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Research and Development

Status Assessment of Toxic Chemicals

Benzidine

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December 1979

STATUS ASSESSMENT OF TOXIC CHEMICALS:
BENZIDINE

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report contains a status assessment of the air emissions, water pollution, health effects, and environmental significance of polynuclear aromatic hydrocarbons. This study was conducted to provide a better understanding of the distribution and characteristics of this pollutant. Further information on this subject may be obtained from the Organic Chemicals and Products Branch, Industrial Pollution Control Division.

Status assessment reports are used by IERL-Ci to communicate the readily available information on selected substances to government, industry, and persons having specific needs and interests. These reports are based primarily on data from open literature sources, including government reports. They are indicative rather than exhaustive.

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ABSTRACT

Epidemiological investigations have clearly demonstrated that benzidine is carcinogenic in humans. Higher than average incidences of bladder cancer among workers in benzidine production facilities and processing facilities have been demonstrated, resulting in increased concern over liquid discharges containing benzidine.

In 1972, 4.72×10^3 metric tons of benzidine were produced in the United States by at least three manufacturers (Allied, GAF, and Fabricolor). Previously the largest producer, Allied phased out production in 1976. The primary method of manufacture of benzidine is reduction of nitrobenzene with zinc and sodium hydroxide; however, a variety of reducing agents are applicable.

Benzidine may enter the environment from benzidine production facilities, from downstream chemical processing, and from use of products containing benzidine or benzidine derivatives. Nitrous acid oxidation is the only wastewater treatment method that has been implemented at the plant scale and shown to be effective for the concentrated benzidine manufacturing wastes.

Data from industry indicate that average benzidine discharges from each of 300 user facilities amount to only 0.68 kg/year. If this can be confirmed, the environmental significance is minimal. In the work place, stringent standards already are in effect under OSHA.

Several areas of information need to be clarified such as the quantity of benzidine produced and consumed, locations of production facilities and consumption sites, and environmental discharge rates and behavior. This information should be obtained in order to devise a management plan for defining regulatory action.

This report was submitted in partial fulfillment of Contract 68-03-2550 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period November 1, 1977 to December 31, 1977. The work was completed as of January 20, 1978.

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CONVERSION FACTORS

To convert from	to	Multiply by
Degree Celsius (°C)	Degree Fahrenheit	$t_F^\circ = 1.8\ t_C^\circ + 32$
Kilogram (kg)	Pound-mass (pound-mass avoirdupois)	2.204
Kilometer^2 (km^2)	Mile^2	3.860×10^{-1}
Meter^3 (m^3)	Foot^3	3.531×10^{1}
Meter^3 (m^3)	Gallon (U.S. liquid)	2.642×10^{2}
Metric ton	Pound-mass	2.205×10^{3}
Pascal (Pa)	Torr (mm hg, 0°C)	7.501×10^{-3}

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
Kilo	k	10^3	1 kg = 1×10^3 grams
Milli	m	10^{-3}	1 mm = 1×10^{-3} meter

[a] Standard for Metric Practice. ANSI/ASTM Designation: E 380-76$^\varepsilon$, IEEE Std 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.

ACKNOWLEDGEMENT

This report was assembled for EPA by Radian Corporation, Austin, TX, and Monsanto Research Corporation, Dayton, OH. Mr. D. L. Becker served as EPA Project Officer, and Dr. C. E. Frank, EPA Consultant, was principal advisor and reviewer.

SECTION 1

INTRODUCTION

Epidemiological investigations have clearly demonstrated that benzidine is carcinogenic in humans. Higher than average incidences of bladder cancer among workers in benzidine production and processing facilities have been demonstrated. Recent research results suggest that some benzidine-derived azo dyes may be converted to benzidine in man or in certain environments. As a result, there is concern over liquid effluent discharges containing benzidine.

This report was prepared from available literature and includes information regarding benzidine chemical properties, producers, uses, and production process. Also included in this report is information concerning the environmental and health effects of benzidine, available pollution control technology, and current regulatory action.

