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ELECTROLYTIC REDUCTION PROCESS USING SILICIC ACID COATED MEMBRANE

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This invention relates to an improvement in processes for electrolytically reducing aromatic nitro compounds. More particularly, it relates to the use of an improved semipermeable membrane to separate the catholyte from the anolyte in such electrolytic processes.

In the past silicic acid has been deposited in porous ceramic cell membranes to reduce the pore size by first soaking the membrane in a basic solution of sodium silicate and then treating with a strong acid. The resulting silicic acid filled membrane when placed in an electrolytic cell would function properly until the silicic acid washed out by the vigorous agitation necessary in the catholyte and/or anolyte baths. Often this useful period did not extend to completion of the electrolysis being carried out. Of course, both the standard ceramic membranes and those filled with silicic acid are fragile and degradation products are nearly impossible to remove therefrom.

It is therefore an object of this invention to provide the improvement in electrolytic reduction processes which comprises the use of a membrane for separating an acidic catholyte from a basic silicate-containing anolyte so that the membrane functions as a self-repairing silicic acid filled membrane.

It is another object to provide an electrolytic reduction process for reducing aromatic nitro compounds which employs an acid and base resistant membrane for separating an acidic catholyte from a basic silicate-containing anolyte.

Briefly described, this invention depends upon the discovery that an acid and alkali corrosion resistant semipermeable membrane can be maintained in a silicic acid filled state of proper porosity by placing it between an acidic catholyte and a silicate compound containing anolyte which is maintained at a high pH. The acid of the catholyte and the silicate of the anolyte mutually diffuse into the membrane and react to form solid silicic acid in situ within the pores of the membrane.

The preferred semipermeable membrane is constructed of a porous material which is resistant to corrosion by acids and bases. The porosity of the material can range from the ionic size of the current conducting ions to an air permeability of less than about 7 cubic feet per square foot of area when measured according to ASTM test D737–46. The conditions of this test are the use of a 0.5 inch water pressure drop across the membrane, air at 21° C. and 65 percent relative humidity, a minimum area of 10 inch by 10 inch, and at least 5 samples. A preferred membrane is a fabric woven of polytetrafluoroethylene fibers and having a porosity in the above range. The fabric should have a minimum total thread count such that the total of the threads per inch in the warp direction plus the threads per inch in the weft direction equal at least 140. There is no maximum thread count because even with the most dense fabrics the pore sizes are still much larger than ionic dimensions. A minimum weight for such fabric is 8 ounces per square yard. For the same reason as above there is no maximum weight. The minimum thickness is about 0.008 inch and there is no maximum as ion transport is not greatly hindered by thick membranes.

A fabric of these characteristics has been found to be resistant to corrosion by concentrated acid (10 N H_2SO_4) and by concentrated base (pH 14). This fabric is nonfragile and is mechanically strong.

The anolyte preferred for use in the improved process is composed of an aqueous solution of about from 15 to 36 weight percent, based on the weight of the water, of a silicate compound which is neutralizable to silicic acid. At silicate concentrations below this range there is sufficient acidity in the vicinity of the anode to cause silicic acid to deposit on the anode. Also insufficient silicic acid is deposited in the membrane so that transfer of anolyte to catholyte makes the process impractical. At silicate concentrations above the upper limit the viscosity of the anolyte becomes so great that oxygen evolved at the anode is entrapped in the anolyte. The cell conductivity also decreases rapidly beyond this concentration. Alkali metal silicates are preferred and of these sodium silicates are preferred. The sodium silicates of water glass formula have been used in the specific examples for purposes of comparison. These silicates have a general formula of $Na_2O \cdot nSiO_2$, where n is usually 2 or more.

The alkaline compound of the anolyte may be an alkali metal hydroxide. Since it is preferable to have a single cation in the anolyte, sodium hydroxide has been used in the examples. Sufficient base should be included so that a pH of at least about pH 12 is attained. This minimum pH should be maintained throughout the electrolytic reduction to assure that excess silicic acid does not form in the body of the anolyte solution. One way of maintaining the minimum pH is to make up the anolyte with a higher pH, such as pH 14, and it will not fall below the lower pH limit during the reduction. The necessary concentration of the alkali metal hydroxide depends upon the concentration of the silicate solution since this is an alkaline solution. For a 15 weight percent silicate solution the concentration of the alkaline compound should be about 25 weight percent based on the weight of the silicate, and for a 36 weight percent silicate solution it should be about 15 weight percent. Even a saturated solution of the base can be used for the anolyte.

