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[54] **PROCESS FOR THE PREPARATION OF A P-AMINO PHENOL BY THE ELECTROLYTIC REDUCTION OF NITROBENZENE**

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[58] **Field of Search** 204/74

[56] **References Cited**

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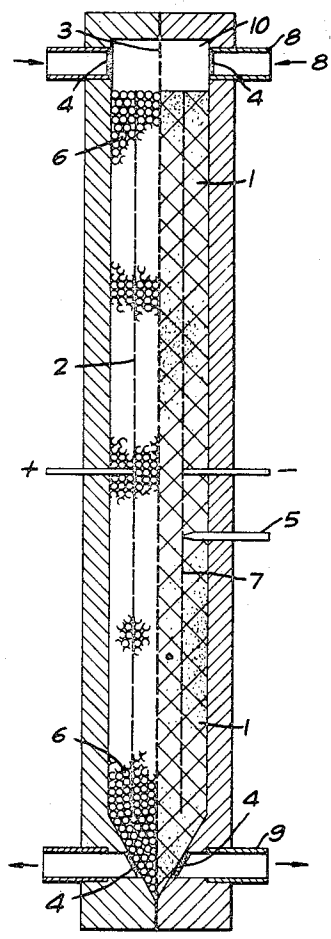
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[57] **ABSTRACT**

A process for the preparation of p-amino phenol and derivatives thereof, which process comprises reducing nitrobenzene electrolytically at a particulate electrode maintained at a cathode potential less negative than −0.40 volts with respect to a saturated calomel electrode, in an acidic medium at a temperature in the range of from 60° to 150° C. Preferably the cathode potential is in the range of from −0.25 to −0.35 volts with respect to a saturated calomel electrode.

