell.

In the reduction of maleic acid, the catholyte may comprise 120 grams of maleic acid in 400 cc. of water containing about 15 cc. of sulfuric acid and a current density of about 8 amperes per square decimeter utilized. In both reductions the anolyte may comprise 5% sulfuric acid in water.

The apparatus and process of this invention are applicable to the selective nuclear partial reduction of other phthalic acids, for example, terephthalic acid may be reduced to Δ2,5 cyclohexadiene dicarboxylic acid-1,4 under process conditions which are substantially those hereinabove described for the reduction of orthophthalic acid.

In some instances, depending upon the organic compound being treated and the reaction desired, it is possible to substitute other liquid electrodes for the liquid mercury electrode body. For example, other low melting metals or metal alloys may be adopted, especially where high over-voltage is not essential to satisfactory reduction. But where high over-voltage is required, as in the reduction of phthalic acid to cyclohexadiene dicarboxylic acid, these metals have not been found satisfactory. However, a sodium amalgam is not precluded where reduction is being effected in an alkaline solution. The sodium in the amalgam will react with the electrolyte in this type operation, but additional amalgam is formed by electrolysis during the electrolytic reduction reaction, so that it may be said that a sodium-mercury amalgam cathode surface rather than pure mercury, is the effective cathode. In such a system for reducing phthalic acid, cyclohexene dicarboxylic acids rather than cyclohexadiene dicarboxylic acids are produced. (Helv. 17 1219 (1934).)

In the cell poison separation step, chemical treating agents other than caustic alkali are operative. Potassium hydroxide is an alternative strongly alkaline treating agent for removing poisons formed in the foregoing synthesis of Δ3,5-cyclohexadiene dicarboxylic acid-1,2. Active oxidizing agents, illustrated by potassium permanganate, may be utilized, and nitric acid has also been found operative, although it attacks the mercury slightly with resulting increase in materials consumption.

The present invention is not limited to specific details set forth in the foregoing examples which should be considered as illustrative and not by way of limitation, and in view of the numerous modifications which may be effected therein without departing from the spirit and scope of the invention, it is desired that only such limitations be imposed as are indicated in the appended claims.

I claim:

1. In a process of electrolytically reducing phthalic acid to a cyclohexadiene dicarboxylic acid by forming a catholyte consisting essentially of about 2% to about 10% by weight of phthalic acid and dilute aqueous sulfuric acid of about 3% to about 20% concentration, contacting said catholyte with a cathode consisting essentially of liquid mercury in an electrolytic cell, maintaining the temperature of said catholyte between about 60° and about 100° C., and passing an electric current of a density of from about 2 to about 40 amperes per square decimeter of cathode area through said cell with said liquid mercury as the cathode, the step of selectively removing cell poisons which would reduce the efficiency of the process by withdrawing liquid mercury from said cathode during continued operation of said cell, separating cell poisons from the withdrawn mercury and returning the thus purified mercury to the cathode of the cell.

2. In a process of electrolytically reducing ortho-phthalic acid to Δ3,5-cyclohexadiene dicarboxylic acid-1,2 by adding phthalic anhydride in an amount of from about 2% to about 10% by weight to a catholyte consisting essentially of a dilute aqueous sulfuric acid of about 3% to about 20% concentration, contacting said catholyte with a cathode consisting essentially of liquid mercury in an electrolytic cell, maintaining the temperature of said catholyte between about 60° and about 100° C., and passing an electric current of a density of from about 2 to about 40 amperes per square decimeter of cathode area through said cell with said liquid mercury as the cathode, the step of selectively removing cell poisons which would reduce the efficiency of the process by withdrawing liquid mercury from said cathode during continued operation of said cell, separating cell poisons from the withdrawn mercury and returning the thus purified mercury to the cathode of the cell.

3. In a process of electrolytically reducing terephthalic acid to Δ2,5-cyclohexadiene dicarboxylic acid-1,4 by adding terephthalic acid in an amount of from about 2% to about 10% by weight to a catholyte consisting essentially of dilute aqueous sulfuric acid of about 3% to about 20% concentration, contacting said catholyte with a cathode consisting essentially of liquid mercury in an electrolytic cell, maintaining the temperature of said catholyte between about 60° and about 100° C., and passing an electric current of a density of from about 2 to about 40 amperes per square decimeter of cathode area through said cell with said liquid mercury as the cathode, the step of selectively removing cell poisons which would reduce the efficiency of the process by withdrawing liquid mercury from said cathode during continued operation of said cell, separating cell poisons from the withdrawn mercury and returning the thus purified mercury to the cathode of the cell.

4. A continuous process of electrolytically reducing phthalic acid to a cyclohexadiene dicarboxylic acid which comprises passing a catholyte consisting essentially of about 2% to about 10% by weight of phthalic acid and dilute aqueous sulfuric acid of about 3 to about 20% concentration into the cathode compartment of an electrolytic cell and over a cathode consisting essentially of liquid mercury, maintaining the temperature of said catholyte between about 60 and about 100° C., passing an electric current of a density of from about 2 to about 40 amperes per square decimeter of cathode area through said cell with the liquid mercury as the cathode, passing the catholyte to a crystallizing zone, crystallizing the cyclohexadiene dicarboxylic acid formed in said cell from said catholyte, separating and recovering the crystals of said dicarboxylic acid from the catholyte, replacing the phthalic acid reduced and removed in the foregoing steps and recycling the catholyte to said cell, withdrawing liquid mercury from said cell during continued operation thereof, separating cell poisons from the withdrawn mercury and returning the thus purified mercury to the cathode of the cell.

5. The process of claim 1 wherein the cell poisons are separated from the mercury by treatment of the mercury with an alkali metal hydroxide.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
809,089	Blackmore	Jan. 2, 1906
1,094,315	Earle et al.	Apr. 21, 1914
1,612,361	Creighton	Dec. 28, 1926
1,730,997	Danckwardt	Oct. 8, 1929
1,961,160	Moulton	June 5, 1934

FOREIGN PATENTS

Number	Country	Date
73,526	Austria	July 10, 1917

OTHER REFERENCES

Mettler, Berichte, vol. 39 (1906), pp. 2933–2942.

Grant, Hackh's Chemical Dictionary, 1944, p. 653.

Rodionov, Chemical Abstracts, vol. 32 (1938), pp. 6554–6555.

Herasymenko, Chemical Abstracts, vol. 31 (1937), p. 4906.