SECTION 2

SUMMARY

Benzidine (p,p'-diaminobiphenyl), with the empirical formula $C_{12}H_{12}N_2$, is used in the manufacture of a wide variety of organic chemicals, as an intermediate for azo dyes, and as a rubber compounding agent. In 1972, 4.72×10^3 metric tons[a] of benzidine were produced in the United States by at least three manufacturers (Allied, GAF, and Fabricolor). Previously the largest producer, Allied phased out benzidine production in 1976. Table 1 highlights available information regarding benzidine.

TABLE 1. BENZIDINE

Emission source	Extent of problem: Emission quantity, kg/day	Extent of problem: County population, persons/km^2	Control technology	Current studies and regulatory action
Production facilities:	0.454	-[a]	-[a]	• OSHA work place standards
GAF Corporation	-[b]	89	Nitrous acid oxidation	• EPA proposed toxic effluent standard
Fabricolor	-[b]	913	-[b]	• Toxicological research by National Center for Toxicological Research
Benzidine-based dye manufacturers, ∿300 sites:	0.56[c]	-[a]	Biodegradation (bench-scale, secondary treatment only)	• EPA drinking water survey
E. I. Dupont	-[b]	345		• Possible inclusion under hazardous spill provisions of the Federal Water Pollution Control Act
Fabricolor	-[b]	913		• Mining Enforcement and Safety Administration proposed standard
J. S. Young	-[b]	987		• Designated a priority pollutant under Federal Water Pollution Control Act

[a]Not applicable.
[b]Not available.
[c]Total for all sites.

[a]1 metric ton = 10^6 grams; conversion factors and metric system prefixes are presented in the prefatory pages of this report.

Benzidine production depends on nitrobenzene, a relatively inexpensive raw material. The primary method of manufacture for this chemical is reduction of nitrobenzene with zinc and sodium hydroxide; however, a variety of reducing agents are applicable. The stepwise reduction may be carried through as a continuous operation, or it may be stopped at any stage for a change in reducing agent, depending upon process economics, equipment availability, quantity produced, plant location, and potential hazards inherent in the reaction.

Benzidine may enter the environment from benzidine production facilities, from downstream chemical processing, and from use of products containing benzidine or benzidine derivatives. Industry reports indicate that benzidine discharges at any production facility do not usually exceed 0.454 kg/day. Free benzidine is present in benzidine-derived azo dyes. According to industry, quality control specifications require that the level not exceed 20 ppm (parts per million), but the discharged benzidine concentration in practice is generally below 10 ppm. Assuming all free benzidine is discharged in the liquid effluent, an estimated total of 204.3 kg/yr is discharged from 300 user facility sites, corresponding to approximately 0.68 kg/yr-facility. If this can be confirmed, the environmental significance is minimal.

Benzidine and its salts are carcinogenic to humans, with the bladder being the site of tumor induction. Carcinogenic hazards to man may result from various types of exposure, including the presence of benzidine carcinogens in drinking water, recreational bodies of water, food processing waters, or fisheries.

Various potential wastewater treatment methods are available to benzidine and benzidine-based dye manufacturers. These include 1) oxidation with nitrous acid (for pretreatment only); 2) oxidation with ozone; 3) adsorption onto activated carbon; 4) adsorption onto polymeric adsorbent; 5) evaporation pond (no discharge); and 6) biodegradation (for secondary treatment only). Only the nitrous acid oxidation method has been implemented at the plant scale and shown to be effective for the concentrated benzidine manufacturing wastes.

As a result of observed inadequate housekeeping procedures at benzidine manufacturing sites, the Occupational Safety and Health Administration (OSHA) has required stringent workplace standards to reduce environmental discharges. Additional studies and regulatory actions are indicated in Table 1.

Based upon information presented in this report, the following items need to be considered in future studies:

- data should be obtained to determine the quantity of benzidine currently produced and consumed including dye manufacture.

- producers should be identified and locations of use determined.

- emission and effluent rates should be determined for production facilities and benzidine-based dye manufacture and other users.

- environmental behavior as well as environmental levels should be defined.

- information should be obtained to describe current industrial practice, commercial significance, and environmental significance.

