PERP Program – New Report Alert

August 2003

Nexant's ChemSystems Process Evaluation/Research Planning program has published a new report, ***Nitrobenzene/Aniline (02/03-2)***.

Nitrobenzene is produced by nitration of benzene with nitric acid in the presence of sulfuric acid as a catalyst and dehydrating agent. Ninety-plus percent of nitrobenzene is converted to aniline by hydrogenation. About 80-85 percent of global aniline goes into production of methylene diphenyl diisocyanate (MDI), a key intermediate for polyurethanes and automotive plastics. Other major applications are antioxidants and vulcanization accelerators for rubber, intermediates for herbicides/pesticides, and intermediates for dyes/pigments. Minor uses include textile and photographic chemicals, pharmaceuticals, amino resins, and explosives.

Both nitrobenzene and aniline technologies are relatively mature, with only incremental improvements in technology anticipated.

Kellogg Brown & Root (KBR) announced a licensing agreement in December 2002 with DuPont Intellectual Assets Business (IAB) designed to offer DuPont's latest nitration/hydrogenation process technology for new aniline plants and retrofits. The arrangement calls for KBR to handle the marketing of the technology through an exclusive global license, with DuPont IAB providing operational expertise.

DuPont became the largest supplier of aniline in the United States with its acquisition in late 2002 of ChemFirst, a global supplier of electronic chemicals and materials to the semiconductor industry and specialty intermediates for polyurethanes and other applications. The deal was delayed by an explosion in a nitrotoluene isomer separation column that idled the entire plant for a time for cleanup and investigation. Aniline production capacity at ChemFirst totals some 500 million pounds per year, accounting for 20 percent of overall production in the United States. DuPont previously had aniline capacity amounting to 115 million pounds per year, so that with ChemFirst capacity DuPont now accounts for 25 percent of U.S. capacity. Air Products and Chemicals, a major participant in polyurethane intermediates that would have also had a fit with ChemFirst's electronic chemicals and materials business, is reported to also have been a bidder. Air Products has been aggressively expanding its electronic chemicals portfolio to complement its leading position in electronic gases. In 2001, it entered the related photoresist developer and chemical mechanical planarization markets.

In December 2002, a proposed merger between Sumitomo Chemical and Mitsui Chemicals was approved by the Fair Trade Commission in Japan. The merger was due to be completed by March 31, 2004. However, the proposed merger fell apart in March 2003 over relative valuations and pension liabilities. The two companies would have held over 90 percent of the Japanese market for aniline, with production capacity amounting to 239,000 metric tons per year. Within two years of the completion of the merger, aniline would have been offered to competitors and intermediaries at cost, to comply with regulatory approvals.

In December 2002, Sunoco Chemicals announced that it was idling its aniline and diphenylamine production facility at Haverhill, Ohio. Reports indicated that “significant mechanical problems” were discovered during a routine inspection of the unit, which was built in 1982. It was the only aniline facility in North America that used phenol feedstock. Citing business returns were insufficient to justify the capital cost to bring the plant back to a safe, reliable operating condition, Sunoco said it intended to focus its resources on phenol and bisphenol A production at the plant.

The chemistry of nitrobenzene production is relatively simple and mature. The nitration of benzene by mixed acid, also called nitrating acid, proceeds by the formation of nitronium ion, NO_2^+, by the reaction of nitric acid with concentrated sulfuric acid:

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

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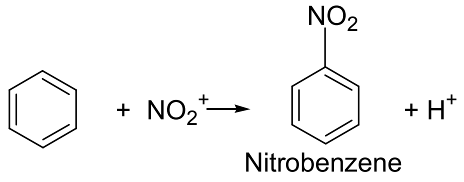
The nitronium ion formed in this way then attacks the aromatic ring to give nitrobenzene:



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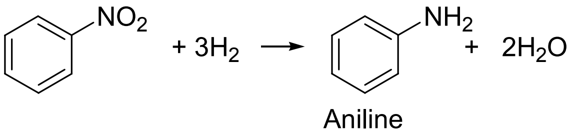
The reaction is exothermic, releasing about 80 kilocalories per mol.

The two commercial nitration processes, isothermal and adiabatic, are different only in the nitration section, where the adiabatic process integrates nitration with sulfuric acid concentration, thus using the heat of nitration to reconcentrate the spent sulfuric acid. This is achieved by circulating a large volume of sulfuric acid through the nitrators, absorbing the heat of nitration without undue temperature rise. In the areas of nitrobenzene purification, effluent treatment, and fume control, the two processes employ equivalent design concepts.

Aniline is typically produced by catalytic hydrogenation of nitrobenzene, but there is also a commercial route involving amination of phenol. The latter process is now practiced only by Mitsui Petrochemicals in Japan, since Sunoco Chemical has recently shut down its U.S. plant.

The highly exothermic catalytic hydrogenation of nitrobenzene (heat of reaction about 130 kilocalories per mol) is carried out commercially in the presence of excess hydrogen in both the vapor phase and the liquid phase.



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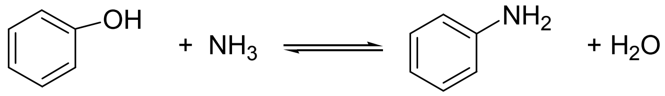
Vapor-phase processes may employ either fixed-bed or fluidized-bed reactors. Copper or palladium on activated carbon or an oxidic support, in combination with other metals (lead, vanadium, phosphorous, chromium) as modifiers/promoters, has been shown to be an effective catalyst for vapor-phase hydrogenation, achieving high activity and selectivity.

Both ICI and DuPont have developed liquid-phase hydrogenation processes that operate at 90-200°C and 100-600 kPa, using slurry or fluidized-bed reactors. ICI's process utilized an excess of aniline as the reaction solvent and removed reaction heat by allowing the reaction mixture to boil off at a reaction pressure usually less than 100 kPa. One preferred catalyst for this process was finely divided nickel on kieselguhr.

DuPont's liquid-phase hydrogenation process uses a platinum-palladium catalyst on a carbon support, with iron as modifier. The modifier provides good catalyst life, high activity, and protection against hydrogenation of the aromatic ring. The continuous process uses a plug-flow reactor. Catalyst inventory is low, and a continuous bleed of catalyst is taken to metals recovery and reprocessing.

Amination of phenol takes place in the vapor phase using excess ammonia in the presence of a silica-alumina catalyst at about 370°C and 1.7 MPa.



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A fixed-bed reactor is suitable, as the reaction exotherm is moderate (about 2 kcal per mol). Use of excess ammonia (mole ratio of 20:1) pushes the reversible reaction to the right and also inhibits the formation of byproducts diphenylamine, triphenylamine, and carbazole.

The lack of new investment in the aniline industry has restricted technology development. Thus, process improvements have centered on reductions in energy usage and waste stream production. This new report from Nexant/ChemSystems assesses the process technology, production economics and market outlook for both nitrobenzene and aniline.

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