Abstract
Process Economics Program Report No. 76C
ANILINE AND DERIVATIVES
(December 1993)

This report supplements previous reports on the subject of aromatic amines. The report includes updated preliminary process designs and estimated economics for the manufacture of nitrobenzene by nitrination of benzene, by the conventional process and an adiabatic nitrination process; the manufacture of aniline by hydrogen reduction of nitrobenzene; and the manufacture of aniline by ammonolysis of phenol. We have also presented a preliminary process design and process economics for the production of 2-mercaptobenzothiazole (MBT), a rubber-processing chemical, made from aniline, carbon disulfide, and sulfur. The estimated economics for the manufacture of diphenylamine by the liquid-phase condensation of aniline have also been updated for this report. A discussion of the industry status is presented in a separate section.
CONTENTS (Continued)

4 NITRATION OF BENZENE (Concluded)
   A CONVENTIONAL NITRATION PROCESS FOR MAKING NITROBENZENE 4-3
      Process Description 4-3
      Process Discussion 4-11
      Cost Estimates 4-11
   AN ADIABATIC NITRATION PROCESS FOR MAKING NITROBENZENE 4-16
      Process Description 4-16
      Process Discussion 4-23
      Cost Estimates 4-23

5 ANILINE BY VAPOR PHASE CATALYTIC REDUCTION OF NITROBENZENE 5-1
   REVIEW OF PROCESSES 5-1
   PROCESS DESCRIPTION 5-1
   PROCESS DISCUSSION 5-9
      Reactor Design 5-9
      Catalyst Regeneration 5-9
      Product Purification 5-10
      Waste Treatment 5-10
      Materials of Construction 5-10
   COST ESTIMATES 5-10

6 ANILINE BY AMMONOLYSIS OF PHENOL 6-1
   REVIEW OF PROCESSES 6-1
   PROCESS DESCRIPTION 6-1
   PROCESS DISCUSSION 6-10
      Product Recovery 6-10
      Ammonia Dissociation 6-10
      Catalyst Life 6-10
      Waste Treatment 6-10
      Materials of Construction 6-12
   COST ESTIMATES 6-12
CONTENTS (Continued)

7 2-MERCAPTOBENZOTHIAZOLE

REVIEW OF PROCESSES 7-1
PROCESS DESCRIPTION 7-2
PROCESS DISCUSSION 7-10
  Reaction Section 7-10
  Hydrogen Sulfide 7-10
Purification Section 7-10
  Caustic Digestion 7-10
  Settling Tank 7-11
  Toluene Extraction 7-11
  Dilution of MBT Salt Solution 7-11
  Oxidation of Sodium MBT Solution 7-11
Benzothiazole and Toluene Recovery Section 7-12
  Product Purity 7-12
  Product Losses 7-12
  Materials of Construction 7-12
  Waste Treatment 7-13
COST ESTIMATES 7-13

8 DIPHENYLAMINE

COST ESTIMATES 8-2
APPENDIX A: PATENT SUMMARY TABLES A-1
APPENDIX B: DESIGN AND COST BASES B-1
APPENDIX C: CITED REFERENCES C-1
APPENDIX D: PATENT REFERENCES BY COMPANY D-1
APPENDIX E: PROCESS FLOW DIAGRAMS E-1
ILLUSTRATIONS

4.1 Nitrobenzene by Conventional Nitration Process
   Process Flow Diagram E-3

4.2 Nitrobenzene by Adiabatic Nitration Process
   Process Flow Diagram E-5

5.1 Aniline by Vapor-Phase Catalytic Reduction of Nitrobenzene
   Process Flow Diagram E-7

6.1 Aniline by Ammonolysis of Phenol
   Process Flow Diagram E-9

6.2 Equilibrium Conversion of Phenol to Aniline 6-11

7.1 2-Mercaptobenzothiazole from Aniline, Carbon Dioxide, and Sulfur
   Process Flow Diagram E-11
TABLES