SECTION 3

SOURCE DESCRIPTION

PHYSICAL AND CHEMICAL PROPERTIES

Benzidine (4,4'-diaminobiphenyl or *p,p*'-diaminobiphenyl) $C_{12}H_{12}N_2$, is used in the manufacture of a wide variety of organic chemicals, as an intermediate for azo dyes, and as a rubber compounding agent (1, 2). Benzidine is reported to be a mixture of three isotropic forms coexisting indefinitely at room temperature (1). Table 2 (3-7) summarizes data regarding the chemical properties of benzidine and its two standard formulations, sulfate and hydrochloride.

Benzidine emits highly toxic fumes when heated to its decomposition point. It has been classified as "dangerous" in the latest edition of Dangerous Properties of Industrial Materials (3). Benzidine is combustible and darkens upon exposure to air and

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(1) Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Vol. 3. John Wiley & Sons, Inc., New York, New York, 1967. pp. 408-414.

(2) Chemical Origins and Markets, Fifth Edition. G. M. Lawler, ed. Stanford Research Institute, Menlo Park, California, 1977. 118 pp.

(3) Sax, N. I. Dangerous Properties of Industrial Materials, Fourth Edition. Van Nostrand Reinhold Company, New York, New York, 1975. 1258 pp.

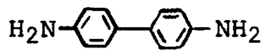
(4) Registry of Toxic Effects of Chemical Substances. H. E. Christensen, ed. U.S. Department of Health, Education, and Welfare, Rockville, Maryland, June 1976. 1245 pp.

(5) Condensed Chemical Dictionary, Eighth Edition. Van Nostrand Reinhold Company, New York, New York, 1971.

(6) Merck Index, Ninth Edition. M. Winholz, ed. Merck & Co., Inc., Rahway, New Jersey, 1976.

(7) Criteria Document: Benzidine. EPA-440/9-76-017 (PB 254 023), U.S. Environmental Protection Agency, Washington, D.C., June 1976. 65 pp.

TABLE 2. CHEMICAL PROPERTIES OF BENZIDINE AND ITS FORMULATIONS (3-7)

Property	Benzidine	Benzidine dihydro-chloride	Benzidine sulfate
Structure			
Crystalline form	Grayish-yellow, white, or reddish-gray crystalline powder		Crystalline powder
Melting point	127.5°C to 128.7°C (98.6 kPa)		
Boiling point	401.7°C		
Density	1.250 at 20°/4°C		
Solubility	1 g in 2,447 g water (12°C) 1 g in 107 g water (100°C) 1 g in 45 g ethyl ether 1 g in 13 g ethanol (28°C)	Soluble in water and alcohol	Very slightly soluble in water, dilute acids and alcohol

light; thus, storage in dark, sealed containers is recommended (6). Chemical reactions of benzidine and its derivatives are well documented in the literature (1).

PRODUCTION

Benzidine, also known as benzidine base or *p,p'*-diaminobiphenyl, is produced as a technical grade paste. It is also available in the hydrochloride form. The 1972 production of benzidine in the United States was 4.72×10^3 metric tons (8).

Eight possible manufacturers were identified, two of which now manufacture benzidine (GAF and Fabricolor). Benzidine manufacturers produce 2.04×10^4 metric tons/yr of azo dyes from benzidine (9). Allied, previously the largest producer, phased

(8) Scoring of Organic Air Pollutants. Chemistry, Production, and Toxicity of Selected Organic Chemicals. Mitre Corporation, McLean, Virginia, 1976.

(9) Keinath, T. M. Benzidine: Wastewater Treatment Technology. EPA-440/9-76-018 (PB 254 024). U.S. Environmental Protection Agency, Washington, D.C., June 1976. 132 pp.

out benzidine production in 1976. Benzidine base is available from Orlex Chemical Corporation; the hydrochloride form is available from Orlex and Conray Chemicals, Inc.; and the dihydrochloride form is supplied by American Drug and Chemical Company (10). City Chemical Corporation is a supplier of the sulfate form of benzidine (11).