9 Claims, 2 Drawing Figures



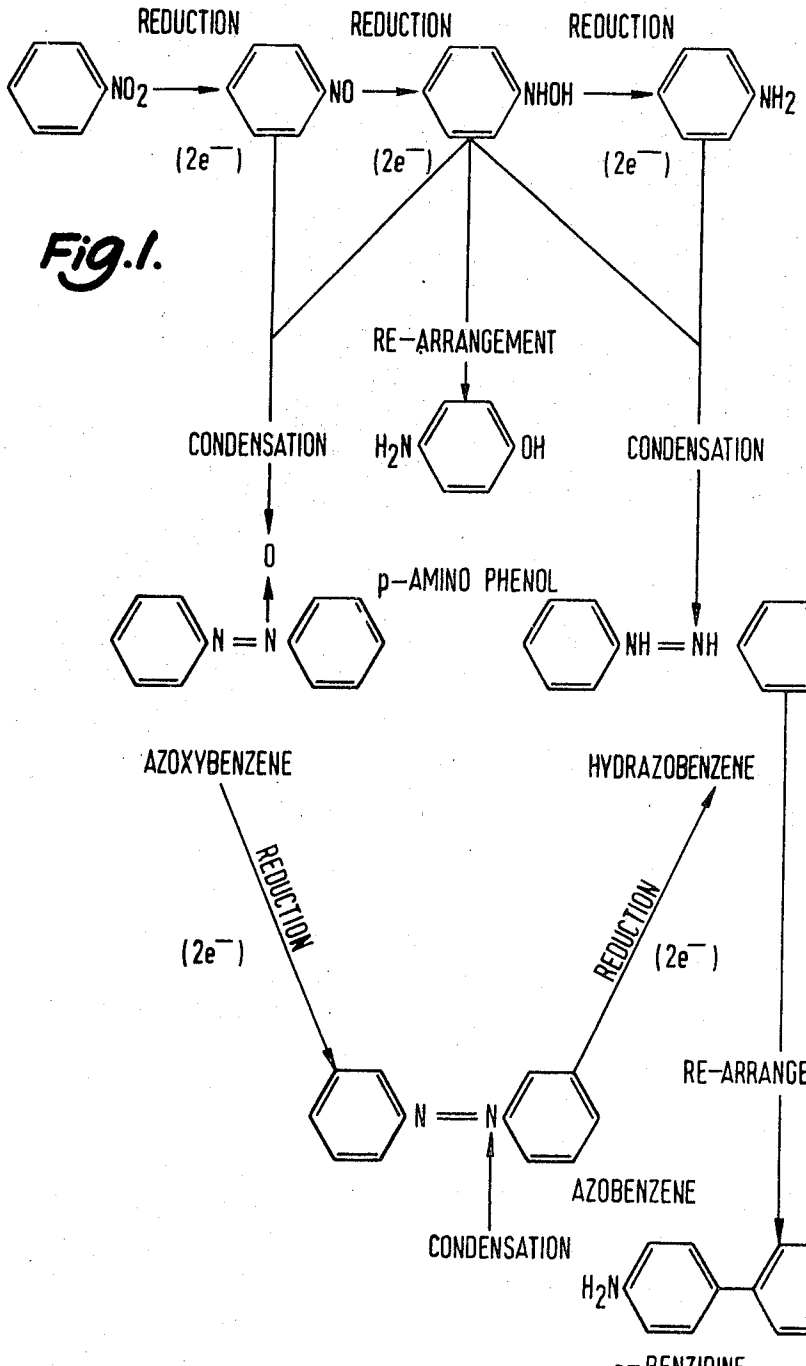
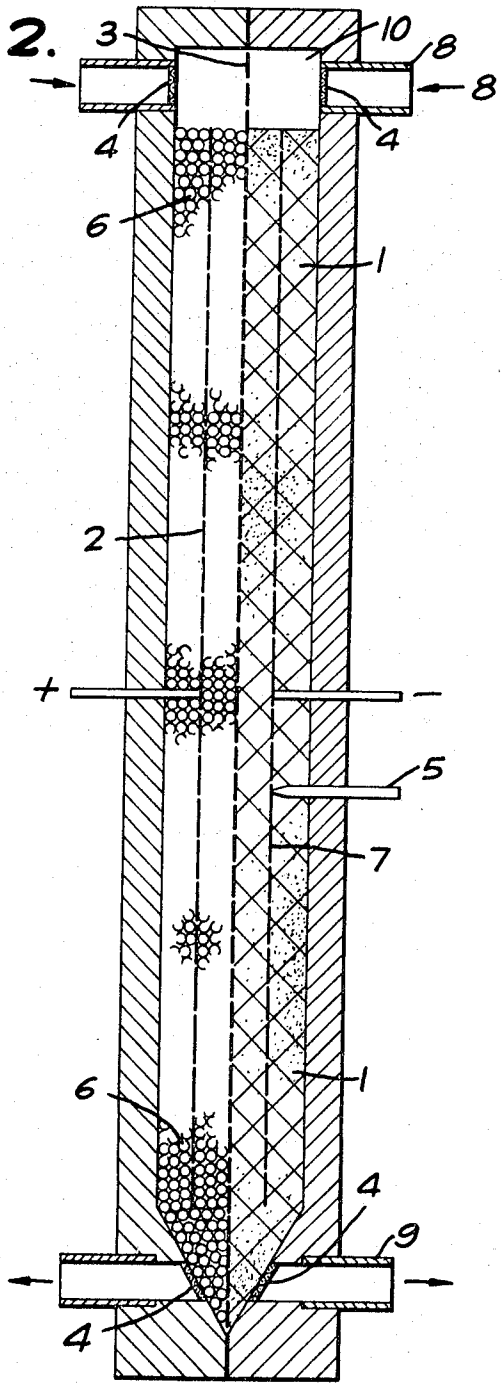


Fig. 1.

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Fig. 2.



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PROCESS FOR THE PREPARATION OF A P-AMINO PHENOL BY THE ELECTROLYTIC REDUCTION OF NITROBENZENE

The present invention relates to an improved process for the preparation of p-amino phenol by the electrolytic reduction of nitrobenzene.

p-Amino phenol is used in the production of rubber antioxidants, dyestuffs, pharmaceuticals and in the production of p-acetamido phenol which is widely used as an analgesic. p-Benzoquinone could be produced by the oxidation of p-amino phenol.

In carrying out the reduction of nitrobenzene a variety of reduction products may be obtained depending upon the pH, temperature and the nature of the reducing agent. In the electrochemical reduction the nature of the reduction is related directly to the electrode potential of the cathode.

FIG. 1 illustrates the possible products of reduction of nitrobenzene under various conditions.

FIG. 2 illustrates an electrolytic cell for carrying out the process.

Referring to FIG. 1, it may be seen that several steps of reduction may occur and that several rearrangements and/or condensation of the reaction products may be expected to occur to form several products in addition to those produced solely by reduction. In the cathodic reduction of nitrobenzene the reaction sequence is, first, the reduction of nitrobenzene involving the transfer of two electrons to form nitrosobenzene. The nitrosobenzene is then further reduced to phenylhydroxylamine with a further transfer of two electrons. Finally, with the transfer of two more electrons the phenylhydroxylamine formed is reduced to aniline. If it desired to form predominantly p-amino phenol by rearrangement of phenylhydroxylamine an acid medium is required and precise potentiostatic control of the cathode potential is important in order to obtain the desired reaction product.

