3,471,381
Patented Oct. 7, 1969

3,471,381

PRODUCTION OF CYCLOHEXADIENE DICARBOXYLIC ACIDS

Hubert Suter, Heinz Nohe, Fritz Beck, and Adolph Hrubesch, Ludwigshafen (Rhine), Germany, assignors to Badische Anilin- & Soda-Fabrik Aktiengesellschaft, Ludwigshafen (Rhine), Germany

No Drawing. Filed Mar. 20, 1967, Ser. No. 624,129
Claims priority, application Germany, Mar. 24, 1966, B 86,344
Int. Cl. C07c *51/40, 61/16*
U.S. Cl. 204—73 5 Claims

ABSTRACT OF THE DISCLOSURE

A process for the manufacture of cyclohexadiene dicarboxylic acids by partial hydrogenation of the corresponding phthalic acids. The process is carried out electrochemically in dilute aqueous sulfuric acid solution at a temperature of more than 70° C. at a current density of 1 to 40 amps per sq. decimeter or a cathode consisting of:

(a) either pure cadmium, tin or bismuth, or
(b) a solid alloy of at least two of the metals lead, mercury, silver, cadmium, tin, thallium and bismuth, or
(c) of amalgamated lead, amalgamated thallium, an amalgamated metal of group (a) or an amalgmted solid alloy of group (b).

Cyclohexadiene carboxylic acids are suitable for the production of cyclic polycarboxylic acids, e.g., by reaction with maleic acid, which are excellent plasticizers, e.g., for polyvinyl chloride.

The present invention relates to a process for the production of cyclohexadiene dicarboxylic acids, more particularly to the use of certain cathodes in the electrochemical production of said carboxylic acids from the corresponding phthalic acids.

It is known that 3,5-cyclohexadiene-1,2-dicarboxylic acid can be prepared by electrochemically hydrogenating o-phthalic acid with dilute sulfuric acid as the catholyte above 60° C. For example, according to "Berichte der Deutschen Chemischen Gesellschaft," vol. 39 (1906), pages 2933 to 2942, and "Zeitschrift für Electrochemie," vol. 35 (1929), pages 769 to 779, the reaction is carried out on specially prepared, very pure lead cathodes in 15% sulfuric acid. In U.S. patent specifications 2,477,579 and 2,477,580 the disadvantages of the lead cathodes are described and the use of mercury cathodes in 5% sulfuric acid recommended. Furthermore, apparatus is described in U.S. patent specification 2,537,304 whose purpose is to prevent poisoning occurring. When lead cathodes are used, poisoning occurs and this considerably reduces the reactivity of the cathodes. Moreover, brown tar-like byproducts are formed which discolor the reaction product and necessitate a special purification process. Even when mercury is used, poisoning of the cathodes still occurs, although not until the reaction has been in progress for some time. It is therefore necessary to continuously remove the mercury from the hydrogenation cell, purify it and return the purified mercury to the cell. The mercury must therefore be recycled in a separate loop which includes at least one purification stage. In this way the cathodes reactivity is maintained but the method required to carry out the electrochemical process over a long period is expensive. Moreover, special saftey precautions must be observed because of the health hazards involved in using mercury and in particular in operating a mercury loop.

It is an object of the invention to provide a new, more effective process for the manufacture of cyclohexadiene dicarboxylic acids from the corresponding phthalic acids. It is another object to provide cathodes for the electrochemical partial hydrogenation of phthalic acids. It is a further object of the invention to provide a process for the manufacture of cyclohexadiene dicarboxylic acids in which long on-stream period can be achieved. A still further object of the invention is to provide a simple process for the manufacture of cyclohexadiene carboxylic acids in which complicated system for mercury recycling is not needed. These and other objects will be better understood from the following detailed description.

We have found that 3,5-cyclohexadiene-1,2-dicarboxylic acid or 2,5-cyclohexadiene-1,4-dicarboxylic acid may be obtained by the electrochemical hydrogenation of o-phthalic acid or terephthalic acid in dilute aqueous sulfuric acid at temperatures above 70° C. and with a current density of 1 to 40 amps per sq. decimeter, if desired using lead or mercury cathodes, without the difficulties usually encountered with lead and mercury cathodes, when the cathode used is amalgamated lead, cadmium, tin, thallium or bismuth, or alloys, which may also be amalgamated, of at least two of the metals lead, mercury, silver, cadmium, tin, thallium and bismuth or pure cadmium, tin or bismuth.

