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## PROCESS FOR THE ELECTROLYTIC REDUCTION OF AROMATIC NITRO COMPOUNDS

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### ABSTRACT OF THE DISCLOSURE

The electrolytic reduction of an aromatic nitro compound is conducted in a cell having acidic catholyte and anolyte baths. The nitro compound is contained in the catholyte bath and hydrogen sulfide is passed through the catholyte during the reduction process. Improved, high yields of the final product are recoverable from serial runs with the same cell without intermittent cleaning of the cell and the electrodes.

### BACKGROUND OF THE INVENTION

This invention relates to an improved process for the electrolytic reduction of aromatic nitro compounds. The improvement is in the passing of hydrogen sulfide through the electrolyte bath which contains the nitro compounds.

The prior reduction processes for aromatic nitro compounds have encountered a number of serious difficulties. Primary among these has been the fouling of the working electrode, which in the case of reduction is the cathode with various metals present in the catholyte. When fouling occurred the surface properties of even a new cathode were quickly changed so that the voltage required rose and the useful period of the reduction process was cut short. Another type of fouling which occurred was the coating of the surface of the cathode with various degradation products. The formation of such products tended to increase as the above metallic fouling occurred. Another related difficulty was that the cathode surface required cleaning and scraping after each full or partial run, thus making prohibitively expensive serial runs required for commercial production. When a high rate of formation of degradation products was encountered the entire cell required frequent dismantling and cleaning. In order to aid in reducing the formation of such degradation products only expensive, highly purified electrolytes and aromatic nitro compounds have been employed heretofore.

It is therefore an object of the present invention to provide an improved electrolytic reduction process for aromatic nitro compounds by which fouling of the working electrode is reduced sufficiently for serial runs to be made without requiring intermittent cleaning.

Another object is to provide a process for electrolytically reducing aromatic nitro compounds more efficiently and with higher yields than was formerly possible.

Yet another object is to provide an efficient process for reducing aromatic nitro compounds wherein unpurified, commercially available electrolytes and aromatic nitro compounds may be used.

### SUMMARY OF THE INVENTION

Briefly, these objects are realized by passing hydrogen sulfide,  $H_2S$ , through the catholyte bath of the electrolytic cell which contains the reducible aromatic nitro compound. Actual recovered, i.e., isolated, yields of between 73% to 84% of theoretical yield have been realized by this process, even for serial runs without intermittent cleaning.

The improved process can be conveniently conducted in a cell having acidic anolyte and catholyte baths separated by a semi-permeable membrane which retains the nitro compound in the catholyte and which has sufficient porosity to allow transport of current conducting ions. An anode and a cathode are placed in contact with the anolyte and catholyte baths, respectively, and are connected to an electrical current source. Reflux condensers and thermometers can be provided for either one or both of the electrolyte compartments. The catholyte compartment, can be provided with means to promote through mixing of the hydrogen sulfide with the catholyte bath. The cell can be preferably constructed of a chemically inert and heat resistant resin.

The improved process is conducted by placing the aromatic nitro compound to be reduced in the catholyte bath, establishing a flow of electrical current, and passing hydrogen sulfide through the catholyte. It is preferable to introduce the hydrogen sulfide near the bottom of the catholyte bath so that greater contact with the liquid bath occurs. This provision of means to promote thorough mixing aids in creating increased contact as well as in forming an emulsion of the generally insoluble aromatic nitro compounds. The hydrogen sulfide need not be passed through the catholyte in great excess. Rather, all that is practically necessary to assure operability is that some hydrogen sulfide pass through the catholyte bath so that the surface portions of the catholyte are contacted by hydrogen sulfide.

Since hydrogen sulfide has a fixed solubility in an acidic catholyte liquid at a particular temperature it would be theoretically possible to add only enough hydrogen sulfide to the catholyte so as to attain thorough contact which would occur at saturation, with no excess passing through the bath. However, assurance of thorough contact requires a condition of equilibrium which in turn requires that some hydrogen sulfide pass through the bath so that the gaseous space above the bath contains an equilibrium concentration of hydrogen sulfide. Thus, for practical operability at least some hydrogen sulfide should pass through the catholyte bath.