It has now surprisingly been found that it is possible to achieve precise control of the electrode potential of a particulate electrode, and that by effecting the electrolytic reduction of nitrobenzene at a particulate cathode under suitably chosen conditions, p-amino phenol may be obtained as the major reduction product.

Accordingly the present invention provides a process for the preparation of p-amino phenol and derivatives thereof, which process comprises reducing nitrobenzene electrolytically at a particulate electrode maintained at a cathode potential less negative than −0.40 volts with respect to a saturated calomel electrode, in an acidic medium at a temperature in the range of from 60° to 150° C., preferably however below 120° C. Generally the electrolytic reduction is carried out at a particulate electrode maintained at a cathode potential in the range of from −0.25 to −0.40 volts, and preferably at a cathode potential in the range of from −0.25 to −0.35 volts, with respect to a saturated calomel electrode.

The particulate cathode at which the electrolytic reduction of nitrobenzene is carried out may be an electrode of the type described in British Pat. specification No. 1,194,181 i.e., an electrode, taking the form of a bed of conducting and/or semiconducting particles which, in use, is fluidized by upward movement of liquid through the bed. Preferably however the particulate cathode will be a restrained particulate bed electrode comprising a mass of substantially stationary discrete particles which are electrically conductive or which are at least partly electrically conductive or semiconductive, and wherein a fluid comprising the electrolyte and/or the reactant or reactants for the electrochemical reaction are caused to flow through the mass of stationary particles. The electrolyte may flow either upward or downward through the bed.

Alternatively the electrode may be of the type described and claimed in British Pat. No. 1,239,983 i.e., an electrode which comprises a mass of discrete particles of particle size from 70μ to 1,000μ which are electrically conductive or which are at least partially electrically conductive, the said mass of particles being supported on a fluid permeable support, and wherein the fluid comprising the electrolyte and/or the reactant or reactants for the electrochemical reaction is caused to flow upwards through the said mass of particles, the degree of upward movement of the particles in the fluid stream being limited by a particle impermeable barrier positioned above the particle bed so that the volume occupied by the moving particles is less than the natural volume which the particles would occupy in the absence of the said particle-impermeable barrier.

The particles forming the electrode may be constituted wholly of an electrically conducting material, such as metal, or may for example comprise a poorly conducting core, such as glass, ceramics or plastics materials having a surface which is conductive or which has parts which are conductive for example glass particles having a metallic layer. Preferably however the particles forming the electrode are wholly conducting, and are comprised of solid metals or alloys, such as copper, nickel, lead, Monel or copper/nickel alloys. The size of the particles is usually in the range from 70μ to 4,000μ, and preferably is in the range 200μ to 1,000μ. The particles are preferably spherical in shape, although nonspherical particles may be used.

The particles constituting the electrode are normally employed in conjunction with an electrically conductive member which can form an effective contact with the mass of particles constituting the electrode and which is capable of conducting an electrical charge between the particles and the exterior of the catholyte half-cell in which the reduction process is being performed. The conductive member may-itself form the wall or part of the wall of the enclosure containing the particulate electrode. The catholyte half-cell comprising a particulate electrode is combined with a suitable anolyte half-cell to form an electrolytic cell in which the reduction is effected. The anolyte half-cell may comprise a platinum mesh, platinized titanium or lead anode, or any other suitable anode.

In carrying out the process of the present invention optimum yields of p-amino phenol are obtained by maintaining the particulate electrode at a cathode potential of −0.300 ± 0.10 volts to a saturated calomel electrode. Good yields are also obtained by maintaining the particulate electrode at a cathode potential of −0.385 ± 0.001 volts to a saturated calomel electrode.

The higher the temperature at which the reduction is effected, the more rapidly the rearrangement of the intermediate phenylhydroxylamine to give p-amino phenol, takes place. Generally the temperature at which the electrolytic reduction is effected will be in the range of from 60° to 150° C., and preferably in the range of 90° to 120° C.