PROCESS DESCRIPTION

Benzidine production depends on nitrobenzene, a relatively inexpensive raw material. The primary manufacturing method for this chemical is reduction of nitrobenzene with zinc and sodium hydroxide, as shown in Reaction 1 (1).

$$\underset{\text{Nitrobenzene}}{2C_6H_5NO_2} + 5Zn + 10NaOH \longrightarrow \underset{\text{Hydrazobenzene}}{C_6H_5NHNHC_6H_5} + 5Na_2ZnO_2 + 4H_2O \quad (1)$$

The resulting hydrazobenzene is then heated with mineral acid in a distillation step. The second step, shown in Reaction 2, results in a double semidine rearrangement (better known as the benzidine rearrangement) with the formation of benzidine and *o,p*'-diaminobiphenyl.

$$\underset{\text{Hydrazobenzene}}{C_6H_5NHNHC_6H_5} \xrightarrow{\text{Mineral acid}} \underset{\text{Benzidine}}{NH_2C_6H_4\text{-}C_6H_4NH_2} + \underset{\substack{o,p'\text{-diaminobiphenyl} \\ (3\text{-}15\%)}}{NH_2C_6H_4\text{-}C_6H_4NH_2} \quad (2)$$

The precipitated dihydrochloride and/or sulfate (depending on which mineral acid is used) is recovered by filtration. The benzidine salt may be used directly in the manufacture of azo dyes. Alternatively, it is converted to the free base by reaction with a weak base and purified by vacuum distillation.

Reaction 1 is allowed to proceed slowly at approximately 100°C. Control of the reaction, accomplished by the gradual addition of reactants, is necessary to avoid side reactions such as complete reduction to aniline. Diluents, such as naphtha, dichlorobenzene, and alcohol, are also used to minimize the chance of such side reactions (1).

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(10) Chemical Marketing Reporter, 1976-77 OPD Chemical Buyers Guide, Sixty-fourth Annual Index. Schnell Publishing Company, Inc., 1976.

(11) 1977 Directory of Chemical Producers. Stanford Research Institute, Menlo Park, California, 1977.

The stepwise reduction may be carried through as a continuous operation using the same reducing agent, or it may be stopped at any stage for a change in reducing agent. Reducing agents, in addition to zinc, include zinc amalgam, iron, electrolytic reduction and others such as noble metal or nickel catalysts in the presence of aqueous alkali. These modifications depend upon process economics, equipment availability, quantity produced, plant location, and potential hazards inherent in the reaction (1).

One modification of this production method is based on electrolysis of nitrobenzene, followed by distillation. A 90% yield of hydrazobenzene can be obtained by electrolysis of an alkaline emulsion of nitrobenzene using an iron cathode. This distillation step is performed in the presence of mineral acid to cause the benzidine rearrangement (1, 5).

Another production sequence involves nitration of diphenyl, followed by reduction of the product with zinc dust in alkaline solution and subsequent distillation (5).

USES

Benzidine is used considerably in analytical chemistry. It is employed in the detection and determination of a large number of inorganic ions and compounds such as cadmium, copper, manganese, chlorine, fluoride, cyanide, ferrocyanide, ferricyanide, phosphate, silica, sulfate, tungsten, hypohalites, permanganate, nitrate, nitrite, and phosphomolybdate. Benzidine has also been used in the determination of naphthalenesulfonic acids and detergents by the formation of an insoluble precipitate (1).

The major use of benzidine is as a starting material in the production of azo dyes and sulfur dyes. Over 250 dyes based on benzidine have been reported, and the more prominent ones manufactured in the United States in 1962 are those presented in Table 3 (1). More recent information indicates that benzidine is no longer used to such a great extent in the production of dyes (12); thus, further investigation is warranted in this area in order to determine the quantity of benzidine used in the production of dyes.

At least two manufacturers of benzidine, GAF and Fabricolor, produce 2.04 x 10^4 metric tons/yr of azo dyes from this intermediate. The dyes are used by approximately 300 major manufacturers

(12) Riegel's Handbook of Industrial Chemistry, 7th Edition. J. A. Kent, ed. Van Nostrand Reinhold Company, New York, New York, 1974.