The presence of hydrogen sulfide in the gaseous space above the catholyte bath can be detected by several means. The utilization of either an ultra-violet spectrophotometer or gas chromatographic equipment for continuous monitoring of the exhaust gas stream. Several analytical chemical methods are available, including passing the exhaust gas through a sodium hydroxide solution to form sodium sulfide which can be precipitated with a copper sulfate solution of known concentration, and thereafter measuring the remaining copper ion concentration with a polarograph or weighing the copper sul-

fide formed. If some hydrogen sulfide is detectable in the exhaust gas the catholyte bath will be saturated with hydrogen sulfide and the benefits of the present invention will be attained. Hence, all that is necessary is for the hydrogen sulfide to be passed through the catholyte bath in an amount sufficient to allow a detectable level thereof to exist in the headspace over the catholyte. If any hydrogen sulfide can be detected in the headspace, a sufficient amount is being used. Due to the elevated temperatures and vigorous agitation of the catholyte bath in most electrolytic reduction processes a condition approaching saturation of the acidic catholyte with the hydrogen sulfide will generally prevail.

The hydrogen sulfide passed through the catholyte bath can be trapped to prevent health hazards or can be recycled after cleaning. Such cleaning is necessary since small volumes of hydrogen are evolved at the cathode in the electrolytic reduction of aromatic nitro compounds and it must be removed from the exhaust gas to prevent explosion hazards.

The anolyte and catholyte baths can contain any of several standard electrolytes. These are generally aqueous solutions of inorganic acids. About from 1.0 N to 10.0 N  $\text{H}_2\text{SO}_4$  may be employed, with the preferred normality being about from 1.0 N to 2.5 N.

Any type of semi-permeable membrane which is mechanically strong, chemically inert, and which allows ionic transport while restricting diffusion of the aromatic nitro compound or its reduction product can be used. Generally, two types of membranes are preferred. The first of these is constructed of an ion exchange resin of either anionic or cationic properties and the second is constructed of porous ceramic material and may optionally include an impregnating resin to reduce porosity.

When a cationic ion exchange membrane is used, the resin employed can be any of those described in U.S. Patents Nos. 2,730,768, 2,731,408, 2,731,411 and Re. 24,865. The most preferred types are composed of a thermoplastic copolymer of styrene and divinyl benzene containing ionizable sulfonic acid groups chemically bonded to the copolymer. The sulfonic acid groups can be represented by the formula  $-\text{SO}_3^- \dots \text{M}^+$ , wherein  $\text{M}^+$  is a metal cation. This resin has a fixed negative charge which prevents anions from the catholyte from migrating into the anolyte where their increased concentration would corrode the anode. This anode protection represents an additional advantage for the use of such a cationic resin membrane.

When an anionic ion exchange membrane is used the resin employed can be any of those described in U.S. Patents Nos. 2,730,768, 2,731,425, 2,732,350, 2,732,351, 2,860,097 and Re. 24,865. The preferred types are prepared by copolymerization of styrene, divinyl benzene, and a monomer containing ionizable amine groups. The amine groups are quaternary in structure and are of the formula  $-\text{N}(\text{R}^1)_3(\text{R}^2)^+ \dots \text{Y}^-$ , wherein  $\text{R}^1$  is a lower alkyl group or a bond of a heterocyclic ring,  $\text{R}^2$  is a lower alkyl group and  $\text{Y}^-$  is an anion. The term "lower alkyl group" as used herein includes groups having from one to four carbon atoms.

These ion exchange resins have the additional advantages of being non-fragile and easily cleaned. They have pore sizes which render them substantially non-porous to the organic compounds present as well as to water, but permeable to current conducting ions. Usually these pores are filled with water at the start of a reduction in an amount of between 30 to 55 weight percent based on the dry resin weight.