The catholyte may comprise a solution containing the nitrobenzene which is to be reduced. Alternatively, the catholyte may be an emulsion containing nitrobenzene provided that a sufficiently high-electrolyte velocity past the electrode is maintained. The electrolyte velocity, or flow rate, past the particulate electrode is an important factor in optimising the conditions under which the process of the invention is effected. The electrolyte velocity in general must be sufficient to avoid substantial polarization and when an emulsion is used as catholyte the electrolyte velocity must be sufficiently high to maintain the nitrobenzene dispersed as an emulsion in the acidic medium. An emulsifying agent may be added to the electrolyte system if desired.

The acidic medium forming the catholyte may comprise for example sulphuric acid, hydrochloric acid, phosphoric acid, perchloric acid, or other suitable mineral acid or an acidic salt which is capable of furnishing protons such as sodium or potassium hydrogen sulphate or the "McKee" salts. Alternatively an organic acid such as acetic acid may be employed. In the latter case the p-amino phenol may be converted into p-acetamido phenol, and may be isolated as such from the reaction mixture. The use of some sodium acetate is helpful in such acetylation reactions as is well known to those versed in the art.

The present invention thus includes within its scope a process for the preparation of p-acetamido phenol which

process comprises reducing nitrobenzene in acetic acid electrolytically at a temperature in the range of from 60° to 150° C. at a particulate electrode maintained at a cathode potential of from −0.25 to −0.35 volts to a saturated calomel electrode.

The catholyte is generally an aqueous medium, but other solvent systems such as dimethylsulphoxide or dimethylformamide may also be employed. The solvents used must however be nonreducible under the conditions of the reaction. If desired, solvent systems which are partly aqueous and partly nonaqueous solvents may be employed.

It has been found that in general acid concentrations in the range 3N to 8N give the optimum results.

The anolyte in the anolyte half-cell will generally have the same composition as the catholyte without the nitrobenzene or its reduction products added thereto. Thus for example if nitrobenzene dissolved in aqueous 4N sulphuric acid is used as the catholyte, the anolyte may suitably comprise aqueous 4N sulphuric acid.

Redox catalysts such as for example stannous chloride or ceric sulphate may be added to the catholyte if desired.

The p-amino phenol obtained by effecting the reduction of nitrobenzene according to the process of the invention may if desired be isolated directly or may be isolated in the form of a derivative, e.g., as its sulphate salts. The p-amino phenol or its derivative may be purified by any suitable known method. For example, cooling of the catholyte may result in the crystallization of p-amino phenol sulphate from the electrolyte. After neutralization, any aniline sulphate present as impurity in the p-amino phenol may be removed using techniques well known to those versed in the art.

It has been found that when using a restrained particulate bed electrode of the type hereinbefore described the fluid flow through the particulate bed electrode may be expressed as a Reynolds number, which is defined by the relationship:

$$R_e = \frac{DQr}{A\mu}$$

where D is the diameter of the spherical particle.

Q is the total volumetric flow rate through the bed.

r is the density of the fluid.

A is the total cross-sectional area of the bed.

μ is the viscosity of the solution.

Of these quantities, D, Q and A are directly recorded; μ and r vary with temperature and are usually obtained experimentally, but reasonable estimates of their value may often be obtained by reference to the literature.

In carrying out the process of the present invention using a restrained particulate bed electrode of the type hereinbefore described it has been found that when the catholyte is in the form of a solution, the flow of solution should preferably have a Reynolds number value in the range 20 to 100. In the case of catholytes which are emulsions, the catholyte flow should have a substantially higher Reynolds number and preferably a Reynolds number in the range 100 to 400. However very much lower Reynolds numbers have been used successfully for both solutions and emulsions where some degree of polarization and a lower power efficiency have been acceptable.

The present invention will now be described by way of example and with reference to FIG. 2 of the accompanying drawings.

FIG. 2 illustrates a diagrammatic representation of a suitable electrolytic cell for the reduction of nitrobenzene to p-amino phenol and,

Referring to FIG. 2, the electrolytic cell of internal dimensions 12 by 4 by 2 cm. comprises a catholyte half-cell 10, having a particulate Monel electrode 1, of particle size between 250 and 400 and a cathode feeder 7 which is connected to a saturated calomel electrode by means of a luggin capillary 5, and an anolyte half cell 11 which comprises a platinum gauze anode 2. The two half-cells are separated by a cation exchange membrane 3. The anode is filled with inert glass ballotini 6 which reduce concentration polarization at the anode by creating turbulence and which also serve to support the membrane. The catholyte inlet 8 and catholyte outlet 9 of the catholyte half-cell are provided with gauze particle filters 4 to prevent the particles forming the particulate electrode escaping from the catholyte half-cell.

