OAR Box 1188

Prepped by Candice Davis

Document Number:

50) II-I-12

Docket Number:

A-90-49

Chemical Products Synopsis

February 1984
Previous Report — October 1980

NITROBENZENE

A-90-49

II-I-12

FOCUS.....Nitrobenzene and derivatives (principally aniline) are used in the production of isocyanates, pesticides, rubber chemicals, and pharmaceuticals. Aniline production accounts for over 96% of the nitrobenzene consumed in the US. Nitrobenzene producers make aniline captively. Nitrobenzene also has a variety of minor derivatives. The major merchant market outlet is the pharmaceutical industry. Nitrobenzene is used as the starting material for the analgesic acetaminophen (APAP). Mallinckrodt, Monsanto, and Penick produce APAP in the United States. Mallinckrodt is reportedly the world's largest producer of APAP, an alternative to aspirin. Mallinckrodt's US capacity is estimated at 15 million pounds per year of APAP. Overseas producers of APAP include Sterling Drug UK, and Rhone-Poulenc of France.

para-Aminophenol is an intermediate precursor for acetaminophen and can be produced by a proprietary process which involves the continuous selective and controlled hydrogenation of nitrobenzene. In addition to use in making APAP, p-aminophenol finds use as a dye intermediate with some quantities reportedly used in producing epoxies.

The increasing use of non-aspirin painkillers has brought continual growth to the merchant market for nitrobenzene. Non-aspirin products, including APAP, now account for about one-third of total painkiller consumption.

Trade sources estimate that the merchant market for nitrobenzene will be in the range of 30-35 million pounds in 1984. US merchant market sellers of nitrobenzene are E.I. DuPont and First Chemical Corporation. The other two current producers of nitrobenzene (Mobay and Rubicon) use material captively for aniline production. Mobay discontinued aniline production by nitrobenzene hydrogenation in 1983, but continues to operate facilities for the acid-iron reduction of nitrobenzene to produce iron oxide pigments as a co-product of aniline. Mobay also purchases aniline on the open market for isocyanates production since stopping production of aniline by nitrobenzene hydrogenation.

OUTLOOK.....Future demand for nitrobenzene depends almost exclusively on aniline requirements. Aniline consumption, in turn, is predominantly dependent on MDI (methyl diphenyldiisocyanate) requirements. Less important derivatives of aniline are rubber processing aids and agricultural chemicals. Although demand for aniline and nitrobenzene was hard hit by the 1982 depression in transportation and construction, requirements rebounded in 1983. Nitrobenzene production will probably exceed 900 million pounds in 1984, but longer-term growth will moderate to a rate of less than 3% annually. Production of aniline from phenol by USS Chemicals will reduce long-term nitrobenzene demand for aniline production. In 1984, USS Chemicals will probably produce about 100 million pounds of aniline, reducing nitrobenzene potential demand by 130-140 million pounds.

PRICING.....Since 1981, the published price for nitrobenzene has been relatively stable in the range of 33 to 34.5 cents per pound, depending on producer and the quantities purchased. Merchant market prices are quoted FOB producing plants for bulk quantities. Based on the average sales values reported by the USITC and trade sources, list prices are relatively meaningless compared to actual selling prices for large volume customers. Negotiated prices depend on quantity. Generally, with a current list price of 33-34 cents per pound, actual selling prices are well below 30 cents for large volume buyers. Future pricing will depend on benzene costs which will probably edge up slowly over the next few years as gasoline pool values for toluene increase with the accelerated phasedown of leaded gasoline in the US and overseas. On the other hand, overcapacity and competitive pressure on aniline and derivatives will tend to hold back increases for nitrobenzene values.

AVERAGE PRICES RANGE–NITROBENZENE
CENTS PER POUND–DOUBLE DISTILLED–TANKS–FOB WORKS

	1960	1965	1970	1975	1980	1981	1982	1983	1984	1985	1987	1989
List Price	11	9½	8½	22	31	33	33	34	34	37	42	45
Ave. Sales Val.	n/a	n/a	n/a	22	n/a	28	25					

SUPPLY AND DEMAND.....Millions of Pounds.....Estimated.....Domestic US

	1960	1965	1970	1975	1980	1981	1982	1983	1984	1985	1987	1989
Capacity	n/a	310	690	915	1670	1670	1575	1425	1425			
Production	162	280	548	570(E)	611	902	775	930	950	1000	1100	1180
Sales	n/a	n/a	n/a	14	n/a	20	19	30(E)				

Historical production statistics, except for the year 1975, are as reported by the US International Trade Commission. In 1975, the ITC reported output of 414 million pounds which is too low based on reported aniline production. Nitrobenzene production is generally in the range of 1.4 times aniline output. Production estimates for nitrobenzene may have to be reduced further if USS Chemicals takes a greater share of the aniline market.

AVAILABILITY.....There has been some rationalization of capacity by nitrobenzene/aniline producers over the past couple of years. With moderated demand growth, it is expected that further facilities will be idled or permanently closed. It is expected that nitrobenzene and aniline producers will attempt to gain better economics by plant improvements and modifications. DuPont is reportedly installing new nitration technology at both nitrobenzene/aniline plants which will reduce energy costs and consumption. The modified facilities are being readied for startup in early 1984.

