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(54) **METHOD FOR THE ELECTROCHEMICAL  
DIRECT AMINATION OF HYDROCARBONS**

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(57) **ABSTRACT**

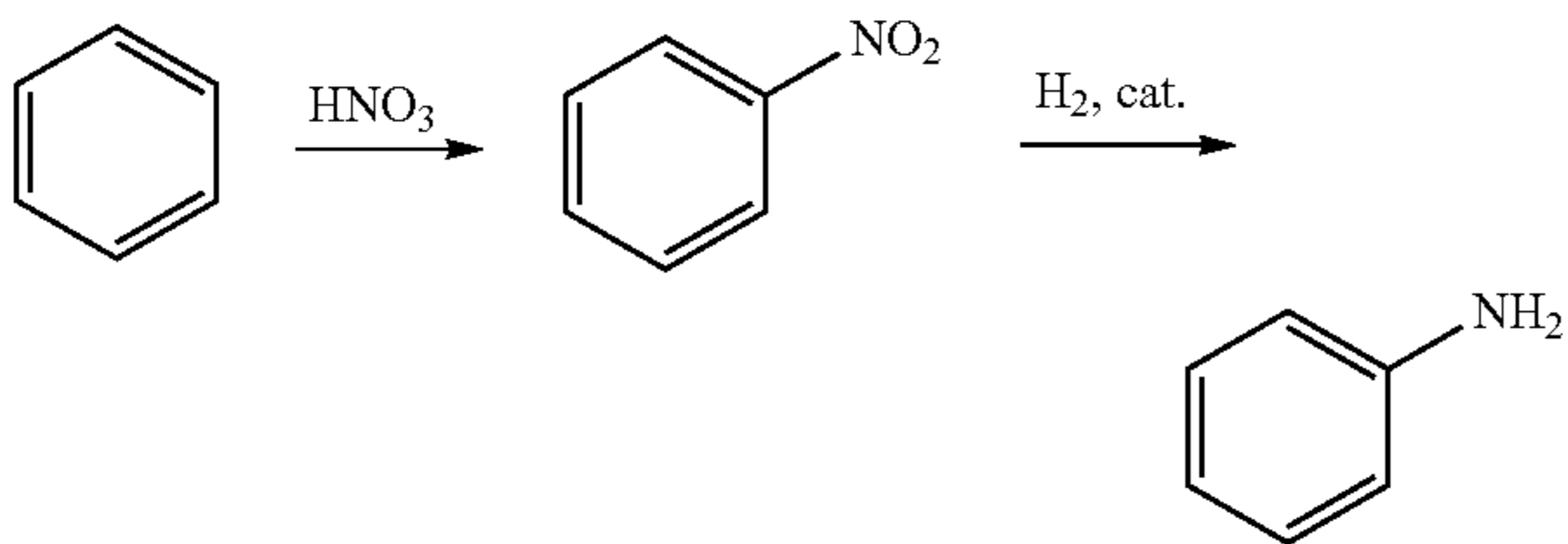
The invention relates to a process for the electrochemical direct amination of hydrocarbons by means of a diamond electrode and also a process for preparing aniline.

### METHOD FOR THE ELECTROCHEMICAL DIRECT AMINATION OF HYDROCARBONS

[0001] The invention relates to a process for the electrochemical direct amination of hydrocarbons by means of a diamond electrode and also a process for preparing aniline.