A solution of 4M sulphuric acid at a temperature of 80° C. is pumped by two separate circulating systems through the anode and cathode compartments of a cell of the type described above. Sufficient nitrobenzene is added to the catholyte solution to make the concentration about 7 g./l. Current is passed through the cell and the cathode is maintained at a potential of −0.30 v. to SCE, the flowrate of the catholyte being in the range 0.9 to 1.2 l/min. The concentration of nitrobenzene in the catholyte is maintained at the initial concentration by periodic suitable additions of nitrobenzene to the catholyte solution.

In the specific embodiment of the invention described above, the nitrobenzene in the catholyte is reduced at the cathode to phenylhydroxylamine, which rapidly re-arranges to give p-amino phenol. As the nitrobenzene is reduced to form p-amino phenol which is soluble in the sulphuric acid catholyte, more nitrobenzene is added. A proportion of the catholyte is withdrawn as a product stream and cooling of this solution results in the crystallization of p-amino phenol as the sulphate salt. The aniline which is present is crystallized with the p-amino phenol. The mother-liquor remaining after crystallization of the p-amino phenol may if desired be recycled to the catholyte reservoir.

The apparatus in which the nitrobenzene reduction is carried out must be constructed from materials which will withstand nitrobenzene and an acidic medium at temperatures of up to 150° C.

Thus, the portions of the electrolytic cell liable to come into contact with the electrolyte solutions and the pumps may be constructed of materials such as a fluorinated ethylenepropylene copolymer, polypropylene polytetrafluoroethylene, high-density polyethylene, glass or ceramics, the choice of materials depending on the temperature to be used.

The invention also includes within its scope p-amino phenol and derivatives thereof whenever prepared according to the process of the invention. The invention also includes p-acetamido phenol when prepared either directly by the electrolytic reduction of nitrobenzene in acetic acid under the process conditions hereinbefore defined, and p-acetamido phenol whenever produced from p-amino phenol produced in accordance with the invention.

The invention also includes within its scope apparatus for the electrolytic reduction of nitrobenzene substantially as described with reference to the accompanying drawings.

We claim:

1. A process for the preparation of p-amino phenol and derivatives thereof, which process comprises reducing nitrobenzene electrolytically at a particulate electrode wherein the size of the particles forming the electrode is in the range 200 to 1,000μ maintained at a cathode potential in the range of −0.25 to −0.40 volts with respect to a saturated calomel electrode, in an acidic medium at a temperature in the range of from 60° to 150° C.

2. A process as claimed in claim 1 wherein the particulate electrode is a restrained particulate bed electrode comprising a mass of substantially stationary discrete particles which are electrically conductive or which are at least partly electrically conductive or semi-conductive, and wherein a fluid comprising the electrolyte and/or the reactant or reactants for the electrochemical reaction are caused to flow through the mass of stationary particles.

3. A process as claimed in claim 1 wherein the particles forming the electrode are wholly conducting particles comprised of a material selected from the group consisting of copper, nickel, lead, Monel and copper/nickel alloys.

4. A process as claimed in claim 1 wherein the acidic medium forming the catholyte is selected from the group consisting

of acetic acid, sulphuric acid, hydrochloric acid, phosphoric acid, perchloric acid, sodium hydrogen sulphate, potassium hydrogen sulphate and McKee salts.

5. A process as claimed in claim 4 wherein the acidic medium has an acid concentration in the range 3N to 8N.

6. A process as claimed in claim 1 wherein the electrolytic reduction is carried out at a cathode potential in the range of from −0.25 to −0.35 volts with respect to a saturated calomel electrode.

7. A process as claimed in claim 6 wherein the cathode potential is -0.300 ± 0.10 volts with respect to a saturated calomel electrode.

8. A process for the preparation of p-amino phenol and derivatives thereof, which process comprises reducing nitrobenzene electrolytically at a particulate electrode wherein the size of the particles forming the electrode is in the range 200 to 1,000μ maintained at a cathode potential in the range of −0.25 to −0.40 volts with respect to a saturated calomel electrode, in an acidic medium at a temperature in the range of from about 90° to 120° C.

9. A process for the preparation of p-acetamido phenol which process comprises reducing nitrobenzene electrolytically in acetic acid having a concentration in the range 3N to 8N at a temperature in the range of from 60° to 150° C. at a particulate electrode wherein the size of the particles forming the electrode is in the range 200 to 1,000μ maintained at a cathode potential of from −0.25 to −0.35 volts with respect to a saturated calomel electrode.

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