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MANUFACTURE OF CYCLOHEXADIENE-DIOIC ACIDS

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ABSTRACT OF THE DISCLOSURE

Manufacture of hexadiene-dioic acids by the electrochemical reduction of benzene-dioic acids in an electrolytic cell containing diaphragms, using a catholyte containing the dioic acid, water and a water-soluble organic solvent, wherein the flow of electrolysis current is periodically interrupted and the cell short-circuited.

This invention relates to the manufacture of 3,5-cyclohexadiene-1,2-dioic acid and 2,5-cyclohexadiene-2,4-dioic acid by the electrochemical reduction of o-phthalic acid or terephthalic acid.

It is known that 3,5-cyclohexadiene-1,2-dioic acid may be obtained from o-phthalic acid by partial electrochemical reduction thereof using specially prepared, highly pure lead cathodes (Zeitschrift für Elektrochemie, vol. 35 (1929), pp. 769–779).

U.S. Pats. 1,477,579 and 2,477,580 describe the drawbacks of lead cathodes and propose the use of mercury cathodes. In addition, U.S. Pat. 2,537,304 describes means for overcoming the occurrence of poisoning at the cathode.

The use of lead cathodes gives rise to poisoning which is manifested by greatly reduced reactivity. Also, brown tar-like products are formed which cause discoloration of the main product and make special purifying operations necessary.

However, the use of mercury also eventually leads to poisoning of the cathode and it is thus necessary to arrange for continuous withdrawal of the mercury from the hydrogenating cell for purification and to recycle the purified mercury to the hydrogenating cell.

Another improvement in the electrochemical reduction of o-phthalic acid or of terephthalic acid is described in Belgian Pat. 709,115 and comprises adding to the catholyte water-miscible organic solvents such as ethers, carboxamides or nitriles. The advantage of this process over the previous processes are that the phthalic acid concentration in the catholyte may be higher, the temperature of the electrolyte may be lower and the deposition of polymeric materials on the cathode and brown discoloration of the product are prevented. One drawback of this process, when operated continuously for long periods, is that sparingly soluble by-products, namely diphthalyl and α,α′-benzoin-dioic acid, are formed which result in a gradual increase in the resistance of the electrolytic cell and a depression of the conversion rate. The said by-products occur after electrolysis times of from 2 to 48 hours and are relatively difficult to remove. Consequently, they are highly detrimental to continuous operation on an industrial scale.

An article by J. Tafel in Chemische Berichte 1900, vol. 33, pp. 2215 ff. relating to the electrochemical reduction of caffeine by means of lead cathodes describes a method of achieving reproducible results in which the lead cathodes are superficially oxidized electrolytically by connecting them as anodes for 30 minutes before the reduction reaction and allowing a current density of, say, 2 a./dm.^{2} to exist and then preparing them by a complicated process.

We have now found that 3,5-cyclohexadiene-1,2-dioic acid and 2,5-cyclohexadiene-1,4-dioic acid may be obtained at a very high degree of purity and without the occurrence of by-products by the electrochemical reduction of o-phthalic acid or terephthalic acid in electrolytic cells in which the anode and cathode chambers are separated by diaphragms, using catholytes containing organic solvents, provided that the flow of electrolysis current is periodically interrupted and the electrolytic cell is short-circuited and, if desired, operated with poles reversed for relatively long periods.

The advantage of the present process is that the formation of the said sparingly soluble by-products diphthalyl and α,α′-benzoin-dioic acid is completely suppressed.

After an electrolysis time of from 6 minutes to 20 hours, especially from 3 to 10 hours, the period during which the flow of current is interrupted and short-circuiting is effected is advantageously from 5 seconds to 15 minutes, especially from 1 to 5 minutes, short electrolysis times being associated with short no-current times. As a rule, the no-current periods are from $\frac{1}{10,000}$ to $\frac{5}{100}$ of the electrolysis time.

