

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.1 PRODUCTION

Benzidine was first prepared in 1845 via the reduction of azobenzene with ammonium sulphide, followed by treatment of the hydrazobenzene with sulfuric acid and treatment with a strong base to release the free benzidine (IARC 1982a). Benzidine can be produced commercially by several methods. The most common is the reduction of nitrobenzene with zinc and sodium hydroxide (Budavari et al. 1996). It can also be produced by the electrolysis of nitrobenzene, followed by distillation, or by the nitration of diphenyl followed by reduction of the product with zinc dust in alkaline solution with subsequent distillation (Lewis 1993). In the production of benzidine-based dyes (dyes characterized as having a biphenyl diazo based linkage that could be derived from benzidine, 3,3'-dichlorobenzidine or a benzidine congener), the benzidine formed as the dihydrochloride salt would not be isolated, but would be reacted directly with so-called chromophore substances to form the dye (EPA 1986c). An estimated production of 500 pounds (227 kg) of benzidine is given for 1983 (EPA 1986c), though this may omit some captive production. In contrast, 10 million pounds (4,720 metric tons) were produced in the United States in 1972 (EPA 1976b).

Benzidine is no longer produced for commercial sale in the United States. In 1973, OSHA regulations effectively banned U.S. production of benzidine. Any benzidine production must be for captive consumption (in-house use), and it must be maintained in closed systems under stringent workplace controls (IARC 1982a). In 1993, the United States International Trade Commission reported that Direct Black 38, a benzidine-based dye, was produced domestically by one manufacturer, but the quantity was not disclosed (USITC 1994).

Although companies that manufacture or process benzidine are required to report maximum quantities stored on-site and quantities released to environmental media or disposed of off-site for the Toxics Release Inventory (TRI), no information has been reported on benzidine from 1987 to 1996. Recent changes have been incorporated into the TRI reporting status of hazardous waste incinerators and waste management companies, and the most recent data indicate that there are four facilities located in California, Illinois, Ohio, and Texas that released minor amounts of benzidine to the environment in 1999. While the absence of TRI data does not confirm that benzidine is not produced or used in the United States since only certain types of facilities are required to report, these TRI results are in keeping with a steadily declining trend in the levels of benzidine produced or used in the United States.

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Commensurate with these results, there are no references on United States-based benzidine production in the latest available edition of SRI's *Directory of Chemical Producers* (SRI 2000).

5.2 IMPORT/EXPORT

In 1980, imports of benzidine were estimated at 8,900 pounds (4.08 metric tons) (SRI 1988). Imports of Direct Black 38, the most widely produced benzidine-based dye, were 200,000 pounds (91 metric tons) in 1978, up sharply from 1976 and 1977; total benzidine-based dye imports in 1979 were 469,000 pounds (213 metric tons), up sharply over the decade (USITC 1986). In recent years, there have been no reported imports of benzidine itself due to concerns over its toxicity. Benzidine-based dyes may still be imported into the United States, although no quantitative data on the amount imported are available (Anonymous 1999; Pfaltz and Bauer 1999; Weber 1991). The benzidine-based dyes, Direct Black 38 and Direct Red 28, are imported into the United States and can be purchased commercially (Aldrich 1998; Anonymous 1999; Pfaltz and Bauer 1999).

5.3 USE

The predominant use of benzidine was for the manufacture of dyes, especially azo dyes in the leather, textile, and paper industries. The Color Index lists over 300 colors of benzidine-based dyes, some 18 of which were found to be commercially available in the United States (AATCC 1984; Gregory 1984). Eleven of these 18 dyes were domestically manufactured. It is unclear whether these dyes were manufactured from benzidine or benzidine congeners such as o-tolidine or o-dianisidine. Some of these dyes, especially direct browns, greens, and blacks, were available as consumer products in the 1970s (Jenkins 1978). Orzeck and Gregory (1981) listed 65 home dyes that contained benzidine or benzidine congeners. Access to such dyestuffs for home use is no longer available, just as remaining industrial uses must embody a stringently controlled captive consumption approach (IARC 1982a). Benzidine or related benzidine congeners may be found as minor impurities in a variety of azo dyes used in coloring prepared for food items.

Benzidine was once used in clinical laboratories for the detection of blood, but this application has been discontinued due to safety concerns and the availability of more specific methods. Other uses listed for benzidine include as a rubber compounding agent, for the manufacture of plastic films, to detect H₂O₂ in milk, for security printing, and for the determination of nicotine. Benzidine was also used in small quantities for the manufacture of organic chemicals and as a laboratory agent (Lawler 1977). While

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diaminobenzidine and related dyes derived from aromatic amines are still in common use as stains in microscopy and similar lab applications (Lunn and Sansone 1991), information is not available to quantify the levels of benzidine (likely as trace impurities) contained in such lab preparations.

5.4 DISPOSAL

Formerly, benzidine may have been released during production or processing, and also from its presence in dyes. Currently, regulations restricting the production and use of benzidine limit the quantity of material discharged. The EPA has listed benzidine as a "priority" chemical that can cause cancer in humans and is subject to rigid inspection and control. The amount of benzidine that can be allowed in waste transported to waste disposal sites is 0.1 ppm (EPA 1980b). Any material products, residues, or container liners containing or in contact with benzidine are considered toxic wastes according to the Resource Conservation and Recovery Act (RCRA). Rotary kiln or fluidized-bed incineration may be appropriate disposal methods for benzidine (HSDB 1999). As a minor impurity in other waste materials, benzidine may still be released in effluent waste water discharges by the dye industry. According to the TRI, benzidine was not transferred to landfills from 1987 to 1999 (TRI87 1989; TRI90 1992; TRI92 1994; TRI99 2001). However, the most recent TRI data indicates that waste containing benzidine has been burned at hazardous waste incinerators (TRI99 2001). It should be noted, however, that many types of commercial facilities are exempt from TRI reporting requirements.