2.1 Aniline, MBT, and Diphenylamine
   Estimated Production Costs 2-2

3.1 Worldwide Producers of Aniline 3-2

3.2 Supply/Demand for Aniline by Major Region in 1992 3-5

3.3 Consumption of Aniline by End Use in 1992 3-6

3.4 Producers of 2-Mercaptobenzothiazole and Its Derivatives 3-8

3.5 Diphenylamine Producers 3-10

4.1 Nitration of Benzene with Nitric Acid
   Patent Summary A-3

4.2 Nitration of Benzene with Nitrogen Oxides
   Patent Summary A-6

4.3 Nitrobenzene by Conventional Nitration Process
   Design Bases and Assumptions 4-4

4.4 Nitrobenzene by Conventional Nitration Process
   Stream Flows 4-6

4.5 Nitrobenzene by Conventional Nitration Process
   Major Equipment 4-8

4.6 Nitrobenzene by Conventional Nitration Process
   Utilities Summary 4-10

4.7 Nitrobenzene by Conventional Nitration Process
   Total Capital Investment 4-12

4.8 Nitrobenzene by Conventional Nitration Process
   Capital Investment by Section 4-13

4.9 Nitrobenzene by Conventional Nitration Process
   Production Costs 4-14

4.10 Nitrobenzene by Adiabatic Nitration Process
    Design Bases and Assumptions 4-17

4.11 Nitrobenzene by Adiabatic Nitration Process
    Stream Flows 4-18

4.12 Nitrobenzene by Adiabatic Nitration Process
    Major Equipment 4-20
TABLES (Continued)

4.13 Nitrobenzene by Adiabatic Nitration Process  
Utilities Summary  4-22
4.14 Nitrobenzene by Adiabatic Nitration Process  
Total Capital Investment  4-25
4.15 Nitrobenzene by Adiabatic Nitration Process  
Capital Investment by Section  4-26
4.16 Nitrobenzene by Adiabatic Nitration Process  
Production Costs  4-27
5.1 Aniline from Nitrobenzene  
Patent Summary  A-9
5.2 Aniline by Vapor-Phase Catalytic Reduction of Nitrobenzene  
Design Bases and Assumptions  5-2
5.3 Aniline by Vapor-Phase Catalytic Reduction of Nitrobenzene  
Stream Flows  5-5
5.4 Aniline by Vapor-Phase Catalytic Reduction of Nitrobenzene  
Major Equipment  5-6
5.5 Aniline by Vapor-Phase Catalytic Reduction of Nitrobenzene  
Utilities Summary  5-8
5.6 Aniline by Vapor-Phase Catalytic Reduction of Nitrobenzene  
Total Capital Investment  5-12
5.7 Aniline by Vapor-Phase Catalytic Reduction of Nitrobenzene  
Capital Investment by Section  5-13
5.8 Aniline by Vapor-Phase Catalytic Reduction of Nitrobenzene  
Production Costs  5-14
5.9 Aniline Production from Benzene via Nitrobenzene  
(Conventional Process)  
Total Capital Investment  5-16
5.10 Aniline Production from Benzene via Nitrobenzene  
(Conventional Process)  
Production Costs  5-17
5.11 Aniline Production from Benzene via Nitrobenzene  
(Adiabatic Process)  
Total Capital Investment  5-19
# TABLES (Continued)

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.12</td>
<td>Aniline Production from Benzene via Nitrobenzene (Adiabatic Process) Production Costs</td>
<td>5-20</td>
</tr>
<tr>
<td>6.1</td>
<td>Aniline by Ammonolysis of Phenol Patent Summary</td>
<td>A-17</td>
</tr>
<tr>
<td>6.2</td>
<td>Aniline by Ammonolysis of Phenol Design Bases and Assumptions</td>
<td>6-2</td>
</tr>
<tr>
<td>6.3</td>
<td>Aniline by Ammonolysis of Phenol Stream Flows</td>
<td>6-5</td>
</tr>
<tr>
<td>6.4</td>
<td>Aniline by Ammonolysis of Phenol Major Equipment</td>
<td>6-7</td>
</tr>
<tr>
<td>6.5</td>
<td>Aniline by Ammonolysis of Phenol Utilities Summary</td>
<td>6-9</td>
</tr>
<tr>
<td>6.6</td>
<td>Aniline by Ammonolysis of Phenol Total Capital Investment</td>
<td>6-13</td>
</tr>
<tr>
<td>6.7</td>
<td>Aniline by Ammonolysis of Phenol Capital Investment by Section</td>
<td>6-14</td>
</tr>
<tr>
<td>6.8</td>
<td>Aniline by Ammonolysis of Phenol Production Costs</td>
<td>6-15</td>
</tr>
<tr>
<td>7.1</td>
<td>2-Mercaptobenzothiazole Patent Summary</td>
<td>A-20</td>
</tr>
<tr>
<td>7.2</td>
<td>2-Mercaptobenzothiazole from Aniline, Carbon Disulfide, and Sulfur Design Bases and Assumptions</td>
<td>7-3</td>
</tr>
<tr>
<td>7.3</td>
<td>2-Mercaptobenzothiazole from Aniline, Carbon Dioxide, and Sulfur Stream Flows</td>
<td>7-5</td>
</tr>
<tr>
<td>7.4</td>
<td>2-Mercaptobenzothiazole from Aniline, Carbon Dioxide, and Sulfur Major Equipment</td>
<td>7-7</td>
</tr>
<tr>
<td>7.5</td>
<td>2-Mercaptobenzothiazole from Aniline, Carbon Dioxide, and Sulfur Utilities Summary</td>
<td>7-9</td>
</tr>
<tr>
<td>7.6</td>
<td>2-Mercaptobenzothiazole from Aniline, Carbon Dioxide, and Sulfur Total Capital Investment</td>
<td>7-14</td>
</tr>
<tr>
<td>7.7</td>
<td>2-Mercaptobenzothiazole from Aniline, Carbon Dioxide, and Sulfur Capital Investment by Section</td>
<td>7-15</td>
</tr>
</tbody>
</table>
### TABLES (Concluded)

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.8</td>
<td>2-Mercaptobenzothiazole from Aniline, Carbon Dioxide, and Sulfur Production Costs</td>
<td>7-16</td>
</tr>
<tr>
<td>8.1</td>
<td>Diphenylamine Patent Summary</td>
<td>A-29</td>
</tr>
<tr>
<td>8.2</td>
<td>Diphenylamine by Liquid Phase Condensation of Aniline Total Capital Investment</td>
<td>8-4</td>
</tr>
<tr>
<td>8.3</td>
<td>Diphenylamine by Liquid Phase Condensation of Aniline Production Costs</td>
<td>8-5</td>
</tr>
</tbody>
</table>