METHYLENEDIANILINE 103

### 4. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

# **4.1 PRODUCTION**

4,4′-Methylenedianiline is produced by the condensation of formaldehyde with aniline in the presence of an acid catalyst. The reaction produces a mixture of di-, tri-, and poly-methyleneanilines. Aniline is removed from the reaction mixture by distillation. The percentage of 4,4′-methylenedianiline in the mixtures manufactured varies from producer to producer. 4,4′-Methylenedianiline can be isolated from the residual mixture by crystallization with a suitable solvent (IARC 1986; Merck 1989; Moore 1978). 4,4′-Methylenedianiline commercially available in bulk quantities contains approximately 96% 4,4′-methylenedianiline, 3% other isomeric amines, and traces of aniline (IARC 1986).

The quantity of 4,4′-methylenedianiline produced by six manufacturers was approximately 230 million pounds (104 million kg) in 1981 (CMA 1982). In 1982, approximately 90-180 million kg (200-400 million pounds) of 4,4′-methylenedianiline was produced in the United States by a total of seven manufacturers (NIEHS 1994; NIOSH 1986). According to data in Toxics Release Inventory (TRI), four companies produced 4,4′-methylenedianiline in the United States in 1994 for distribution and sale, as well as their own use, captively or otherwise (TR194 1996): Dow Chemicals, U.S.A., La Porte, Texas; an unidentified company in New Martinsville, West Virginia; Rubicon, Inc., Geismar, Louisiana; and Uniroyal Chemical Co., Inc., Naugatuck, Connecticut. Another report indicates three companies producing 4,4′-methylenedianiline in the United States (SRI 1994): Dow Chemicals, U.S.A., La Porte, Texas; Bayer Corporation, Polymers Division, New Martinsville, West Virginia; and Uniroyal Chemical Co., Inc., Naugatuck, Connecticut.

The data on production capacity or the amount of 4,4′-methylenedianiline produced in the United States in recent years are not available. Table 4-l lists the facilities in each state that manufacture or process 4,4′-methylenedianiline, the intended use, and the range of maximum amounts of 4,4′-methylenedianiline that are stored on site. The data listed in Table 4-l are derived from the Toxics Release Inventory (TRI94 1996). Only certain types of facilities were required to report; therefore, this is not an exhaustive list.

Table 4-1. Facilities That Manufacture or Process 4,4'-Methylenedianiline

Facility	Location a	Range of maximum amounts on site in pounds	Activities and uses
CIBA GEIGY CORP.	MC INTOSH, AL	100,000-999,999	As a reactant
A. O. SMITH CORP.	LITTLE ROCK, AR	10,000-99,999	As a reactant
A. O. SMITH CORP.	LITTLE ROCK, AR	1,000-9,999	As a reactant
NA	MAGNOLIA, AR	10,000-99,999	As a reactant
HEXCEL CORP.	CHATSWORTH, CA	10,000-99,999	As a formulation component
AIR PRODS. & CHEMICALS INC.	LOS ANGELES, CA	10,000-99,999	As a reactant
UNIROYAL CHEMICAL CO. INC.	СТ	100,000-999,999	Produce; For on-site use/processing; For sale/distribution
			As a formulation component
UOP	MC COOK, IL	10,000-99,999	As a reactant
ALLCO ACQUISITIONS	ELK GROVE VILLAGE, IL	10,000-99,999	
AIR PRODS, & CHEMICALS INC.	WICHITA, KS	1,000,000-9,999,999	As a reactant
A. O. SMITH CORP.	WICHITA, KS	10,000-99,999	As a reactant
BASF CORP.	GEISMAR, LA	100,000-999,999	Produce; For on-site use/processing; As a reactant
RUBICON INC.	GEISMAR, LA	1,000,000-9,999,999	Produce; For on-site use/processing; For sale/distributio
			As a reactant
NA	SAINT LOUIS, MO	100,000-999,999	As a reactant; As a formulation component
COOK COMPOSITES & POLYMERS CO.	NORTH KANSAS CITY, MO	1,000-9,999	As a reactant
UNIROYAL CHEMICAL CO. INC.	GASTONIA, NC	10,000-99,999	Import; For on-site use/processing; As a reactant; As a
			formulation component
COOKSON AMERICA	GRANITE FALLS, NC	1,000-9,999	As a reactant; As a formulation component; As a product component
AMOCO CORP.	PIEDMONT, SC	10,000-99,999	As a reactant
AMERON INC.	SPARTANBURG, SC	1,000-9,999	As a reactant; As a formulation component
DOW CHEMICAL CO.	LA PORTE, TX	1,000,000-9,999,999	Produce; For on-site use/processing; For sale/distribution
			As a reactant
NA	BAYTOWN, TX	1,000,000-9,999,999	Produce; For on-site use/processing; As a reactant
AMERON INC.	BURKBURNETT, TX	10,000-99,999	As a reactant; As a formulation component
HERCULES INC.	CLEARFIELD, UT	10,000-99,999	As a reactant
3M CO.	PRAIRIE DU CHIEN, WI	10,000-99,999	As a reactant
RPM INC.	GREEN BAY, WI	1,000-9,999	As a formulation component