Mechanically strong membranes may be formed of these ion exchange resins by polymerizing them in situ on a porous support member according to the teachings of the above patents. These members may be constructed of fabrics woven from such materials as: Dynel (vinyl chloride-acrylonitrile copolymer), glass, polyvinylidene chloride, and vinyl chloride-vinyl acetate copolymers.

The fabrics of these materials are tightly woven, usually in the range of about 24 threads per inch and have weights of about from 14 to 28 mg./cm.<sup>2</sup>. The pore size range is nearly identical for the two types of ion exchange resins and is about from 1 to 10 Angstrom units, which renders the membranes substantially impermeable under the hydraulic pressures normally encountered in the present process.

The ceramic semi-permeable membranes are prepared by the controlled sintering of alumina or alumina-silica powders. Optional control of the porosity can be achieved by adding a material inert to the acid, such as furfural-formaldehyde resin, to the pores of the ceramic material. This impregnation is carried out by soaking the porous material in a solvent solution of the resin and its curing catalyst until the desired amount of resin is deposited within the pores, removing excess solvent from the pores and curing the resin. Furfural-formaldehyde resin has been added to porous alumina-silica membranes in amounts of about from 0.5 to 2.2 weight percent. The resulting ceramic-resin filled membrane has a pore-size of below 0.6 micron and a permeability of from about 0.05 cc. to about 1 cc. water/hour/square inch of diaphragm area measured under a hydrostatic head of 70 inches.

The anode can be constructed of lead, platinum, or carbon. The submerged area of the anode is not critical, but is usually maintained equivalent to the submerged surface area of the cathode. Various metals may be employed as cathode materials, including commercially pure (+99%) silver, lead, titanium, and molybdenum. "Hastelloy C," a trade named alloy can also be used and is preferred. Its composition in approximate weight percentages is: 54% nickel, 15 to 17% molybdenum, 14.5 to 16.5% chromium, 4 to 7% iron, 3 to 5% tungsten, 2.5% cobalt, 1% silicon, 1% manganese, 0.35% vanadium, 0.08% carbon, 0.04% phosphorus and 0.03% sulfur. Another trade named alloy which can be used is "Ni-O-Nel" alloy which has an approximate weight composition of 40% nickel, 31% iron, 21% chromium, 3% molybdenum, 1.75% copper, 0.60% manganese, 0.40% silicon, and 0.5% carbon. The percentages of the individual alloy components may be varied within limits of above 10% of the stated values. Also the nonmetallic components are believed unnecessary but are present in the alloys as obtained commercially.

The anode and cathode may be in bar, rod, or mesh form. While great variation in submerged electrode areas is possible, 0.6 to 1.7 dm.<sup>2</sup> (square decimeter) areas can generally be used for small scale production. The effective area of a mesh screen electrode is measured by the peripheral dimensions of the submerged screen.

While any electrolytically reducible aromatic nitro compound may be reduced by the improved process of the present invention, the use of hydrogen sulfide is described by reference to the reduction of nitrobenzene. By focusing upon a given nitro compound, comparison of process parameters is facilitated. The reduction of nitrobenzene represents one of the most important commercial electrolytic reductions of an aromatic nitro compound since phenylhydroxylamine is the direct reduction product and rearranges in the heated catholyte acid bath to an acid salt of p-aminophenol (PAP). By treatment with an alkaline material the PAP can then be liberated. 2,4-dinitrotoluene, 2,4,6-trinitrotoluene and other unstable nitro compounds are normally excluded from the term "electrolytically reducible aromatic nitro compounds" due to the difficulties in handling the same.

Other aromatic nitro compounds which are electrolytically reducible according to the present process are: o-chloronitrobenzene; m-nitrotoluene; 2-chloro-2-nitrotoluene, o-ethylnitrobenzene, m-nitrodiphenyl amine, 5-nitroisoquinoline, 2-nitroparasyrene, and 2,5-dichloronitrobenzene.