PRODUCERS AND CAPACITIES–NITROBENZENE–MM LBS

PRODUCER	LOCATION	1983 CAPACITY
DuPont	Beaumont, TX	375
DuPont	Gibbstown, NJ	240
First Chemical Corp.	Pascagoula, MS	350
Mobay	New Martinsville, WV	60
Rubicon	Geismar, LA	400
	TOTAL	1425

Based on announced capacities and trade estimates. Capacity generally equates to aniline capabilities at the same location. Some capacities may be overstated. Although Uniroyal sold its share of Rubicon's isocyanates business to ICI, it continues as a joint venture partner in the nitrobenzene/aniline production unit at Geismar. At the end of 1982, American Cyanamid closed a plant at Willow Island, WV with a nitrobenzene capacity of about 75 million pounds per year. With about 85 MM lbs. of capacity already mothballed at Bound Brook, NJ, American Cyanamid thus effectively left the nitrobenzene and aniline markets. By the second quarter of 1983, Mobay had shut down about 90 million pounds of aniline capacity, equivalent to about 130 MM lbs. of nitrobenzene feed. Of the total of about 130 MM lbs. of aniline capacity at New Martinsville, only 40 MM (equivalent to about 60 MM lbs. of nitrobenzene) was left operating for use in making iron oxide pigments.

END USES.....Nitrobenzene, often referred to as nitrobenzol or oil of mirbane, is among the best known and one of the oldest derivatives of benzene. Nitrobenzene is probably the most important technical nitration product, except for wartime explosives like trinitrotoluene, tetryl picric acid, and cyclonite. Most nitrobenzene, over 95%, is used for aniline manufacture and is therefore made on a large scale by aniline producers only. Crude nitrobenzene may be used directly for aniline manufacture, whereas purified technical grade can be obtained by washing and distillation. For sales to the merchant market, nitrobenzene is available as technical grade, redistilled crystals, or a 97% concentration yellow oily liquid (oil of mirbane). Nitrobenzene is soluble in ethanol, ether, and benzene, but only very slightly soluble in water (0.2% at room temperature). While aniline is the principal derivative of nitrobenzene, it is also used as the raw material for benzidine, metanilic acid – as well as dinitrobenzene and dyes such as nigrosine and magenta. Nitrobenzene is also used as an industrial solvent and in consumer products. Redistilled as oil of mirbane, it has been used as an inexpensive perfume for soaps. The most significant merchant market outlet is the production of an analgesic by Mallinckrodt, Monsanto, and Penick.

Aniline can be produced commercially from nitrobenzene by reduction or hydrogenation. The dominant technology involves the hydrogenation of nitrobenzene. In the catalytic vapor phase hydrogenation process, nitrobenzene is vaporized in a stream of hydrogen and passed through a reactor bed of copper catalyst. In the liquid phase process, nitrobenzene is hydrogenated under pressure using a Raney nickel catalyst. Hydrogenation processes are relatively high-energy consumers. Obtaining sufficient quantities of economic iron filings is a limiting factor in the batch method of reducing nitrobenzene. Mobay currently operates a reduction unit to produce iron oxide as a co-product.

While aniline was initially important as an intermediate for dyestuffs, dyes and intermediates only account for about 5% of domestic demand today. Isocyanates and rubber chemicals are now the principal end uses for aniline. Methylene diphenyldiisocyanate and polymeric isocyanates are the largest and fastest growing outlet accounting for about 60% of aniline (and consequently nitrobenzene) production. Rubber chemical's share of the end use pattern has dropped from about 65% of aniline demand in the mid-1960's to somewhat less than 20% today. Rubber processing agents include vulcanization accelerators and activators, antioxidants, inhibitors, stabilizers, peptizers, and plasticizers.

In addition to major end uses, there are perhaps 200-300 other derivatives and products made commercially from aniline, used in the paper industry and in the preparation of surfactants, pesticides, herbicides, and many other areas. Aniline is used to make alkylanilines, diphenylamine, and sulfanilic acid.

Aniline is also made from phenol reacted with ammonia. The new plant of USS Chemicals, started up in 1982, has begun to alter the demand for nitrobenzene.

END USE PATTERN–1983 ESTIMATED

DERIVATIVE	PERCENT
Aniline	96
Other	4

MANUFACTURING.....Nitrobenzene is prepared by the direct nitration of benzene, using a nitric acid – sulfuric acid mixture. Since raw materials represent such a high percentage of the manufacturing cost, operating procedures are generally directed toward maximizing yields. While batch operations had been common, all large plants now use continuous processes. Continuous operations generally involve the use of small stainless steel nitrators with high-speed agitators and efficient cooling to speed the reaction. The reaction is exothermic and requires adequate cooling. In the process, benzene is charged to react with all of the nitric acid in the low nitric acid concentration mixed acid. The reaction mixture is subsequently run to a separator where the spent acid is drawn off. The spent acid is generally recovered for recycle. The crude nitrobenzene is drawn off and may be used directly for aniline manufacture. If a pure grade nitrobenzene is required, the crude material is washed and then distilled.

ENVIRONMENTAL ASPECTS.....Nitrobenzene is a highly-toxic chemical. Its toxicity consists primarily of methemoglobin formation in the blood, but it also affects the nervous system and liver. It is readily absorbed through the skin in dangerous amounts and may be fatal if swallowed or inhaled as vapor. Absorption in toxic quantities, as with aniline, is followed by cyanosis (blue discoloration of lips, nails, and skin). The generally allowable threshold limit value for nitrobenzene is 1 PPM (skin) on a time-weighted average basis.