Table 4-1. Facilities That Manufacture or Process 4,4'-Methylenedianiline (continued)

Facility	Location <sup>a</sup>	Range of maximum amounts on site in pounds	Activities and uses
NA	NEW MARTINSVILLE, WV	1,000,000-9,999,999	Produce; For on-site use/processing; For sale/distribution;
		·	As a reactant
BASF CORP.	HUNTINGTON, WV	1,000-9,999	Produce; For on-site use/processing; As a reactant

Source: TRI94 1996

<sup>a</sup> Post office state abbreviations used

NA = not available

# 4.2 IMPORT/EXPORT

The exports of 4,4'-methylenedianiline from the United States to other countries in 1989, 1990, 1991, 1992 and 1993 were 13.1 million kg (28.9 million pounds), 13.5 million kg (29.8 million pounds), 5.8 million kg (12.8 million pounds), 7.1 million kg (15.7 million pounds), and 4.5 million kg (9.9 million pounds), respectively (NTDB 1994). There was a marked decrease in amounts of 4,4'-methylenedianiline exported to other countries during the period 1990-1993. The imports of 4,4'-methylenedianiline from other countries to the United States in 1989, 1990, 1991, 1992, and 1993 were 1.5 million kg (3.3 million pounds), 1.3 million kg (2.9 million pounds), 1.1 million kg (2.4 million pounds), 0.9 million kg (2.0 million pounds), and 0.5 million kg (1.1 million pounds), respectively (NTDB 1994). These figures indicate a continual and gradual decrease in the amounts of 4,4'-methylenedianiline imported into the United States from other countries from 1989 to 1993.

# 4.3 USE

Over 90% of 4,4′-methylenedianiline produced in the United States is used captively for the production of 4,4′-methylenedianiline diisocyanate and other polymeric isocyanates (IARC 1986). These di- or poly-isocyanates are used in a variety of polymer and resin production, including polyurethane foam, isocyanate resins and elastomer (e.g., Spandex® fiber). Small amounts of 4,4′-methylenedianiline are used as an azo dye intermediate; as a chemical reagent for the determination of tungsten and sulfates; as a corrosion inhibitor; as an antioxidant and curative agent in rubber; as a raw material in the production of resins; and as an epoxy-resin hardening agent in adhesives, encapsulants, coatings, filament windings and binders (CMA 1982; IARC 1986; Lewis 1993; Tucker et al. 1993).

#### 4.4 DISPOSAL

Incineration is one of the feasible methods for disposal of wastes containing 4,4′-methylenedianiline. Gas-fired incinerators in which first-stage combustion takes place with a less than stoichiometric airfuel ratio, followed by a second-stage combustion with excess air, are suitable for disposal of 4,4′-methylenedianiline wastes (HSDB 1996). The temperature and the residence time inside the combustion zone of the incinerators should be such that they ensure complete destruction (>99.99%) of the compound (HSDB 1996).