If desired, one of a number of short-circuit periods may be replaced by a period of operation with poles reversed, for which purpose a current strength of from $\frac{1}{100}$ to $\frac{1}{5}$ of the electrolysis current, preferably of from $\frac{1}{50}$ to $\frac{1}{10}$ thereof, is used. The reversed-pole periods are usually equal to the short-circuit periods. Optionally, in a series of no-current periods resulting from short-circuiting of the electrolytic cell, one of them—selected at relatively large intervals as desired, usually every 100th to 500th no-current period—may be replaced by a period of operation with poles reversed.

The measures of removing current and short-circuiting and, where used, of operating the electrolytic cell with poles reversed are well suited for continuous operation for long periods. By such means, not only the occurrence of the said sparingly soluble by-products is suppressed but also the occurrence of troublesome deposits on cathodes and diaphragms is prevented, so that the resistance of the electrolytic cell and the conversion of material are not adversely affected.

Conveniently, an electric time-switch is adjusted to switch off the rectifier at predetermined intervals and to short-circuit the electrolytic cell. Indeed, in a long-term experiment lasting for more than one year, the catholyte remained completely clear and no deposit of by-product could be found either on the diaphragms or on the cathodes. The current consumption, conversion rate and bath voltage remained constant throughout the entire period.

The process is eminently suitable for the partial electrochemical reduction of terephthalic acid and, preferably, of o-phthalic acid. The reduction is carried out in all other respects under known conditions and in conventional electrolysis apparatus in which the anode and cathode chambers are separated by diaphragms. The concentration of phthalic acid is usually in the range of from 5 to 25%, especially from 10 to 20% by weight.

The catholyte used is usually a mixture of ethers, carboxamides and/or nitriles which are liquid at room temperature and are miscible with water, for example dioxane, tetrahydrofuran, glycol monoethyl ether, dimethyl formamide or acetonitrile, together with water and sulfuric acid. The concentration of water and sulfuric acid in the catholyte is conveniently such that the catholyte shows good conductivity. The concentration of sulfuric acid is usually from 1 to 20%, especially from 2 to 10%, by weight, based on the total system of water, sulfuric acid, aromatic carboxylic acid and organic solvent. The concentration of water in the catholyte is usually between 5 and 40%, especially between 10 and 25%, by weight.

The concentration of organic solvent should be as high as possible consistent with maintaining good catholyte conductivity whilst achieving high phthalic acid solubility. The concentration of the organic solvent is usually in the range of from 40 to 80%, in particular from 50 to 70%, by weight. A mixture of organic solvents may be used if desired.

The anolyte used is generally dilute aqueous sulfuric acid having a concentration of from 2 to 10% by weight.

The anode and cathode chambers are separated by a diaphragm. Ion exchanger diaphragms or plastics tissues may be used in place of the more commonly used ceramic materials if desired.

The anode is normally made of lead, lead dioxide, graphite or platinum metals. The cathode may be made of the usual cathode materials with the necessary hydrogen overvoltage. No special alloys need be employed, and normal lead may be used for the cathode with good results without the cathode suffering from poisoning or fatigue.

The current densities are in the range of from 1 to 30, preferably from 2 to 20 a./dm.^{2}. The temperatures may be between 20 and 70° C. The process is usually carried out at temperatures ranging from 25° C. to 45° C., this temperature range being maintained by cooling if necessary. Lower temperatures have the advantage that in the hydrogenation of o-phthalic acid the rearrangement of the 3,5-cyclohexadiene-1,2-dioic acid formed to 2,5-cyclohexadiene-1,2-dioic acid is substantially avoided.

Isolation of the product is simple. For example, the organic solvent may be removed by distillation, whereupon the cyclohexadiene-dioic acid precipitates, which may also be achieved by diluting the reaction solution with water. The precipitated product is then filtered off, washed and dried.

In a preferred embodiment of the process six bipolar, plate-shaped electrodes of lead are used which are connected in series and are assembled in the manner of a filter press. The electrodes may conveniently also be designed as cooling elements for water cooling. The five cathode and anode surfaces are separated by cation exchanger diaphragms, based on sulfonated polystyrene for example.