The formation of a small quantity of degradation prod-

ucts in the catholyte bath can not be completely avoided by the present process. It has been found that the presence of these products can be satisfactorily tolerated by adding a small quantity of a surfactant to the catholyte bath for the purpose of forming a better emulsion of these products. They are then retained by the catholyte liquor and can be drained from the cell with only a light coating remaining on the cell component. Both ionic and non-ionic surfactants can be employed. The preferred ionic surfactants are quaternary tetra-alkyl ammonium chlorides. Only a small amount of surfactant is needed for this purpose, i.e., less than about 1% based on the weight of the reducible aromatic nitro compound. Preferably, concentrations of about 0.1% based on the weight of the reducible aromatic nitro compound are employed.

The present improved electrolytic reduction process can be carried out in either a batch-type cell or a continuous flow-type cell. The first of these cells is comprised of two relatively wide compartments separated by a semi-permeable membrane. One compartment is used to hold the catholyte bath and the other is used to hold the anolyte bath. The inter-electrode distance is about 4 inches in such a cell. Mechanical stirring means are provided for the catholyte and/or the anolyte baths. This type of cell is used for catholyte bath volumes of under about 1000 ml.

The continuous flow-type cell is comprised of two relatively narrow compartments separated by a semi-permeable membrane. Both compartments are designed to accept electrode plates which are of the same general dimensions as the semi-permeable membrane. One of these compartments is connected to an anolyte holding tank and the other is connected to a catholyte holding tank. Pumps are arranged to force the electrolytes into their respective compartments and past the planar electrode surfaces at a minimum flow rate of about 1.5 ft./sec., with rates of 2 to 7 ft./sec. being preferred. This continuous flow causes sufficient mixing of the added hydrogen sulfide with the catholyte bath as it flows through the catholyte compartment. The inter-electrode distance for this cell is about 1/4 inch to 1/2 inch and the catholyte holding tank can be arranged to hold a large volume of fluid, e.g., about 40 liters.

Many of the process parameters depend upon which type of cell is used. For the continuous flow-type cell the following parameters can be used: catholyte temperature, 72° C. to 92° C.; potential, 3 to 7 volts; current density, about 16 amperes/dm.<sup>2</sup>; hydrogen sulfide added to catholyte, about from 1 to 1000 mg. H<sub>2</sub>S/g. nitrobenzene; and total reduction time, 6 to 7 hours. For the batch-type cell the following parameters can be used: catholyte temperature 72° C. to 92° C. potential, 7 to 12 volts; current density, 6 to 13 amperes/dm.<sup>2</sup>; hydrogen sulfide added to catholyte, about from 50 to 200 mg. H<sub>2</sub>S/g. nitrobenzene; and total reduction time, 6 to 7 hours. The above parameters for addition of the hydrogen sulfide are working levels only and do not constitute minimum quantities.

The nitrobenzene to be reduced is added once the cell has been raised to working temperature and after the electrical current through the cell has been established. Usually it is added in small amounts so that about 6 to 10 weight percent nitrobenzene based on the total catholyte weight is present at any one time. The total ampere-hours of direct current supplied vary with the total amount of nitrobenzene added to the cell. Four Faradays per gram molecular weight are required for reduction of nitrobenzene.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The reduction of an aromatic nitro compound to an intermediate product and conversion thereof to a product