Even when the cathodes according to this invention are used in continuous operation no poisoning is observed. In the course of time the cathode potential is negativated which becomes apparent from the formation of small amounts of hydrogen; said formation of hydrogen, however, improves convection and advantageously changes the concentration of the phthalic acid to be hydrogenated or of the hydrogenation product at the cathode. The advantages of the new process are obvious: in contrast to processes where lead cathodes are used no disturbances occur, and in contrast to processes where mercury cathodes are used a considerably simpler method of operation is possible.

By amalgamation we mean the coating of metals or alloys with a mercury alloy by applying small amounts of mercury to the metal or alloy.

The amalgamated cathodes which may be used are of lead coated with an alloy of lead and mercury, cadmium coated with an alloy of cadmium and mercury, tin coated with an alloy of tin and mercury, thallium coated with an alloy of thallium and mercury or bismuth coated with an alloy of bismuth and mercury. The binary, ternary or higher alloys which may be used are alloys of lead and mercury; lead and silver; lead and cadmium; lead and tin; lead and bismuth; lead and thallium; mercury and silver; mercury and cadmium; mercury and tin; mercury and bismuth; mercury and thallium; cadmium and tin; cadmium and bismuth; cadmium and thallium; tin and bismuth; tin and thallium; bismuth and thallium; lead, mercury and silver; lead, mercury and cadmium; lead, mercury and tin; lead, mercury and bismuth; lead, mercury and thallium; lead, silver and cadmium; lead, silver and tin; lead, silver and bismuth; lead, silver and thallium; lead, cadmium and tin; lead, cadmium and bismuth; lead, cadmium and thallium; lead, tin and bismuth; lead, tin and thallium; lead, thallium and bismuth; mercury, silver and cadmium; mercury, silver and tin; mercury, silver and bismuth; mercury, silver and thallium; mercury, cadmium and tin; mercury, thallium and bismuth; mercury, cadmium and bismuth; mercury, cadmium and thallium; mercury, tin and bismuth; mercury, tin and thallium; silver, cadmium and tin; silver, cadmium and bismuth; silver, cadmium and thallium; silver, tin and bismuth; silver, tin and thallium; silver, thallium and bismuth; cadmium, tin and bismuth; cadmium, tin and thallium; cadmium, thallium and bismuth; and tin, thallium and bismuth; examples of higher, e.g., quaternary, alloys are alloys of lead, mercury, silver and tin; lead, mercury, silver and thallium; and lead, thallium, cadmium and tin, all of which may be amalgamated.

The relative proportions of the individual metals may vary within a wide range, the limits being determined by the mechanical processability of the resulting alloy. In the case of cadmium, tin and bismuth pure, i.e. 100%, metals may be used. When mercury is used as amalgam or in an alloy, the content of mercury should be chosen in such a way that the mercury alloy or the amalgamated metal remains solid at the reaction temperature. The limits with lead:mercury are, therefore, from 30:70 to 99.5:0.5 or 0.1 to 2 g. of mercury per square decimeter of lead in the amalgamation, or, for example, with thallium:mercury the limits are from 50:50 to 99.9:0.1, with lead:mercury:silver from 30:65.9:0.5 to 99.5:0.5:0 to 30:0.5:69.5 parts by weight. The proportions are similar with other mercury-containing cathodes. It is preferred to use cadmium, cadmium:tin=100:0 to 50:50, lead:mercury=50:50 to 90:10, lead:mercury:silver=50:30 to 90:9.5:0.5, lead:bismuth=30:70 to 80:20, lead:tin=20:80 to 80.20, lead:cadmium=0.5:99.5 to 80:20, cadmium:bismuth=100:0 to 20:80 are used, all the cathodes with and without amalgamation, as well as amalgamated lead. Lead or platinum metal is usually used for the anode. Lead dioxide, graphite, silicon carbide and other substances which are resistant, or at least substantially, resistant to anodic dissolution.