The cathode chambers are interconnected by means of glass tubes and plastics tubing. The catholyte is pumped continuously through the five cathode chambers successively, in each case flowing upwardly through the chamber to be withdrawn at the top. The catholyte preferably consists of a mixture of from 50 to 70% of dioxane or tetrahydrofuran, from 10 to 25% of water, from 2 to 10% of sulfuric acid and from 10 to 20% of o-phthalic acid, by weight. We prefer to use dilute, 2–20% w./w. sulfuric acid as anolyte.

The overall dimensions of the electrodes are 30 mm. x 730 mm., the internal dimensions of the effective area of the electrode being 250 mm. to 680 mm., equal to an area of 17 dm.^{2}.

EXAMPLE

The electrolytic unit described above and comprising 6 lead electrodes connected in series and forming 5 cathode and anode chambers separated by cation exchanger diaphragms of sulfonated polystyrene is used. The anolyte used is 5% w./w. sulfuric acid. The catholyte consists of a mixture of 60% of dioxane, 20% of water, 5% of sulfuric acid and 15% of o-phthalic acid. Electrolysis is carried out under the following conditions:

current density: 10 a./dm.^{2}
catholyte throughput: 13.6 kg./hr.
reaction temperature: 30–35° C.
current supplied: 130%
total cell voltage: 58 v.
phthalic acid conversion: 92–94%
3,5-cyclohexadiene-1,2-dioic acid: 99% yield based on phthalic acid converted
current efficiency: 70.2–71.6%
current consumption: 5–5.3 kw.h./kg.

An electric time switch is set to switch off the rectifier automatically every 6 hours, the electrolytic cell then being short-circuited for 2 minutes. At intervals of four months one of the short-circuit periods is replaced by a period of operation with poles reversed using a current at a strength $\frac{1}{20}$ of that of the working current, giving a current density of 0.5 a./dm.^{2}. The discharged catholyte remains completely clear and the electrodes and diaphragms remain free of deposits. No diphthalyl or α,α'-benzoin-dioic acid could be detected. The conditions stated remained constant for a period of operation lasting longer than one year.

COMPARATIVE EXAMPLE

Operating under exactly the same conditions, the results are the same during the first 4 to 8 hours of operation. After 4 to 8 hours cloudiness is observed in the discharged catholyte, the voltage rises, the conversion rate falls and the evolution of hydrogen increases. After an operating period of from 15 to 18 hours the voltage has risen to 100 volts and the rate of conversion is only 75%. The pressure in the cell also rises considerably. After about 24 hours the catholyte outlets from the last two cathode chambers have become stopped up and the cell has to be dismantled. A crystalline layer is seen to have been deposited on the diaphragms and, to some extent, on the cathodes also.

The total amount of by-products—comprising approximately equal of diphthalyl and α,α'-benzoin-dioic acid—is 0.2% by weight of the phthalic acid introduced or 0.03% by weight of the catholyte solution.

Since the by-products are only soluble in high-boiling solvents at elevated temperatures, only mechanical cleaning is feasible.

We claim:

1. A process for the manufacture of 3,5-cyclohexadiene-1,2-dioic acid and 2,5-cyclohexadiene-1,4-dioic acid by the electro-chemical reduction of o-phthalic acid or terephthalic acid in electrolytic cells in which the anode and cathode chambers are separated by diaphragms, using catholytes containing organic solvents, wherein the flow of electrolysis current is periodically broken and the electrolytic cell is short-circuited, said flow of electrolysis current being broken for a period of from 5 seconds to 15 minutes at intervals ranging from 6 minutes to 20 hours.

2. A process as claimed in claim **1** wherein the ratio of the length of the electrolysis periods to that of the no-current periods is from 1,000:1 to 100:5.

3. A process as claimed in claim **1** wherein at relatively long intervals a no-current period is replaced by a period in which the electrolytic cell is operated with its poles reversed instead of being short-circuited.

4. A process as claimed in claim **1** wherein the flow of electrolysis current is broken for a period of from 1 minute to 5 minutes at intervals ranging from 3 hours to 10 hours.

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