The catholyte preferred for use in the improved process is composed of an aqueous acidic solution having a concentration of from 1 to 10 N. About 2.5 N is most preferred. An acid concentration within the indicated range provides sufficient acidity to effect an instantaneous formation of silicic acid in the pores of the membrane when the catholyte and anolyte are added simultaneously to their respective chambers. Also, acidity in this range prevents conversion of silicic acid in the membrane pores to silicate. Sulfuric and phosphoric acids are preferred.

Standard cathode and anode materials may be used in the improved process as long as the cathode is acid resistant and the anode resists corrosion by the base of the anolyte. The preferred cathode is Monel metal, while the preferred anode is of platinum.

To conduct the electrolytic reduction a cell is set up with the semipermeable membrane separating the catholyte and anolyte compartments, the anolyte and catholyte are then simultaneously added to minimize stresses on the membrane. Silicic acid is formed instantaneously in the pores of the membrane and effectively checks crossflow of the electrolytes.

The formation of silicic acid reduces the membrane pore size to the point where the relatively large silicate ion will no longer migrate into the catholyte portion of the membrane, and therefore further silicic acid buildup does not occur after this degree of pore size reduction is achieved. According to the usual practice a slightly greater liquid head is maintained in the anolyte than in the catholyte. The electrodes are then inserted and the cell is heated to about 60° C. and current imposed. The reducible aromatic nitro compound is then added to the

catholyte and the reduction carried out until hydrogen begins to evolve from the cathode.

The reduction can best be conducted at a temperature of between about 70° C. to about 95° C. The preferred range is from about 80° C. to about 90° C. Of course lower starting temperatures of about 60° C. can be used. The current is maintained between about from 5 to 20 amperes per square decimeter of effective cathode area. The effective area of a solid bar is its submerged surface area. The effective area of a metal screen is measured by its peripheral dimensions. The potential drop depends upon cell design and electrode spacing but is generally in the range of about from 5 to 30 volts. The time required for the reduction process is not critical and is determined by the coulomb requirement for the particular compound being reduced.

The aromatic nitro compounds which can be reduced, except as noted below, include all of the general class of aromatic nitro compounds which are ordinarily reduced by such process, hence they may be more specifically termed "reducible aromatic nitro compounds." 2,4-dinitrotoluene and 2,4,6-trinitrotoluene are normally excluded from this term due to difficulties in handling. Nitrobenzene is one of the most important of such compounds since it can be reduced to phenylhydroxylamine which rearranges at the temperatures used to form the acid salt of p-aminophenol from which the basic form p-aminophenol (PAP) can be recovered by neutralization.

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.

In the electrolytic reduction of nitrobenzene concentrations of up to 8 weight percent based on the weight of the catholyte may be introduced in either a stepwise fashion during the reduction or stirred in at the start of the reduction process. Above this concentration aniline tars form which make recovery procedures difficult.

The conversion of the reduction products to products of ultimate utility can be by standard recovery procedures. One such procedure is briefly described by reference to nitrobenzene as follows. When the end of the reduction is indicated by hydrogen evolution at the cathode, the catholyte is removed and distilled to approximately one-half its original volume. The concentrate is then adjusted to pH 3.5 with NH_4OH solution and filtered to remove insoluble tars. The filtrate is then treated with bleaches, stirred, and passed through a carbon column which generally contains 50 g. of activated carbon. The bleaches used are aqueous solutions of $NaHSO_3$ and

$$Na_2S_2O_4 \cdot 2H_2O$$

The activated carbon column is then washed with H_2O and the effluent is adjusted to pH 7.0 to 7.2 with NH_4OH solution and is 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_4OH solution. It is cooled to about from 15° C. to 20° C., filtered, washed with H_2O and one percent $NaHSO_3$, and dried under vacuum at 50° C.

The following examples are illustrative and are not to be construed as 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.

Example 1

Two flanged heat-resistant glass elbows of 3 inch inside diameter were bolted together with a semipermeable membrane interposed between the flanges. One leg of the resulting U-cell provided a catholyte compartment while the other leg was used as the anolyte compartment. Each compartment was fitted with a thermometer and an agitator. The catholyte compartment was fitted with a reflux condenser and a heat exchange coil was placed about the entire cell. A cylindrically shaped Monel metal screen of 20 mesh size having an effective area of 0.6 square decimeter was inserted into the catholyte compartment and connected with the negative pole of a direct current source. A platinum bar was then inserted in the anolyte compartment and connected to the positive pole of the direct current source. The distance separating the anode from the cathode was 12 inches.

The Monel metal of the cathode contained elements in the following weight percentage ranges: 60 to 70 nickel, 25 to 35 copper, 1 to 3 iron, 0.25 to 2 manganese, 0.02 to 1.5 silicon and 0.3 to 0.5 carbon.

The membrane was a fabric woven of polytetrafluoroethylene fibers having an air permeability of 1.79 cubic feet per square foot of area measured by ASTM test D737–46. The warp thread count was 143 threads per inch while the weft thread count was 44 threads per inch. The fabric was 0.0161 inch thick and weighed 13.91 ounces per square yard. A woven fabric of these specifications is marketed by Stern and Stern Textiles, Hornell, New York under trade designation "T–10–42."

The catholyte consisted of 750 ml. of a 2.3 N-aqueous solution of H_2SO_4 and the anolyte consisted of 800 ml. of an aqueous solution containing 200 ml. of a 40 weight percent solution of sodium silicate ($Na_2O \cdot 3.3SiO_2$) and 20 g. of sodium hydroxide in 600 ml. of water.

The cell was then heated to 78° C. and current density of 8.33 amperes per square decimeter of effective cathode area was established at a potential of 18.5 volts. The amounts of nitrobenzene set out in Table 1 were added at the times given. While the cell temperature and voltage varied, the current was held constant at the above current density. The cumulative ampere-hours at each of the reaction times is also set out.

TABLE 1

Reaction time hr.	Nitrobenzene added, ml.	Temperature, ° C.	Potential, volts	Cumulative, ampere-hours
0	5	78	18.5	0
0.5	3.7	87	17.0	2.5
1.0	0	86	18.0	5.0
2.0	5	88	18.5	10.0
3.0	5	89	21.0	15.0
4.0	10	83	23.5	20.0
5.0	0	89	23.0	25.0
5.5	0	88	21.5	27.5
Total	28.7			

The total of 28.7 ml. of nitrobenzene added is equivalent to 34.5 g., and the cumulative total of nitrobenzene thus amounted to approximately 4.6 weight/volume percent (g./ml.×100) of the weight of the catholyte. A polarograph assay of the catholyte bath showed 79 percent of theoretical yield.

The catholyte liquor was then run through the standard recovery procedure to isolate 24.0 g. of PAP, which represented a 67 percent isolated yield.

Example 2

Two runs were then conducted in the U-cell of Example 1 employing identical polytetrafluoroethylene woven cloth membranes. These membranes had an air permeability of 7.0 cubic feet per square foot of area as measured by ASTM test D737–46. The thread count in the warp direction was 154 threads per inch, while the weft count was 120 threads per inch. The thickness was 0.0164 inch and the weight 16.24 ounces per square yard. A fabric of these specifications is marketed by Stern and Stern Textiles under trade designation "T–43."

For both runs the cathode was "Hastelloy C" alloy and the anode was a platinum bar. "Hastelloy C" alloy has a composition in weight percent of: 54 nickel, 15 to 17 molybdenum, 14.5 to 16.5 chromium, 4 to 7 iron, 3 to 4.5 tungsten, 2.5 cobalt, 1 silicon, 1 manganese, 0.35 vanadium, 0.08 carbon, 0.04 phosphorous, and 0.03 sulfur.

The catholyte for both runs was 750 ml. of a 2.5 N aqueous solution of H_2SO_4. The anolyte for Run 1 was composed of 373 g. of a 40 weight percent aqueous solution of sodium silicate ($Na_2O \cdot 3.3SiO_2$), 40 g. of sodium hydroxide and 600 ml. of water. For Run 2 the anolyte was composed of 650 g. of a 40 weight percent aqueous solution of sodium silicate, 20 g. of sodium hydroxide and 20 ml. of water. The concentrations of sodium silicate in the two runs were 14.7 weight percent for Run 1, and 35.5 weight percent for Run 2, based on the total weight of the anolyte.

In both cases the cathode area was 0.75 square decimeter and the current density maintained was 13.3 amperes per square decimeter of effective cathode area. In both runs 30.75 g. of nitrobenzene were added in the stepwise fashion set out in Table 2.

The cells were heated to the initial temperatures shown for the respective runs and the above current density established at the indicated initial potentials prior to adding the first quantity of nitrobenzene.

TABLE 2.—RUN 1

Reaction time hr.	Nitrobenzene added, ml.	Temperature, ° C.	Potential, volts	Cumulative, ampere-hours
0	10	60	20.0	0
1	0	77	20.3	5
2	10	90	20.2	10
3	0	87	23.5	15
4	5.6	85	25.1	20
4.5	0	85	26.0	22.5
5	0	83	26.0	25
6	0	82	26.3	30
Total	25.6			

RUN 2

Reaction time hr.	Nitrobenzene added, ml.	Temperature, ° C.	Potential, volts	Cumulative, ampere-hours
0	10	70	40.0	0
0.5	0	77	19.2	2
2	5	83	20.0	9.5
3	5	88	26.5	14.5
4	5.6	84	23.2	19.5
5	0	86	25.8	24.5
6	0	88	27.0	30
Total	25.6			

In Run 1, 20 g. of sodium hydroxide were added to the anolyte at 4.5 hours in order to maintain the pH above pH 12.

In Run 2 the high starting potential was due in part to the high concentration of sodium silicate in the anolyte which caused some silicic acid to be formed on the anode. To further protect the anode 20 g. of sodium hydroxide dissolved in 20 ml. of water was added at 0.5 hour and the anode was removed and cleaned before continuing the run. This additional base prevented the formation of the silicic acid on the anode and resulted in a successful run.

The polarograph assay for Run 1 showed a yield of 64%. The polarograph assay on the catholyte of Run 2 showed 74 percent yield while the actual isolated yield was 64 weight percent.

This example shows that the sodium silicate concentration of the anolyte may vary from about 15 weight percent to about 36 weight percent of the weight of the anolyte. In Run 1, with the lower concentration, the anolyte remained colorless indicating that no nitrobenzene had migrated through the silicic acid filled membrane. The silicate concentration was thus sufficiently high to produce enough silicic acid to reduce the membrane pore size into the desired range.

In summary, the invention provides an improvement in electrolytic processes for the reduction of aromatic nitro compounds in which silicic acid is continually deposited from the anolyte onto a semipermeable membrane separating the anolyte and catholyte, to thereby provide replacement of silicic acid washed out by the continuous agitation in the anolyte and/or catholyte baths.

What is claimed is:

1. In an electrolytic process for reducing a reducible aromatic nitro compound in a cell having an anolyte bath and an acidic catholyte bath separated by a semipermeable membrane, the improvement comprising employing as the membrane an acid and alkali corrosion resistant porous material having an air permeability of less than about 7 cubic feet per square foot of fabric area measured under a 0.5 inch water pressure drop with air at 21° C. and 65% relative humidity, and using as said anolyte an aqueous solution containing a silicate compound which forms silicic acid upon neutralization in a concentration of about from 15 to 36 weight percent based upon the weight of the water and containing an alkaline compound in an amount sufficient to maintain a pH of at least about pH 12.

2. The process of claim 1 wherein said porous material is a woven fabric formed of polytetrafluoroethylene fibers.

3. The process of claim 1 wherein said porous material is a woven fabric having a minimum total thread count for both directions of at least 140 threads per inch.

4. The process of claim 1 wherein said silicate compound is sodium silicate having a water glass formula.

5. The process of claim 1 wherein the reducible aromatic nitro compound is present in said catholyte in a concentration of less than about 8 weight percent based on the total weight of said catholyte.

6. The process of claim 1 wherein said catholyte bath is comprised of an aqueous solution of sulfuric acid of at least 1.0 N concentration.

7. A process for the electrolytic reduction of a reducible aromatic nitro compound by application of electrical current in a cell having anolyte and catholyte baths separated by a semipermeable membrane, an anode, and a cathode comprising the steps of using for said membrane an acid and alkali resistant porous material having an air permeability of less than about 7 cubic feet per square foot of fabric area measured under a 0.5 inch water pressure drop with air at 21° C. and 65% relative humidity, employing as said anolyte bath an aqueous solution containing a silicate compound which forms silicic acid upon neutralization in a concentration of about from 15 to 36 weight percent based upon the weight of water and containing an alkaline compound in an amount sufficient to maintain a pH of at least about pH 12, and using as said catholyte bath an aqueous solution of sulfuric acid having a concentration of at least 1.0 N and containing a reducible aromatic nitro compound.

8. The process of claim 7 wherein said porous material is a woven fabric formed of polytetrafluoroethylene fibers.

9. The process of claim 7 wherein said porous material is a woven fabric having a minimum total thread count for both directions of at least 140 threads per inch.

10. The process of claim 7 wherein said silicate compound is sodium silicate having a water glass formula.

11. The process of claim 7 wherein said reducible aromatic nitro compound is present in said catholyte bath in a concentration of less than about 8 weight percent based on the total weight of said catholyte.

12. The process of claim 7 wherein the aromatic nitro compound is nitrobenzene wherein said electrical current is supplied at a current density of about from 5 to 20 amperes per square decimeter of effective cathode area until evolution of hydrogen at the cathode, and wherein the temperature of said catholyte bath is maintained at about from 70° C. to 90° C.

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