TABLE 3. COMMERCIAL DYES DERIVED FROM BENZIDINE (1)

Colour Index name	Colour Index No.	Colour Index name	Colour Index No.
Mordant Yellow 36	14135	Direct Blue 6	22610
Pigment Red 39	21080	Direct Brown 1	30045
Direct Red 28	22120	Direct Brown 1A	30110
Direct Orange	22130	Direct Brown 154	30120
Direct Red 10	22145	Direct Brown 6	30140
Direct Red 13	22155	Direct Brown 85	30145
Direct Red 37	22240	Direct Black 38	30235
Direct Red 1	22310	Direct Black 4	30245
Direct Brown 2	22311	Direct Green 1	30280
Direct Orange 1	22370, 22375	Direct Green 6	30295
	22430	Direct Green 8	30315
Direct Violet 1	22570	Direct Brown 31	35660
Direct Blue 2	22590	Direct Brown 74	36300

of textiles, papers, and leather (13); however, no recent production figures are available to indicate the extent of benzidine usage in the various dye products.

Azo dyes are typically manufactured in small batches with the amine (benzidine) initially in acid in a well-stirred tub. The solution is cooled to 0°C to 5°C, and sodium nitrite is added until the diazotization is complete. The diazonium compound is added at a slow rate to a second tub containing a coupling compound (phenol, naphthol ether, or a compound with an active methylene group). As the coupling reaction proceeds, the dye precipitates. Upon completion of the coupling reaction, the tub is warmed with steam. The finished dye is recovered in filter presses and dried in tray dryers (12, 14).

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(13) Summary Characterizations of Selected Chemicals of Near-Term Interest. EPA-560/4-76-004 (PB 255 817), U.S. Environmental Protection Agency, Washington, D.C., April 1976. 50 pp.

(14) Steadman, T. R., et al. Industrial Process Profiles for Environmental Use, Chapter 7, Organic Dyes and Pigments Industry. EPA-600/2-77-023g, U.S. Environmental Protection Agency, 1977.

SECTION 4

ENVIRONMENTAL SIGNIFICANCE AND HEALTH EFFECTS

ENVIRONMENTAL SIGNIFICANCE

Benzidine may enter the environment from benzidine production facilities, from downstream chemical processing (most notably dye manufacture and application), and from use of products containing benzidine or benzidine derivatives.

The principal environmental concern at benzidine production facilities has been the quantity of benzidine discharged to municipal wastewater treatment plants. Discharge measurements to date, however, have only been made by the industry, and reported benzidine discharges at any facility usually do not exceed 0.454 kg/day. Benzidine is believed to be present in the sludge removed from industrial waste pretreatment plants, and the environmental adequacy of land disposal of these sludges is unknown. Industry data indicate that discharges from municipal wastewater treatment plants contain benzidine at a level lower than its limit of detection. Levels of benzidine exceeding 5 g/m^3 can inhibit anaerobic digestion wastewater treatment processes; concentrations above this level thus present a problem to treatment plants using this process plus a possible hazard to the receiving waters (13).

Free benzidine is present in the benzidine-derived azo dyes. Industry quality control specifications require that the discharged benzidine level not exceed 20 ppm, and in practice this level is usually below 10 ppm. Assuming all free benzidine is discharged in the liquid effluent, an estimated total of 204.3 kg/yr is discharged from 300 dye user facility sites, corresponding to approximately 0.68 kg/yr-facility (13).

In 1951, concentrations of benzidine in a chemical plant workroom atmosphere averaged 0.024 mg/m^3; however, no measurements for benzidine in ambient air have been reported (15).

The following programs are in progress to develop and evaluate analytical techniques for environmental monitoring of benzidine:

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(15) Documentation of the Threshold Limit Values, Third Edition. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1971.

Monitoring Method Development - Appropriate analytical methods for benzidine were to be selected by August 1976. Three EPA laboratories investigated reliability, detection limits, and feasibility of analytical methods. Initial evaluations were completed in June 1976, and the recommendations were to follow (personal communication with John Moran, Office of Research and Development, Washington, D.C.).

Field Monitoring - Monitoring activities will be considered when an appropriate method is available (personal communication with Vincent DeCarlo, Office of Toxic Substances, Washington, D.C.).