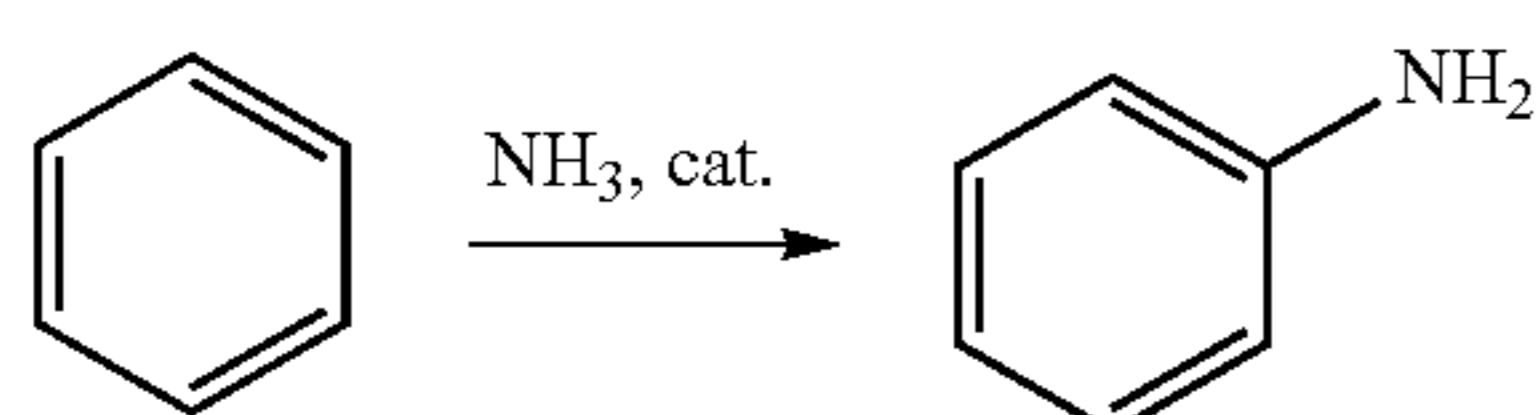
[0002] Amines are starting materials for many chemical compounds and branches of industry. Aromatic organic compounds are required, for example, as starting materials for the preparation of isocyanates which are used for producing polyurethanes. However, amines are also used for producing dyes. Furthermore, amines have numerous uses as reactants in nucleophilic substitutions to form imines, carboxamides/carboximides. In addition, amines are building blocks for agrochemicals and pharmaceuticals and also for surfactants, coatings and lubricants.

[0003] The industrial preparation of aromatic amines, in particular aniline, is at present effective in industry by means of a two-stage process. Here, the aromatic is converted by means of nitrating acid, viz. a mixture of  $H_2SO_4$  and  $HNO_3$ , into the corresponding nitro compound. The aromatic nitro compound is subsequently catalytically hydrogenated by means of 3 equivalents of hydrogen according to the following scheme.



[0004] A disadvantage of this process is the handling of large waste streams which have to be disposed of appropriately. The waste stream comprises various aromatic nitro compounds such as nitrophenols or nitrocresoles. Direct incineration of this stream is not possible since it is a predominantly aqueous discharge. The water thus has to be evaporated before the residue can be "disposed of thermally". This represents a very energy-intensive process. An alternative process is described in U.S. Pat. No. 6,245,242, where ozonolysis is utilized for the oxidative degradation of the organic constituents in the wastewater from the nitrobenzene plant.

[0005] Catalytic direct amination has been described in DE-A 10 2004 062 253. However, the aromatic hydrocarbon is in this case oxidatively aminated in ammonia by means of a catalyst system.



[0006] Disadvantages of this process are the conversions which are too low for an industrial process and the stoichiometric use of an oxidant, for example atmospheric oxygen, for the removal of hydrogen. Another disadvantage is that this process does not make do with benzene and ammonia as sole

reagents but additionally requires an oxidant. The aniline yield is so low that it brings the economics of this process into question.

[0007] There is therefore a great need for a single-stage process for preparing amine compounds without the use of nitrating acid, which would result in costly waste streams, with conversions of more than 5% and without the use of further oxidants.

[0008] This object is achieved by a process for preparing amines, wherein the amination is carried out in one step and electrochemically on an organic compound.

[0009] The process of the invention is advantageous when a doped diamond electrode is used as electrode.

[0010] The process of the invention is advantageous when a boron-doped diamond electrode is used as cathode and anode.

[0011] The process of the invention is advantageous when it is carried out at a current density in the range from 1 to 20  $A/dm^2$ .

[0012] The process of the invention is advantageous when the electrolysis is stopped after an amount of charge in the range from 2 to 8 F/mol of substrate.