Electrolysis is carried out in conventional electrolytic cells, in which the anode and cathode are separated by a diaphragm, for example of porous clay. The anode and cathode are arranged in conventional manner, for example a double-walled tube may be used which may be heated or cooled and in which the cylindrical cathode is arranged on the inner wall of the tubular cell or is the inner wall of the tube and surrounds the likewise cylindrical diaphragm. The anode is for example, a water-cooled lead pipe. However, throughlike cells with electrodes in the form of plates and with suitable cooling elements may be used equally well.

The process may be used for the partial hydrogenation of both o-phthalic acid, which may also be in the form of phthalic anhydride, and terephthalic acid. The particular phthalic acid may be dispersed in a concentration of 2 to 8%, preferably 3 to 6%, by weight, in dilute aqueous sulfuric acid which generally contains more than 2% but not more than 50%, preferably 3 to 20%, by weight of sulfuric acid. At temperatures above 70° C. a sufficiently large amount of the particular phthalic acid goes into solution for the partial hydrogenation to proceed smoothly. It is advisable to exploit the maximum solubility of the phthalic acid at the particular reaction temperature and with the given sulfuric acid content. The values can be easily determined by simple experiments, e.g., 4.95 g. of o-phthalic acid dissolves in 100 g. of 5% sulfuric acid at 85° C. In general it is not necessary to use temperatures above 100° C. It is preferably to carry out the process at temperatures between 80° and 98° C. Dilute sulfuric acid is advantageously used as the anolyte as well—in approximately the same concentration as in the case of the catholyte. The concentration may, however, be slightly higher.

Electrolysis may be carried out with a current density of 1–40, preferably 3–20, amps./sq. decimeter (cathode current). In a preferred, continuous method of operation the catholyte is fed to the cathode chamber of the electrolytic cell by means of a metering pump, the mixture of phthalic acid and sulfuric acid being allowed to flow from the bottom to the top of the cell. The hydrogen formed provides additional convection. After residence times of for example 0.1 to 5 hours in the electrolytic cell the reaction mixture is cooled, preferably to below 15° C. The cyclohexadiene dicarboxylic acid which has been formed then crystallizes out. It is separated in conventional manner and the mother liquor, after phthalic acid has been added to it, can be returned to the electrolytic cell.

After being simply washed with water the cyclohexadiene dicarboxylic acids prepared in this way are obtained in extremely pure form. Since the cyclohexadiene dicarboxylic acids are very reactive on account of their double bonds, it is recommendable to work them up at relatively low temperatures, preferably below 20° C.

The process according to the present invention is further illustrated by the following examples.

EXAMPLE 1

The hydrogenation cell consists of a double-walled glass tube provided with a cylindrical amalgamated lead cathode, a cylindrical clay diaphragm and a water-cooled lead tube as anode. The catholyte is introduced at the bottom of the cell by means of a metering pump and withdrawn at the top.

Height of cell	57 cm.
Diameter of cell	6.5 cm.
Cathode area	10 sq. decimeters.
Anode area	3.1 sq. decimeters.
Cathode chamber	1 liter.
Reaction temperature	85° C.
Current density	10 amps./dm.^{2}.
Applied current	150% of theoretical.
Catholyte	5% H_2SO_4+4.5% o-phthalic acid.
Anolyte	5% H_2SO_4.
Catholyte throughput	4.6 kg./h. (206.5 g. of o-phthalic acid).
o-Phthalic acid conversion	100%.
3,5-cyclohexadiene-1,2-dicarboxylic acid	88% of the theory.
Space-time yield	0.184 kg. of 3,5-cyclohexadiene-1,2-dicarboxylic acid per reaction space per hour.
Current efficiency	58.75%.

In sustained operation over a period of eight days there was no change in the result ownig to poisoning of the cathode. Analysis of the reaction product showed no traces of 2,6-cyclohexadiene dicarboxylic acid. There were no tar-like impurities.

EXAMPLES 2–26

The following results were obtained using various cathodes and operating under the same conditions as described in Example 1.