HEALTH EFFECTS

Although many chemicals have been shown to induce cancer in laboratory animals, only a few have been positively identified as human carcinogens. Benzidine and its salts, without question, are carcinogenic to humans (9), with the site of tumor induction being the bladder (7).

Carcinogenic hazards to man may result from various types of exposure, including the presence of carcinogens in drinking water, recreational water bodies, food processing waters, or fisheries. It is believed reasonable that the presence of benzidine in the aquatic environment poses a threat to man and the environment (9).

A high occurrence of bladder tumors in the dye industry has been established. In a 1949 study, 186 workmen were examined to follow the evolution of bladder lesions. The study indicated that benzidine and β-naphthylamine have the highest carcinogenic potential among the aromatic amines studied. A 1952 study investigated the incidence of bladder tumors in an English dyestuffs factory. Sixty-six cases of bladder tumor were reported. Of the 66 cases there were 30 (23 in the manufacturing section and 7 in the handling section) who were exposed to benzidine and who had never been exposed to β-naphthylamine (7).

A 1954 study involved workmen engaged in the manufacture and use of aniline, benzidine, and α- and β-naphthylamines in the British chemical industry. The data indicated that the incidence of bladder cancer among persons exposed to benzidine greatly exceeded that among the general population. The study also showed bladder cancer to be a fatal disease, only 20% of all cases having survived more than 10 years from the first detection of the disease (7).

In 1962, the incidence of urinary bladder tumors in workers exposed to α-naphthylamine, β-naphthylamine, and benzidine was studied to determine the average incubation period, the average survival time, and the incidence of malignant tumors other than those of the bladder. The population studied consisted of 366 male workers in a coal tar dye factory employed between 1912-1962. Of the 366 workers studied, 76 were exposed to benzidine alone. Bladder cancer developed in 17, or 21.3%, of these 76 workers. The induction of bladder cancer from benzidine had an average incubation period of 18.7 years, calculated from the first exposure to diagnosis of malignancy (7).

Following diagnosis of bladder malignancy in workers exposed to benzidine, the longest period of survival was 10 years, the shortest was less than a year. The mean survival time between diagnosis of cancer and death was approximately three years (7).

There was no evidence of any unusual incidence of malignancies other than those of the urinary bladder. Among the 366 men studied, there were 11 recorded malignant tumors other than cancer of the bladder (7).

Previous cases of bladder cancer have occurred among Allied Chemical Buffalo Dye Plant workers. In all cases these workers were exposed to early processes and operations. New manufacturing facilities, a catalytic reduction process, elimination of all base operations, and institution of a variety of process and administrative controls have drastically reduced exposure levels. No new cases have occurred among those workers whose only exposure has been to the latest process and equipment commissioned in 1955. The nature of the risk is such, however, that exposure must be maintained at the lowest practicable limit through the promulgation and enforcement of administrative, engineering, and processing controls, and industrial hygiene practices (7).

POPULATION AT RISK

Industries handling benzidine are 1) the manufacturers of benzidine, 2) the dye manufacturers who use benzidine as a starting material or intermediate, and 3) users of benzidine-based dyes (e.g., textile industry). Workers in these industries risk exposure. Because benzidine is widely used in clinical and forensic laboratories as a detection reagent, an additional segment of the population is potentially exposed through this end use. Also, benzidine is a contaminant in many disperse dyes. A large population may risk exposure to benzidine from use of products dyed in this manner (e.g. benzidine may enter the environment through wash water from cleaning these materials or through skin absorption). Table 4 lists some companies identified as possible producers and users of benzidine and benzidine-derived chemicals. It was not possible to list all users of benzidine-based dyes, and industry contact may be necessary to obtain a more precise list of producers. Since Congo Red reportedly constitutes a major use of benzidine, manufacturers of this product are listed as a category of possible benzidine exposure.