[0013] The process of the invention is advantageous when the electrolysis is carried out continuously.

[0014] The process of the invention is advantageous when the temperature is in the range from  $-50$  to  $50^\circ C$ . during the electrolysis.

[0015] The process of the invention is advantageous when the pressure is in the range from 1 to 30 bar during the electrolysis.

[0016] The process of the invention is advantageous when the electrolysis takes place in an undivided cell.

[0017] The process of the invention is advantageous when from 1 to 99% strength ammonia is used as electrolyte.

[0018] The process of the invention is advantageous when it is carried out at temperatures in the range from  $-50^\circ$  to  $-33^\circ C$ . at atmospheric pressure.

[0019] The process of the invention is advantageous when it is carried out at room temperature and pressures in the range from 1 to 30 bar.

[0020] The process of the invention is advantageous when an aromatic is used as organic compound.

[0021] The process of the invention is advantageous when benzene is used as organic compound.

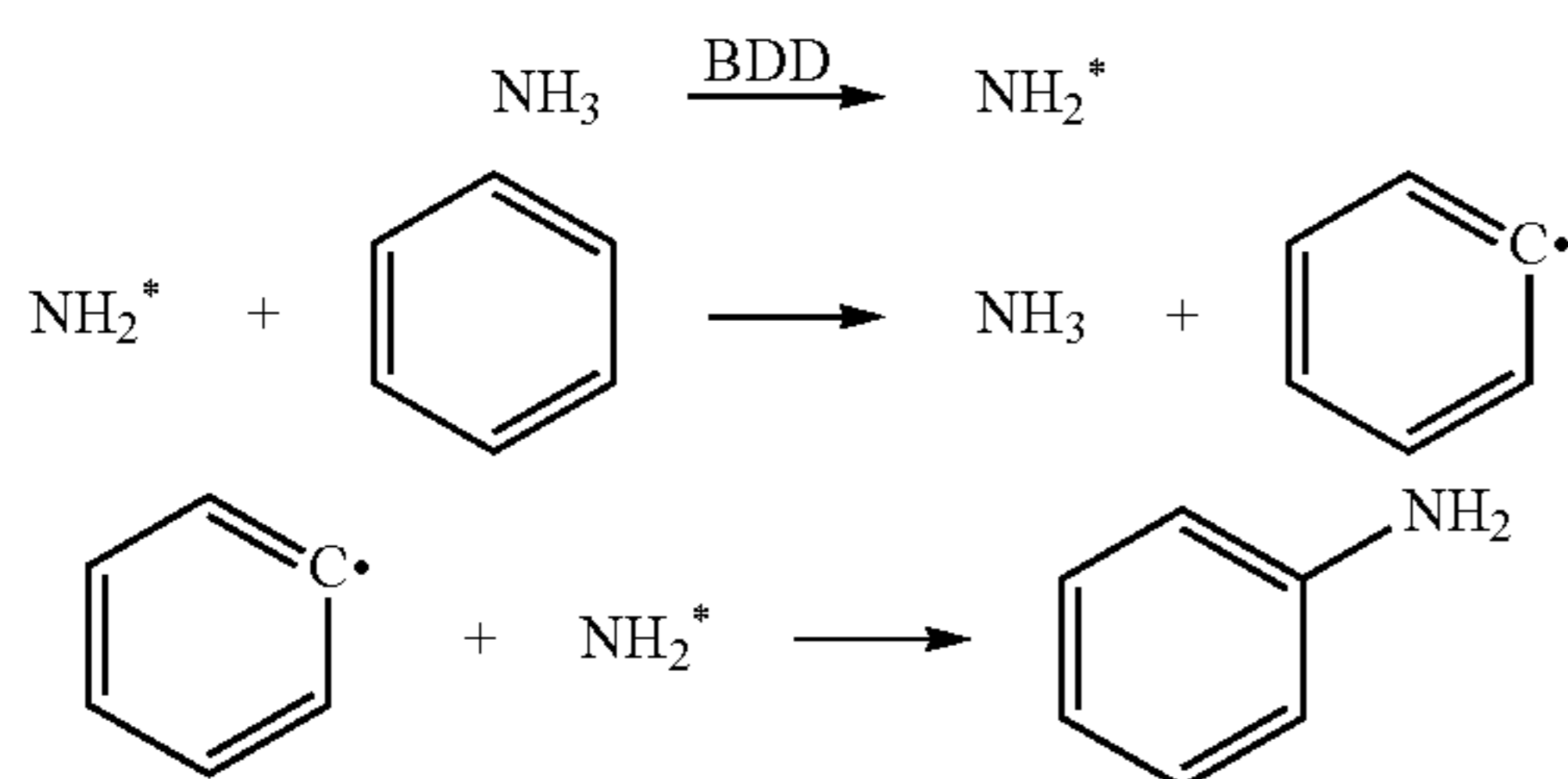
[0022] Any organic compound known to those skilled in the art can be aminated by the process of the invention. These organic compounds are hydrocarbons selected from the group consisting of substituted and/or unsubstituted, aliphatic, cyclic and/or acyclic and/or aromatic compounds. These substituted and/or unsubstituted, aliphatic, cyclic and/or acyclic and/or aromatic compounds can bear heteroatoms selected from the group consisting of oxygen, nitrogen, phosphorus and sulfur and/or functional groups such as alcohol, carboxylic acid, ester, amine, amide, thiol and thione groups. Preferred organic compounds are methane, ethane, n-propane, isopropane, n-butane, isobutane, tert-butane, n-pentane, isopentane, n-hexane, benzene, toluene, o-xylene, m-xylene, p-xylene, diphenylmethane, aniline and pyridine, imidazole, styrene, ethylbenzene, methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, ethylene glycol, propylene glycol, butanediol, ethylene, propylene, butene, butadiene, acrolein, acrylic acid, acrylonitrile, adipic acid. Particular preference is given to aromatic compounds. Very particular preference is given to benzene.



**[0023]** The electrodes used for the electrolysis are selected from the group consisting of platinum, graphite, vitreous carbon, steel and doped diamond electrodes. Preferred anode materials are graphite, vitreous carbon, platinum and doped diamond electrodes. Preferred cathode materials are graphite, vitreous carbon, platinum, steel and doped diamond electrodes. Doped diamond electrodes are very particularly preferred both for the cathode and for the anode. Here, it is possible to use either nitrogen-doped or boron-doped diamond electrodes. Especial preference is given to boron-doped diamond electrodes both for the cathode and for the anode.

**[0024]** The electrode material of the anode and cathode can, but does not have to be, identical. However, preference is given to both the cathode and the anode comprising a boron-doped diamond electrode.

**[0025]** These boron-doped diamond electrodes display a high oxygen overvoltage in aqueous electrolytes, so that hydroxy radicals can be specifically generated. The electrolysis according to the invention used in the boron-doped diamond electrodes in an  $\text{NH}_3$  electrolyte leads by a similar mechanism to free  $\text{NH}_2$  radicals.



**[0026]** The free  $\text{NH}_2$  radicals are highly reactive and lead to H abstraction on organic compounds followed by amination by recombination of free radicals.

**[0027]** It is possible to use doped diamond electrodes which have been produced by the CVD (chemical vapor deposition) process. Such electrodes are commercially available, for example from the manufacturers: Condias, Itzehoe; Diacon, Fürth (Germany) or Adamant Technologies, La-Chaux-de-Fonds (Switzerland).

**[0028]** Cheaper doped diamond electrodes which have been produced by the HTHP process (high temperature high pressure: industrial diamond powder is mechanically introduced into the surface of a metal sheet as support) can likewise be used.

**[0029]** HTHP-BDD electrodes are commercially available from pro aqua, Niklasdorf (Austria), and their properties are described by A. Ciecwiwa, R. Wüthrich and Ch. Comninellis in *Electrochem. Commun.* 8 (2006) 375-382.

**[0030]** The electrolysis can be carried out using any electrolysis cells known to those skilled in the art, e.g. divided or undivided flow cells, capillary gap cells or stacked plate cells. Particular preference is given to the undivided flow cells. A bipolar arrangement of a plurality of electrodes is advantageous for achieving optimum space-time yields.

**[0031]** The electrochemical direct amination according to the invention is carried out in a liquid ammonia solution as electrolyte. Preference is given to a from 1 to 99% strength ammonia solution.

**[0032]** The electrolysis in the liquid ammonia is carried out at temperatures of from  $-50$  to  $50^\circ\text{C}$ ., particularly preferably in the range from  $-40$  to  $30^\circ\text{C}$ . Depending on the electrolyte

temperature employed, the pressure during the reaction is in the range from 1 to 30 bar, preferably in the range from 0.1 to 20 bar.

**[0033]** A supporting electrolyte is preferably additionally present in the electrolyte during the electrolysis. It is possible to use any supporting electrolytes known to those skilled in the art for the electrolysis. The supporting electrolytes which are preferably used in the process of the invention are selected from the group consisting of ammonium salts, quaternary ammonium salts and metal salts. The ammonium salts are selected from the group consisting of ammonium acetate, ammonium hydrogencarbonate and ammonium sulfate. The quaternary ammonium salts are selected from the group consisting of methyltributylammonium methylsulfate, methyltriethylammonium methylsulfate, tetrabutylammonium tetrafluoroborate and tetraethylammonium tetrafluoroborate. Particular preference is given to methyltributylammonium methylsulfate. The metal salts are preferably selected from the group consisting of alkali metal and alkaline earth metal salts, particularly preferably from the group consisting of sodium amide, sodium acetate, sodium alkylsulfonates, sodium arylsulfonates, sodium alkylsulfates, sodium arylsulfates, sodium hydrogencarbonate, potassium amide, potassium acetate, potassium alkylsulfonates, potassium alkylsulfates and potassium hydrogencarbonate.

**[0034]** The current density in the process of the invention is preferably in the range from 1 to  $20\text{ A/dm}^2$ , particularly preferably in the range from 2 to  $10\text{ A/dm}^2$ . To avoid a deposit on the electrodes, the polarity can be changed at short intervals when using diamond electrodes as anode and cathode material. The reversal of the polarity can occur at an interval of from 30 seconds to 60 minutes, and preference is given to an interval of from 60 seconds to 30 minutes.

**[0035]** Mixing of the contents of the cell can be effected using any mechanical stirrers known to those skilled in the art, but also other mixing methods such as the use of an Ultraturax or ultrasound.

**[0036]** The reaction is stopped after introduction of an amount of charge in the range from 2 to 8 F/mol of substrate, particularly preferably in the range from 2 to 4 F/mol of substrate. In the case of atmospheric pressure electrolysis in a discontinuous process, the reaction is stopped by switching off the power supply and warming the reaction mixture to RT and then distilling off the excess  $\text{NH}_3$  from the reaction mixture. To stop the reaction in the case of low-pressure electrolysis (low pressure means from 0 to 40 bar) in a discontinuous process, the power supply is switched off, the pressure vessel is then brought to atmospheric pressure and the excess  $\text{NH}_3$  is distilled off from the reaction vessel. In the case of a continuously operated process, parts of the electrolytes are discharged and are then warmed to RT and/or brought to atmospheric pressure. The ammonia gas given off during this reaction is appropriately taken off with suction. The residue which remains is worked up by methods known to those skilled in the art, e.g. dissolution, crystallization, distillation and/or filtration.

**[0037]** An organic compound can also be multiply aminated by the process of the invention. To separate the multiply aminated products from the singly aminated products, it is possible to use all separation methods known to those skilled in the art. It can be effected, for example, by separating off the



singly or multiply aminated product from the reaction mixture by means of distillation and/or crystallization.

#### EXAMPLES ACCORDING TO THE INVENTION

##### Example 1

###### Amination of Anisole in Liquid Ammonia at $-40^{\circ}\text{C}$ .

**[0038]** 4.7 g of anisole and 1.2 g of methyltributylammonium methylsulfate are placed in a glass beaker cell having a BDD anode and BDD cathode (electrode dimensions in each case  $70\times 20\times 5$  mm, immersed area  $45\times 20$  mm, spacing: 9 mm) at  $-40^{\circ}\text{C}$ . After addition of 70.0 g of ammonia (liquid), the electrolysis is started at a current density of  $2\text{ A/dm}^2$ . During the electrolysis, the voltage increases from 9.7 V to 10.6 V. After introduction of an amount of charge of 2 F/mol of anisole, the electrolysis is stopped and the electrolyte is brought to room temperature. The residue remaining after evaporation of the  $\text{NH}_3$  is analyzed by gas chromatography.

**[0039]** Diaminobenzene is detected in an amount of 18 GC-% by area as amination product in the reaction mixture.

##### Example 2

###### Amination of Benzene in Liquid Ammonia at Room Temperature

**[0040]** 4.0 g of benzene and 2.0 g of methyltributylammonium methylsulfate are placed in an autoclave having a BDD anode and BDD cathode (electrode dimensions in each case  $70\times 20\times 5$  mm, immersed area  $45\times 20$  mm, spacing: 9 mm) at room temperature. The autoclave is pressurized with 113.8 g of ammonia and the electrolysis is started at a current density of  $2\text{ A/dm}^2$ . During the course of the electrolysis, the voltage drops from 5.2 V to 4.7 V, while the pressure in the apparatus rises from 12.1 bar to 17.9 bar. After introduction of an amount of charge of 2 F/mol of benzene, the electrolysis is stopped and the autoclave is vented. The residue remaining after evaporation of the  $\text{NH}_3$  is analyzed by gas chromatography.

**[0041]** Phenylhydrazine is detected in an amount of 0.6 GC-% by area as amination product in the reaction mixture.

1. A process for preparing an amine, the process comprising:

carrying out an amination in from 1 to 99% strength ammonia as electrolyte in one step and electrochemically, in an electrolysis, on an organic compound,

wherein a doped diamond electrode is an electrode.

2. The process according to claim 1, wherein a boron-doped diamond electrode is employed as a cathode and an anode of the electrode.

3. The process according to claim 1, carried out at a current density in a range from 1 to  $20\text{ A/dm}^2$ .

4. The process according to claim 1, wherein the electrolysis is stopped after an amount of charge in a range from 2 to 8 F/mol.

5. The process according to claim 1, wherein the electrolysis is carried out continuously.

6. The process according to claim 1, wherein temperature is in a range from  $-50$  to  $50^{\circ}\text{C}$ . during the electrolysis.

7. The process according to claim 1, wherein a pressure is in a range from 1 to 30 bar during the electrolysis.

8. The process according to claim 1, wherein the electrolysis takes place in an undivided cell.

9. The process according to claim 1 carried out at temperature in a range from  $-50$  to  $-33^{\circ}\text{C}$ . at atmospheric pressure.

10. The process according to claim 1, carried out at room temperature and a pressure in a range from 1 to 30 bar.

11. The process according to claim 1, wherein the organic compound is an aromatic.

12. The process according to claim 1, wherein the organic compound is benzene.

13. The process according to claim 2, carried out at a current density in a range from 1 to  $20\text{ A/dm}^2$ .

14. The process according to claim 2, wherein the electrolysis is stopped after an amount of charge in a range from 2 to 8 F/mol.

15. The process according to claim 3, wherein the electrolysis is stopped after an amount of charge in a range from 2 to 8 F/mol.

16. The process according to claim 13, wherein the electrolysis is stopped after an amount of charge in a range from 2 to 8 F/mol.

17. The process according to claim 2, wherein the electrolysis is carried out continuously.

18. The process according to claim 3, wherein the electrolysis is carried out continuously.

19. The process according to claim 13, wherein the electrolysis is carried out continuously.

20. The process according to claim 4, wherein the electrolysis is carried out continuously.

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