of ultimate utility may be described by reference to nitrobenzene. The electrolytes are placed in the catholyte and anolyte compartments and the initial current established. The cell is simultaneously heated to at least about 55° C. and preferably to near the final temperature. Nitrobenzene is then added in small amounts, so that not more than 10 weight percent based on the catholyte weight is present at any one time. The completion of the reduction of available nitrobenzene is signaled by H<sub>2</sub> evolution at the cathode. The catholyte containing the acid salt of p-aminophenol (PAP) is removed and steam distilled to about one half of its original volume. The concentration is then adjusted to pH 3.5 with NH<sub>4</sub>OH solution and filtered to remove insoluble tars. The filtrate is then treated with NaHSO<sub>3</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, stirred, and passed through a column containing activated carbon. The column is washed with H<sub>2</sub>O and the total eluate adjusted to pH 6.8 to pH 7.2 with NH<sub>4</sub>OH solution and thereafter distilled to remove aniline and water until PAP starts to precipitate at 100° C., at which time distillation is terminated. The liquid residue is then adjusted to pH 7.0 with NH<sub>4</sub>OH solution. It is cooled to about from 15° C. to 20° C., filtered washed with H<sub>2</sub>O and 1% NaHSO<sub>3</sub>, and dried under vacuum at 50° C. The resulting PAP may be employed to produce acetyl p-aminophenol, a well known analgesic or may be used as a dye intermediate, as an antioxidant, or as PAP-HCl in photographic developers.

The following examples are illustrative only and are not to be limitative since those skilled in this art will understand that various modifications may be made therein without departing from the spirit and scope of the invention. Particularly, a wide variety of aromatic nitro compounds can be reduced by the present process.

#### EXAMPLE I

A continuous flow-type cell was set up with a cationic resin semi-permeable membrane separating the two compartments. The membrane was composed of a glass fabric backing impregnated with cationic resin and weighed 27.6 mg./cm.<sup>2</sup> of area. The cationic resin was styrene-divinyl benzene copolymer containing ionizable sulfonic acid radicals electrically neutralized by sodium ions. The membrane exhibited a specific resistance of 22 ohm-cm.<sup>2</sup> and a specific conductance of 3×10<sup>-3</sup> mho./cm. both measured in 0.01 N NaCl. A membrane of this type is marketed by Ionics Incorporated under trade designation "Nepton 61 DYG 067." When installed the resin contained 33 weight percent water based on the total weight of resin plus water.

The catholyte holding tank of the cell was charged with 35.3 liters of deionized water and then with 2500 g. of a 98% technical grade H<sub>2</sub>SO<sub>4</sub> solution. The anolyte tank was charged with a smaller volume of a 2.5 N aqueous solution of H<sub>2</sub>SO<sub>4</sub>. The pumps for both baths were operated during this start-up procedure. The cathode was of "Hastelloy C" in plate form and the anode was of lead in plate form. As installed in their respective compartments they each had submerged areas of about 25 dm.<sup>2</sup>. The cathode and anode were connected to a source of direct electric current and a current of about 80 amps. was established. The catholyte bath was then steam heated to 81° C. and the current raised to 400 amps., or 16 amps./dm.<sup>2</sup>. Hydrogen sulfide was then fed into the input catholyte line at a rate whereby about two bubbles of exhaust gas per second were recovered from the cell headspace. This exhaust gas was then fed through a caustic scrubber to trap the excess H<sub>2</sub>S. Commercially available nitrobenzene (unpurified) was then added in small quantities to the catholyte feed line at the times set out in Table 1. The electrical potential and current, catholyte and anolyte temperatures and cumulative vent gas volume measured by a wet volume meter are also set out for each nitrobenzene addition time.

TABLE 1.—REDUCTION OF NITROBENZENE

Addition Times, hr.:	Nitrobenzene added, ml.	Potential, volts	Current, Amps.	Catholyte Temp., °C.	Anolyte Temp., °C.	Cumulative Vent Gas Volume, liters
0.....	0	3.95	400	81	56	0
0.5.....	230	4.05	400	83.5	63.5	38.0
1.0.....	180	4.28	400	81	61	54.0
1.5.....	170	4.19	400	85	63.5	72.5
2.0.....	210	4.30	400	83	63	82.0
2.5.....	200	4.61	400	83	62.5	93.0
3.0.....	150	4.65	400	84	63.5	105.0
3.5.....	210	4.87	400	85	64	114.5
4.0.....	190	5.35	400	83	63.5	123.5
4.5.....	220	5.92	400	83.5	63	135.0
5.0.....	200	6.60	400	85	64	150.0
5.5.....	130	7.00	400	84.5	64	169.5
6.0.....	0	6.23	400	83.5	64	192.0
Total.....	2,000					192.0

During the reduction process a total of 250 g. of H<sub>2</sub>S gas were fed into the catholyte inlet stream and a great portion thereof recovered in the caustic scrubber. After the catholyte had been subjected to electrolysis for 6 hours and all of the nitrobenzene had been added, hydrogen gas began to evolve at a rate of about 2 liters/minute. This hydrogen evolution was taken as the end point of the electrolytic reduction.

The cumulative total of the nitrobenzene added was 2500 g. which amounted to approximately 7 weight/volume percent (g./ml.×100) of the catholyte bath.

A polarographic assay was conducted on an aliquot portion of the catholyte with the result that 90% conversion of the nitrobenzene to PAP was found.

Another aliquot portion of the catholyte liquor was filtered after cooling to about room temperature and the liquor was placed in a flask and distilled to remove residual nitrobenzene along with about 50 weight percent of the excess water. The resulting liquor was cooled to about 40° C. and neutralized to pH 3.6 with NH<sub>4</sub>OH solution. The tars were then removed by adding NaHSO<sub>3</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O and filtering through an activated charcoal column. The eluate was neutralized to pH 7.0 with NH<sub>4</sub>OH solution and another distillation was conducted to remove further nitrobenzene. The mixture was then neutralized to pH 7.0 and cooled to 10° C. After filtering and oven drying 49.3 g. of PAP were recovered which amounted to an isolated yield of 73%.

#### EXAMPLE II

A continuous flow-type cell similar to that of Example I was set up for reduction of a number of batches of nitrobenzene with the same semi-permeable membrane material and the catholyte and anolyte holding tanks filled in the same manner. The same electrode materials, but newly cleaned, and the same start-up procedures as used for Example I were followed and the hydrogen sulfide was fed into the input catholyte line at the same rate as in that example. Two (2) ml. of quaternary trimethyl dodecyl ammonium chloride were added with the first charge of nitrobenzene for each run.

A number of preliminary runs were made with the cell during which the cell components and electrodes came to equilibrium with the electrolyte baths and during which the activated carbon column used during the recovery procedure was saturated with that amount of p-amino phenol which it would absorb.

A series of eight serial runs was then made following the same procedure as used for Example II. The electrical potential and current for this series of runs varied between 3.75 to 6.15 volts, and 400 to 405 amps., respectively. The catholyte temperature varied 79° C. to 85° C., while the anolyte temperature varied between 59° C. to 69° C. The total time of reduction for each run was held constant at 6 hours. The cumulative total of unpurified, commercially available nitrobenzene fed in, the amount of H<sub>2</sub>S added, the cumulative volume of vent gas, the

polarographic and isolated yields are as set out in Table 2 for each of the runs.

The pump system for the catholyte bath was held constant during these eight runs to establish a flow rate of 4.1 ft./sec. past the cathode.

TABLE 2.—SERIAL ELECTROLYTIC REDUCTIONS

Run. No.:	Nitrobenzene Added, grams	H <sub>2</sub> S added, grams	Cumulative Vent Gas Volume, liters	Polarographic Yield, weight percent	Isolated Yield, weight percent
1.....	2,500	4.5	126.0	92	73
2.....	2,500	31.5	180.0	92	75
3.....	2,500	14	147.5	90	76
4.....	2,500	30	138.0	97	80
5.....	2,500	11	154.0	92	75
6.....	2,500	26	165.0	92	74
7.....	2,500	8	81.0	87	78
8.....	2,500	43	125.8	92	74
Average.....					70

The electrodes were not removed for cleaning between these runs nor was the cell cleaned or disrupted in any way. While frequent cleaning has been necessary in the prior reduction processes none was required here to attain the average isolated yield of 76% for eight consecutive runs. Such efficient serial runs on large volume cells have not been heretofore possible and the running of consecutive runs at such high isolated yields without intermittent cleaning is unexpected.

After completion of these runs the cell was drained, torn down, and cleaned, and only a small amount of degradation products were found on the membrane and electrode surfaces. Such serial runs can be employed on a commercial basis.

#### EXAMPLE III

Nitrobenzene was reduced in a batch-type cell using the following three different cathode materials: "Hastelloy C" alloy, silver, and lead.

Two cell halves constructed from a heat resistant chemically inert resin were bolted together with a cationic semi-permeable membrane interposed therebetween. The catholyte compartment was fitted with a thermometer, an agitator, and a reflux condenser. A steam heating device was then inserted into the catholyte compartment. A plate of "Hastelloy C" alloy was inserted into the catholyte compartment to a depth sufficient to have an effective area of 1.65 dm.<sup>2</sup> and connected to an electric current source. A lead strip was then inserted in the anolyte compartment to provide a submerged area of 1.65 dm.<sup>2</sup> and connected to the electric current source.

The catholyte bath was made up by mixing 123 g. of technical grade (+98%) H<sub>2</sub>SO<sub>4</sub> with sufficient deionized water to bring the total volume up to 900 ml. The anolyte compartment of the cell was filled with a 5% (v./v.) H<sub>2</sub>SO<sub>4</sub> solution and 123 g. of commercially available nitrobenzene was added thereto in the portions set out in Table 3.

The cell was heated to the initial temperature set out in

Table 3 and a low current of about 2 amps. was established for a few minutes. Then the full current density of 11 amps./dm.<sup>2</sup> was established. This current density was held constant during the reduction and amounted to a constant current of 17.5 amps.

Hydrogen sulfide was introduced into the bottom of the catholyte bath through a capillary glass tube at a rate sufficient to produce about 2 bubbles per minute of exhaust gas.

TABLE 3.—BATCH CELL REDUCTION

Reaction Time, Hr.:	Potential, Volts	Temperature, ° C.	Cumulative Amp., Hr.	Nitrobenzene added, grams
0.-----	9	72	0	41
1.0-----	7.5	83	17.5	41
2.0-----	7.0	82	35.0	41
3.0-----	7.0	83	52.5	0
4.0-----	7.2	84	70.0	0
5.0-----	7.5	85	87.5	0
6.0-----	8.0	86	105.0	0
7.0-----	8.5	88	122.5	0
Total-----				123

During the reduction about 8 liters of H<sub>2</sub>S were introduced into the catholyte bath. This amounted to 12 g. of H<sub>2</sub>S or 0.098 g. H<sub>2</sub>S/g. of nitrobenzene.

A polarographic assay on an aliquot portion of the cooled catholyte showed 93.5 percent reduction of the nitrobenzene to p-aminophenol.

The catholyte liquor was then removed from the cell and the p-aminophenol recovered by following the recovery procedure of Example I. The PAP recovered weighed 86.9 g. which resulted in an isolated yield of 80%.

The cell was thereafter cleaned with acetone and fitted with a commercially pure silver cathode using the same effective area of 1.65 dm.<sup>2</sup>. An identical run was made except that the catholyte temperature varied between 84° C. to 86° C. and 4.0 liters of H<sub>2</sub>S or 0.049 g. H<sub>2</sub>S/g. nitrobenzene were introduced into the catholyte bath. The polarographic assay showed 102.2% yield. The PAP isolated by the recovery procedure weighed 91.5 g. which resulted in an isolated yield of 84%.

The cell was then fitted with a lead cathode of the same effective area of 1.65 dm.<sup>2</sup>. An identical run was made except that the catholyte temperature varied between 83° C. to 86° C. Four (4.0) liters of H<sub>2</sub>S were introduced into the catholyte bath. The polarographic assay showed 108% yield. The PAP isolated amounted to 88.5 g. which resulted in an isolated yield of 81%.

This example demonstrates that a variety of cathode materials can be used.

## EXAMPLE IV

Two identical runs were made in the batch-type cell used for Example III, the first using carbon dioxide gas and the second using hydrogen sulfide. The anode was a lead plate and the semipermeable membrane was of the same material as the membrane of Example I. The cathode was a plate of "Hastelloy C" alloy and was cleaned with steel wool and emery cloth prior to installation. It was inserted to a depth sufficient to have an effective area of 1.65 dm.<sup>2</sup>. A 5% (v./v.) solution of H<sub>2</sub>SO<sub>4</sub> was added to the anolyte chamber and 61.5 g. of chemical pure (C.P.) H<sub>2</sub>SO<sub>4</sub> solution plus sufficient deionized water to make 1000 ml. was added to the catholyte chamber.

Sixty one and one-half (61.5) g. of nitrobenzene were added to the catholyte after the catholyte was brought up to about 80° C. For the first run carbon dioxide was in-

roduced into the catholyte bath through a capillary glass tube at a rate sufficient to produce about 2 bubbles per minute of exhaust gas. The current was established at 10 amps. and continued for 6 hours for a cumulative total of 60 amp.-hours. The catholyte bath temperature varied from 85° C. to 89° C. during the reduction and approximately 6 liters of CO<sub>2</sub> were introduced. The catholyte bath after cooling and purification according to Example I yielded 33 g. of PAP or 60.5% yield.

For the second run H<sub>2</sub>S was substituted for the CO<sub>2</sub> and the same volume was introduced, i.e., 0.146 g. H<sub>2</sub>S/g. nitrobenzene.

Upon cooling and purifying the catholyte bath 45 g. of PAP were recovered for an 82.5% isolated yield.

Thus it can be concluded that introducing another gas for the hydrogen sulfide does not result in the same process since the electrolytic reduction is markedly different when hydrogen sulfide is used.

In summary, an improved electrolytic reduction process for aromatic nitro compounds is provided by passing hydrogen sulfide through the catholyte bath during electrolysis.

What is claimed is:

1. In a process for the electrolytic reduction of a reducible aromatic nitro compound by application of electrical current in a cell having an anode, a cathode, and anolyte and catholyte baths separated by a semi-permeable membrane, the aromatic nitro compound being present in the catholyte bath, the improvement comprising passing hydrogen sulfide through said catholyte bath during said reduction in an amount sufficient to allow a detectable level thereof in the headspace over said catholyte bath.

2. The process of claim 1 wherein said hydrogen sulfide is thoroughly mixed with said catholyte bath.

3. The process of claim 1 wherein the semi-permeable membrane is formed from an ion exchange resin which is substantially non-porous to water and is ion-permeable.

4. The process of claim 1 wherein the cathode is selected from the group consisting of silver, titanium, molybdenum, lead, and an alloy of about 54% nickel, about 15 to 17% molybdenum, about from 14.5 to 16.5% chromium, about from 4 to 7% iron, about from 3 to 5% tungsten, about 2.5% cobalt, about 1.0% silicon, about 1.0% manganese, and less than about 1.0% of vanadium, carbon, phosphorous and sulfur.

5. The process of claim 1 wherein the aromatic nitro compound is nitrobenzene.

6. The process of claim 1 wherein said catholyte bath contains a tar-emulsifying surfactant.

7. The process of claim 1 wherein said anolyte bath comprises an aqueous solution of sulfuric acid having a normality in the range of about from 1 N to 10 N, said catholyte bath comprises an aqueous solution of sulfuric acid having a normality in the range of about from 1 N to 10 N and wherein said catholyte bath contains said aromatic nitro compound in an amount of less than about 10 weight percent.

8. The process of claim 7 wherein the normalities of said catholyte and anolyte baths are about from 1.0 N to 2.5 N.

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