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-I 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-I 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.

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| Location ^a | Range of maximum amounts on site in pounds | Activities and uses | |
|-----------------------|--|--|--|
| MC INTOSH, AL | 100,000-999,999 | As a reactant | |
| LITTLE ROCK, AR | 10,000-99,999 | As a reactant | |
| LITTLE ROCK, AR | 1,000-9,999 | As a reactant | |
| MAGNOLIA, AR | 10,000-99,999 | As a reactant | |
| CHATSWORTH, CA | 10,000-99,999 | As a formulation component | |
| LOS ANGELES, CA | 10,000-99,999 | As a reactant | |
| СТ | 100,000-999,999 | Produce; For on-site use/processing; For sale/distribution; | |
| | | As a formulation component | |
| MC COOK, IL | 10,000-99,999 | As a reactant | |
| ELK GROVE VILLAGE, IL | 10,000-99,999 | | |
| WICHITA, KS | 1,000,000-9,999,999 | As a reactant | |
| WICHITA, KS | 10,000-99,999 | As a reactant | |
| GEISMAR, LA | 100,000-999,999 | Produce; For on-site use/processing; As a reactant | |
| GEISMAR, LA | 1,000,000-9,999,999 | Produce; For on-site use/processing; For sale/distribution | |
| | | As a reactant | |
| SAINT LOUIS, MO | 100,000-999,999 | As a reactant; As a formulation component | |
| NORTH KANSAS CITY, MO | 1,000-9,999 | As a reactant | |
| GASTONIA, NC | 10,000-99,999 | Import; For on-site use/processing; As a reactant; As a | |
| | | formulation component | |
| GRANITE FALLS, NC | 1,000-9,999 | As a reactant; As a formulation component; As a product component | |
| PIEDMONT, SC | 10,000-99,999 | As a reactant | |
| SPARTANBURG, SC | 1,000-9,999 | As a reactant; As a formulation component | |
| LA PORTE, TX | 1,000,000-9,999,999 | Produce; For on-site use/processing; For sale/distributic | |
| | | As a reactant | |
| BAYTOWN, TX | 1,000,000-9,999,999 | Produce; For on-site use/processing; As a reactant | |
| BURKBURNETT, TX | 10,000-99,999 | As a reactant; As a formulation component | |
| CLEARFIELD, UT | 10,000-99,999 | As a reactant | |
| PRAIRIE DU CHIEN WI | 10 000-99 999 | As a reactant | |

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

| NA |
|-----|
| 200 |

Facility

NA

UOP

CIBA GEIGY CORP.

A. O. SMITH CORP. A. O. SMITH CORP.

HEXCEL CORP.

AIR PRODS. & CHEMICALS INC.

UNIROYAL CHEMICAL CO. INC.

AIR PRODS. & CHEMICALS INC.

ALLCO ACQUISITIONS

A. O. SMITH CORP. BASF CORP.

RUBICON INC.

COOK COMPOSITES & POLYMERS CO. UNIROYAL CHEMICAL CO. INC.

4

COOKSON AMERICA

AMOCO CORP. AMERON INC. DOW CHEMICAL CO.

NA AMERON INC. HERCULES INC. 3M CO. **RPM INC.**

BAYTOWN, TX BURKBURNETT, TX CLEARFIELD, UT PRAIRIE DU CHIEN, WI GREEN BAY, WI

10,000-99,999 1,000-9,999

As a reactant

As a formulation component

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

| acility Location ^a | maximum amounts on site in pounds | s Activities and uses |
|-------------------------------|--------------------------------------|---|
| A NEW MARTIN | ISVILLE, WV 1,000,000-9,999,99 | Produce; For on-site use/processing; For sale/distribution; |
| | | As a reactant |
| ASF CORP. HUNTINGTON | 1 , WV 1,000-9,999 | Produce; For on-site use/processing; As a reactant |
| | | As a reactant |

Source: TRI94 1996

^a Post office state abbreviations used

NA = not available

METHYLENEDIANILINE

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).