Ex.	Cathode	o-Phthalic acid yield, percent	Yield of 3,5-cyclohexadiene-1,2-dicarboxylic acid, percent of theory	Current efficiency, percent
2	Pb:Hg=75:25 amalgamated.	97	90	58.7
3	Pb:Hg=75:25 not amalgamated.	96	91	59
4	Pb:Hg:Ag=80:19:1 not amalgamated.	99	86	57.6
5	Cd:Sn=90:10 not amalgamated.	100	87	56.8
6	Sn	84	79	53
7	Bi	87	81	54.5
8	Cd	99	91	58.5
9	Tl	96	89	56.5
10	Tl amalgamated	97	90	56.8
11	Tl:Hg=85:15	97.5	90.5	57
12	Tl:Pb=80:20	96.5	89.5	56
13	Pb:Cd=50:50	99	90.5	55.5
14	Cd:Bi=50:50	100	89	56.8
15	Sn:Bi=50:50	86.5	83.5	54
16	Pb:Sn=36:64	98	88	55
17	Pb:Bi=50:50	99	88.5	56
18	Pb:Bi=50:50 amalgamated.	100	90	56.5
19	Pb:Ag=90:10 amalgamated.	99	89.5	56.5
20	Ag:Cd=10:90	100	90.5	58
21	Pb:Cd:Ag=50:40:10 amalgamated.	99	89.3	57.2
22	Bi:Sn:Hg=40=50:11	98	88.7	56.1
23	Cd:Tl:Ag=80:10:10	100	88.9	57.5
24	Pb:Cd:Bi:Hg=40:30:25:5.	98	87.8	55.8
25	Sn:Tl:Cd:Ag=30:10:51:10.	97	87.5	56.8
26	Pb:Sn:Tl:Cd=40:20:20:20 amalgamated.	97.5	88.1	56.3

EXAMPLE 27

120 cc. of a suspension of very finely ground terephthalic acid (10 g.) in 5% sulfuric acid is hydrogenated at a temperature of 90° to 95° C. in a cylindrical glass electrolytic vessel containing a trough-like clay diaphgram surrounded by a cylindrical cathode of an amalgamated lead/mercury allow (90% Pb+10% Hg). 15% sulfuric acid is used as the anolyte. The anode is of platinum and the current density is 5 amps per sq. decimeter. The reaction is stopped after one hour, the suspension is cooled to 15° C. and the precipitate is filtered and dried. NMR analysis shows a yield of 89% of the theory of 2,5-cyclohexadiene-1,4-dicarboxylic acid with reference to the reacted terephthalic acid.

We claim:

1. A process for the production of 3,5-cyclohexeadiene-1,2-dicarboxylic acid or 2,5-cyclohexadiene-1,4-dicarboxylic acid which comprises electrochemical hydrogenation of o-phthalic acid or terephthalic acid in aqueous sulfuric acid at temperatures of from 70° to 100° C. and with a current density of 1 to 40 amps per sq. decimeter on a cathode consisting of cadmium, tin, bismuth, amalgamated lead, amalgamated cadmium, amalgamated tin, amalgamated thallium, amalgamated bismuth or an alloy of at least two of the metals lead, mercury, silver, cadmium, tin, thallium and bismuth or an amalgamated alloy of the said metals.

2. A process as claimed in claim **1** in which o-phthalic acid or terephthalic acid is used in a concentration of from 2 to 8% by weight dispersed in aqueous sulfuric acid of a concentration of 2 to 50% by weight.

3. A process as claimed in claim **1** in which the current density is 3 to 20 amps per sq. decimeter.

4. A process as claimed in claim **1** in which sulfuric acid of a concentration of 3 to 20% by weight is used.

5. A process as claimed in claim **1** in which o-phthalic acid or terephthalic acid is used in a concentration of 3 to 8% by weight.

References Cited

UNITED STATES PATENTS

2,477,579	8/1949	Condit	204—73
2,477,580	8/1949	Condit	204—73
2,537,304	1/1951	Condit	204—73

PATRICK P. GARVIN, Primary Examiner

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,471,381 Dated October 7, 1969

Inventor(s) Hubert Suter et al

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

Column 3, line 41, "50:30" should read "50:30:20".

Column 5, in the table, example 25, under "Cathode", "51:10" should read "50:10".

SIGNED AND
SEALED
FEB 17 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents