

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
28 April 2005 (28.04.2005)

PCT

(10) International Publication Number  
**WO 2005/037767 A2**

(51) International Patent Classification<sup>7</sup>: **C07C 209/00**

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(21) International Application Number:  
PCT/US2004/033199

(22) International Filing Date: 6 October 2004 (06.10.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/510,690 10 October 2003 (10.10.2003) US  
10/798,083 11 March 2004 (11.03.2004) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: SPEARATION OF AMINE FROM A PHENOLIC COMPOUND

(57) Abstract: A process comprises contacting a product mixture with a base, optionally in the presence of a polyhydric alcohol, to produce a base-treated mixture and distilling the base-treated mixture in which the product mixture comprises an aromatic amine and a phenolic compound.



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## SEPARATION OF AMINE FROM A PHENOLIC COMPOUND

### FIELD OF THE INVENTION

The invention relates to a process for separation of an aromatic amine from a phenolic compound in a mixture comprising the aromatic amine and phenolic compound.

### BACKGROUND OF THE INVENTION

Aromatic amines are important industrial chemicals. They can be used to produce a very important class of industrial compounds such as azo dyes. Aromatic amines can be produced by chemical reduction of nitro compounds with a metal and acid such as, for example, iron or tin and hydrochloric acid or by catalytic hydrogenation using molecular hydrogen and a hydrogenation catalyst such as nickel or platinum. Nitro compounds can be readily made by direct nitration of aromatic compounds.

The product mixture produced by catalytic hydrogenation of an aromatic nitro compound generally comprises the desired amine, a corresponding phenolic compound, and unreacted aromatic nitro compound. These by-products, because of their color and deleterious effects on product properties, are undesirable and are difficult to separate from the amines by distillation. Therefore, there is an increasing need for the reduction of impurities to increase the amine purity.

### SUMMARY OF THE INVENTION

A process comprises contacting a product mixture with a base, optionally in the presence of a polyhydric alcohol, to produce a base-treated mixture and distilling the base-treated mixture in which the product mixture comprises an aromatic amine and a phenolic compound.

### DETAILED DESCRIPTION OF THE INVENTION

An aromatic amine can be produced by catalytic reduction or hydrogenation of an aromatic nitro compound, either under liquid phase or gas phase. The reduction or hydrogenation can be carried out under any suitable conditions known to one skilled in the art, continuously, semi-continuously, or

batch-wise. A suitable condition can include a temperature in the range of from about 30°C to about 300°C, preferably about 80°C to about 250°C; a pressure that can accommodate the temperature such as about 1 atm (103 kPa) to about 20 atm (300 psig, 2000 kPa), preferably about 150 kPa to about 800 kPa; and for a  
5 sufficient period of time such as from about one to about 100 minutes.

Any hydrogenation catalysts known to one skilled in the art such as, for example, nickel, iron, platinum, copper, cobalt, palladium, iridium, and combinations of two or more thereof can be used in the production of aromatic amine. Generally, a catalyst can be present in a catalytic amount effective to  
10 catalyze the hydrogenation or reduction and can be in the range of from about 1 to about 10,000 ppm (mg per kg) aromatic nitro compound.

The hydrogenation or reduction process produces a product mixture or crude product, which comprises desired amine and impurities. A desired amine can have the formula of  $\text{RAr}(\text{CH}_2)_p\text{NR}^1$  where Ar is an arylene group; R and each  
15  $\text{R}^1$  can be the same or different; each  $\text{R}^1$  is independently selected from the group consisting of hydrogen, halogen, alkyl group, aryl group, and combinations of two or more thereof; and p is a number from 0 to 3. Examples of amine products include, but are not limited to, aniline, toluidines, chloroanilines, bromoanilines, iodoanilines, chlorotoluidines, bromotoluidines, iodotoluidines, benzylamine, N-  
20 benzylamine, ethylanilines, fluoromethylanilines, chloromethylanilines, bromomethylanilines, and combinations of two or more thereof. These disclosed examples include all possible isomers.

For example, aniline can be produced by the reduction of nitrobenzene with hydrogen either in the liquid phase using a supported hydrogenation catalyst  
25 such as nickel or precious metal, or in the gas phase using supported catalysts. Phenol is a byproduct, in trace amounts ranging from about 50 to about 1000 mg per kg amine product (ppm). Aniline can also be produced by conversion of phenol in the Halcon process.

Also for example, toluidine can be produced by reduction of nitrotoluene. Nitrotoluene can be vaporized at a temperature in the range of from about 150°C  
30 to about 400°C to obtain a vapor or gas phase of nitrotoluene. The vapor phase nitrotoluene is then introduced or fed to suitable equipment such as a gas phase

vessel or reactor, preferably a fixed bed reactor containing a hydrogenation catalyst. Hydrogen can be introduced into the equipment, preferably contemporaneously with the vapor phase nitrotoluene.

Impurities or by-products associated with the production of aromatic amines include, but are not limited to, unreacted nitro compounds, cyclohexanones, phenolic compounds, ketones, and combinations of two or more thereof. Examples of phenolic compounds include, but are not limited to, phenol, cresols, chlorophenols, bromophenols, iodophenols, chlorotoluidines, bormotoluidines, iodotoluidines, benzylamine, N-benzylamine, ethylphenols, fluoromethylphenols, chloromethylphenols, bromomethylphenols and combinations of two or more thereof. These disclosed examples include all possible isomers.

Any unreacted nitro compound can be present in the product mixture in the range of from 0 to about 1000 ppm and can be readily removed from the crude product by any means known to one skilled in the art such as, for example, distillation. Because such means are well known, the description of which is omitted herein for the interest of brevity.

Ideally, a desired amine compound contains lower than 500, preferably lower than 100, and more preferably lower than 50 parts per million (mg/kg) of such phenolic compound.

According to the invention, the product mixture (or crude product) can be contacted with a base before it is distilled. Any base, organic or inorganic, can be used. For example, suitable bases can include, without limitation, lithium hydroxide, sodium hydroxide, sodium hydrosulfide, sodium bisulfide, potassium hydroxide, potassium hydrosulfide, potassium bisulfide, calcium hydroxide, magnesium hydroxide, sodium bicarbonate, sodium carbonate, sodium sulfide, sodium oxide, magnesium oxide, calcium oxide, calcium carbonate, sodium phenoxide, barium phenoxide, calcium phenoxide, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetramethylammonium bisulfide, tetraethylammonium bisulfide, and combinations of any two or more thereof. Potassium hydroxide and sodium hydroxide are preferred for they are readily available and inexpensive.

A base can be combined with the crude product at any concentration effective to reduce the phenolic compound contamination to the desired level disclosed above. Generally, the molar ratio of base to phenolic compound can be in the range of from about 0.5:1 to about 10:1, preferably about 1:1 to about 3:1 or about 1:1 to about 2:1. The contacting of the crude product with a base can be carried out under any suitable conditions. For example, such condition can include a temperature in the range of from about 0°C to about 200°C, preferably about 20°C to about 50°C, a pressure that can accommodate the temperature such as about 1 kPa to about 300 kPa, preferably about 10 kPa to about 110 kPa, and for a sufficient period of time such as from about 0.01 to about 10,000 minutes.

Combining a base and an amine can also be carried out in the presence of a polyhydric alcohol. Examples of polyhydric alcohol include, but are not limited to trimethylene glycol, triethylene glycol, glycerols, ethylene glycol, diethylene glycol, 1,2-propane diol, 1,3-propane diol, tripropylene glycol, polyethylene glycols, polypropylene glycols, and combinations of two or more thereof. The polyhydric alcohol can be present in the base-amine combination in the range of from about 1 to about 10,000 mg per kg of the total combination.

Thereafter, a desired amine can be recovered from the base-treated crude product (or product mixture) by, for example, distillation. Suitable apparatus for the distillation is any customary apparatus as described for example in *Kirk-Othmer, Encyclopedia of Chemical Technology*, 3rd Ed. Vol. 7, *John Wiley & Sons*, New York, 1979, pages 870-881, such as sieve plate columns, bubble cap columns or columns packed with arranged or dumped packing. The distillation can be carried out in a single column or a plurality of columns, such as 2 or more columns. Any distillation techniques known to one skilled in the art can be used. A suitable distillation can include a temperature in the range of from about 100 to about 400, preferably about 100 to about 250°C, a pressure that can accommodate the temperature such as about 0.1 kPa to about 200 kPa, preferably about 5 kPa to about 30 kPa, and for a sufficient period of time such as from about 1 to about 1500 minutes.

### EXAMPLES

Example 1. This example illustrates reduction of phenol in aniline using KOH.

To a distillation flask was added 100 ml of commercial aniline containing  
5 122 ppm (mg/kg) phenol (a final product produced from a DuPont commercial  
plant at Beaumont, Texas, USA) and potassium hydroxide (53.5 mg) dissolved in  
64.4 mg of water. This was connected to a distillation head containing a short  
vigreux column. Reduced pressure (42 mmHg (5.6 kPa)) distillation was  
continued until 75 ml of aniline was in the receiver. GC analysis of the distillate  
10 revealed the phenol content was 7.4 ppm. The phenol content of the material still  
in the distilling flask was 321 ppm based on 25 ml aniline remaining in the flask.

Similarly, 100 ml of commercial aniline and potassium hydroxide (52 mg)  
in 66 mg of water was added to a distillation flask. This was vacuum distilled at  
40 mmHg (5.33 kPa) and three cuts taken, 79.4g, 8.1g and 8.4g. The phenol  
15 content of these cuts were respectively 4 ppm, 3 ppm, and <1 ppm (non-detect).  
The phenol content of the distillation residue was 2391 ppm.

Example 2. This example shows reduction in phenol content in aniline using NaOH.

To a distillation flask was added 100 ml of commercial aniline (phenol  
20 122 ppm) and sodium hydroxide (35.7 mg) dissolved in 93 mg of water. The  
same procedure as Example 1 was followed. The distillate (75 ml) had a phenol  
content of 19 ppm. The phenol content of the material remaining in the distilling  
was 374 ppm.

Example 3. This example shows using KOH and unrectified crude aniline.

25 A series of runs was conducted using a sample of crude, unrectified,  
aniline obtained from a commercial plant, which had a phenol content of 107 ppm  
to determine the efficiency of removing phenol with various doses of potassium  
hydroxide. An unrectified aniline was a crude plant aniline which had been  
dewatered but not detared in the final (rectifying) distillation column.

To a distillation flask was added 50 ml of crude aniline and 35  $\mu$ l of 50% potassium hydroxide in water. Distillation was performed at 90 mm Hg (12 kPa) pressure using a five plate Oldershaw column and vacuum distillation head. Distillation was stopped on obtaining 48.9 g of aniline distillate. This had a phenol content of 2.7 ppm. The results are shown in the following table.

KOH (ppm)	Phenol (ppm)
0	107
216	43
289	18
361	17
433	6.8
433	10.4
505	2.7
578	0

Example 4. This example illustrates using a polyhydric alcohol.

To a distilling flask was added 50 ml of crude aniline, 40  $\mu$ l of 50% potassium hydroxide and 100  $\mu$ l of polyethylene glycol (avg. Mn ca. 400, "PEG 400", Aldrich Chemical Company, Milwaukee, Wisconsin). The resulting mixture was vacuum distilled at 90 mm giving 46.6 g of aniline distillate containing 1.1 ppm of phenol.

Example 5. This example shows treating o-toluidine with KOH.

Aqueous potassium hydroxide solution (45%; 0.1055 g) was charged into a three neck round bottom flask (500 ml) followed by 123.5g of o-toluidine (OTOL) containing 489.1 ppm of o-cresol. OTOL was a commercial product commercially available from First Chemical Corp., Pascagoula, Mississippi. An Aldrich Oldershaw column (ten stages) with a short path distillation head on top of the column was attached to the flask. The mixture in the flask was agitated with a magnetic spin bar while vacuum was gradually pulled down to 90 mmHg (12 kPa). The pot temperature was raised using a heating mantle to distill OTOL. The typical distillation conditions were: pot temperature 130°C, overhead temperature 125°C, vacuum 90 mmHg (12 kPa). The distillation was stopped when boil up slowed down and the overhead temperature started falling. Distillate

(108.5 g) was collected and was analyzed with GC to find o-cresol non-detectable.

In separate runs, a plant distilled OTOL sample, obtained from a storage tank, having 133.3 ppm of o-cresol was used. A different amount of o-cresol was added to the sample to make OTOL with different concentrations of o-cresol. The OTOL was then mixed with aqueous KOH solution (45%) at different KOH/o-cresol mole ratios and distilled through a ten-stage Oldershaw column under vacuum. The distillation conditions were similar to the plant OTOL distillation conditions disclosed above. The results summarized in the following table (ND denotes non-detectable) demonstrate that the invention process substantially reduced the o-cresol content in OTOL.

Run No.	Initial o-Cresol Content (ppm)	KOH/o-Cresol mole ratio	o-Cresol in Distillate (ppm)
1	489.1	1.51/1	ND
2	489.1	1.20/1	ND
3	489.1	1.08/1	31.7
4	489.1	0.99/1	220.9
5	286.5	2.00/1	ND
6	286.5	1.60/1	ND
7	286.5	0.99/1	68
8	133.3	1.22/1	ND
9	133.3	1.07/1	29.6
10	133.3	0.99/1	38.4

Example 6. This example shows using a polyhydric alcohol to stabilize excess KOH.

In another separate run, o-cresol was added to OTOL to raise the o-cresol concentration to 8.8%. About 1.6 equivalent of KOH (45%) was charged. The pot temperature was raised under vacuum to strip water and then to reflux OTOL for 8 hours. At the end of the reflux, OTOL (20% of the charge) was distilled through the ten-stage column. The overhead sample showed 10.1 ppm of o-cresol. The potassium o-cresolate concentration was about 14% in the pot. It was noted that some white salt (excess KOH) coated on the flask bottom. Poly(ethylene glycol) was then added to the pot. The amount of PEG charged was the same as the KOH



(45%) charge. After being agitated at 120°C for 20 minutes, all the salts went into the solution.

### CLAIMS

1. A process comprising contacting a product mixture with a base, optionally in the presence of a polyhydric alcohol, to produce a base-treated mixture and introducing said base-treated mixture to a distillation apparatus  
5 wherein said product mixture comprises an aromatic amine and a phenolic compound.

2. A process according to claim 1 wherein the molar ratio of said base to said phenolic compound is in the range of from about 1:1 to about 4:1 and said base is lithium hydroxide, sodium hydroxide, sodium hydrosulfide, sodium  
10 bisulfide, potassium hydroxide, potassium hydrosulfide, potassium bisulfide, calcium hydroxide, magnesium hydroxide, sodium bicarbonate, sodium carbonate, sodium sulfide, sodium oxide, magnesium oxide, calcium oxide, calcium carbonate, sodium phenoxide, barium phenoxide, calcium phenoxide, tetramethylammonium hydroxide, tetraethylammonium hydroxide,  
15 tetrapropylammonium hydroxide, tetramethylammonium bisulfide, tetraethylammonium bisulfide, or combinations of any two or more thereof.

3. A process according to claim 2 wherein the molar ratio of said base to said phenolic compound is in the range of from 1:1 to 2:1 and said base is potassium hydroxide, sodium hydroxide, or combinations thereof.

20 4. A process according to claim 1, 2, or 3 wherein said amine is aniline, toluidines, chloroanilines, bromoanilines, iodoanilines, cholortoluidines, bormotoluidines, iodotoluidines, benzylamine, N-benzylamine, ethylanilines, fluoromethylanilines, chloromethylanilines, bromomethylanilines, or combinations of two or more thereof; and is preferably aniline, toluidines, or  
25 combinations of two or more thereof.

5. A process according to claim 1, 2, 3, or 4 wherein said phenolic compound is phenol, cresols, chlorophenols, bromophenols, iodophenols, cholortoluidines, bormotoluidines, iodotoluidines, benzylamine, N-benzylamine, ethylphenols, fluoromethylphenols, chloromethylphenols, bromomethylphenols,  
30 or combinations of two or more thereof; and is preferably phenol, cresols, or combinations of two or more thereof.

6. A process according to claim 1, 2, 3, 4, or 5 wherein said contacting is carried out in the presence of said polyhydric alcohol, which is trimethylene glycol, triethylene glycol, glycerol, ethylene glycol, diethylene glycol, 1,2-propane diol, 1,3-propane diol, tripropylene glycol, polyethylene glycol, polypropylene glycol, or combinations of two or more thereof; and said polyhydric alcohol is preferably polyethylene glycol.

7. A process comprising contacting a product mixture with a base to produce a base-treated mixture introducing said base-treated mixture to a distillation apparatus wherein  
10 said product mixture comprises an aromatic amine and a phenolic compound;

the molar ratio of said base to said phenolic compound is in the range of from about 1:1 to about 4:1 and is preferably in the range of 1:1 to 2:1;

said base is lithium hydroxide, sodium hydroxide, calcium hydroxide, magnesium hydroxide, sodium bicarbonate, sodium carbonate, sodium oxide, magnesium oxide, calcium oxide, calcium carbonate, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetramethylammonium bisulfide, tetraethylammonium bisulfide, or combinations of any two or more thereof and said base is preferably is potassium hydroxide, sodium hydroxide, or combinations thereof; and

said amine is aniline, toluidines, chloroanilines, bromoanilines, iodoanilines, cholortoluidines, bormotoluidines, iodotoluidines, benzylamine, N-benzylamine, ethylanilines, fluoromethylanilines, chloromethylanilines, bromomethylanilines, or combinations of two or more thereof; and said amine is preferably aniline, toluidines, or combinations of two or more thereof.

8. A process according to claim 7 wherein said contacting is carried out in the presence of a polyhydric alcohol, which is trimethylene glycol, triethylene glycol, glycerol, ethylene glycol, diethylene glycol, 1,2-propane diol, 1,3-propane diol, tripropylene glycol, polyethylene glycol, polypropylene glycol, or combinations of two or more thereof and which is preferably is polyethylene glycol.

9. A process for separating o-cresol from o-toluidine in a mixture, which comprises said o-cresol and said o-toluidine, comprising contacting said mixture with potassium hydroxide to produce a base-treated mixture and distilling said base-treated mixture.
- 5 10. A process according to claim 9 wherein said polyhydric alcohol is polyethylene glycol.