TABLE 4. COMPANIES AND LOCATIONS OF POTENTIAL BENZIDINE RISK AREAS

	Location/population			
Company	City	Population density, people/km^2	County	Population
Benzidine producers:				
GAF Corporation Chemical Products	Rensselaer, NY	89	Rensselaer	153,800
			Albany	288,700
			Schenectady	159,900
			Saratoga	140,700
			Total	743,100
Fabricolor Chemical Corp.	Paterson, NJ	913	Passiac	456,200
			Bergen	874,600
			Total	1,331,000
Manufacturers of Direct Red 28 (Congo Red, CI 22120):				
E. I. duPont de Nemours and Co., Inc.	Wilmington, DE	345	New Castle	395,000
			Salem Co., NJ	61,700
			Cecil Co., MD	56,300
			Total	513,000
Fabricolor Chemical Corp.	Paterson, NJ	(see above)		
J. S. Young Co., Young Aniline Works, Inc., Subsidiary	Baltimore, MD	987	5 county total	2,140,400

SECTION 5

CONTROL TECHNOLOGY

Various potential wastewater treatment methods are available to benzidine manufacturers and benzidine-based dye manufacturers including: 1) oxidation with nitrous acid (for pretreatment only); 2) oxidation with ozone; 3) adsorption onto activated carbon; 4) adsorption onto polymeric adsorbent; 5) no discharge (evaporation pond); and 6) biodegradation (for secondary treatment only). A comparison of these potential treatment methods is presented in Table 5 (9).

Of the potential treatment technologies that are available for the removal of benzidine from process wastewaters, only the nitrous acid oxidation method has been implemented at the plant scale (GAF Corporation) and shown to be effective for the concentrated benzidine manufacturing wastes. It is to be noted that this process was employed only for the treatment of benzidine manufacturing wastewaters. Residual levels of benzidine in the nitrous acid treated effluent usually were found to be less than 10 ppb (parts per billion) (9).

Benzidine-based dye manufacturing wastewaters can be treated relatively inexpensively by the patented biodegradation process (see Table 5). Due to biological toxicity, however, this process probably cannot be employed for the direct treatment of benzidine manufacture wastewaters prior to a pretreatment step such as the nitrous acid oxidation process (9).

Fabricolor, Inc. and GAF Corporation discharge their wastewaters to municipal biological wastewater treatment systems. The final product wastewaters, after biological treatment, should show no detectable benzidine.

No other benzidine treatment technologies have been implemented at the plant scale; in fact, none have been evaluated beyond the bench scale. Consequently, plant-scale process efficiencies and costs have not been established for any of the processes considered other than the nitrous acid oxidation process (9).

The ranges for actual or projected process costs given in Table 5 are broad because benzidine production methods vary considerably with respect to the quantity of process wastewaters generated.

TABLE 5. COMPARISON OF POTENTIAL TREATMENT METHODS (9)

Type of treatment	Level of development and/or application	Effectiveness	Waste treatment cost, ¢/kg benzidine produced
Benzidine manufacturing wastewaters:			
Oxidation with nitrous acid (pretreatment only)	Full scale	10 ppb	4.4 - 26.4 (actual)
Oxidation with ozone	Bench scale (preliminary only)	1 - 10 ppb (projected)	220 - 1100 (projected)
Adsorption onto activated carbon	Bench scale (preliminary only)	1 - 10 ppb (projected)	2.2 - 22 (projected)
Adsorption onto polymeric adsorbent	None	1 - 10 ppb (projected)	Unknown
No discharge/evaporation	None	N/A[a]	55 (projected)
Benzidine-based dye manufacturing wastewaters:			
Biodegradation (secondary treatment only)	Bench scale	Unknown	0.04 (projected)[b]

[a]Includes pretreated benzidine manufacturing wastes.

[b]For treatment of dye mother liquors (basis 0.05 kg/m^3).

If the wastewater volumes produced are high, then the associated costs are also respectively higher (9).

Substitution of less toxic compounds is another possible control method; however, it is estimated that substitute compounds are three to five times as expensive as benzidine, and substitutes for some derivatives (especially halogenated benzidine compounds) may not be available.

SECTION 6

REGULATORY ACTION

As a result of inadequate housekeeping procedures at benzidine manufacturing sites, the Occupational Safety and Health Administration (OSHA) has required stringent workplace standards.

In December 1973, the U.S. Environmental Protection Agency (EPA) proposed a toxic pollutant effluent standard, and the agency is planning to resubmit a similar standard and a pretreatment requirement. The results of the current animal experiments at the National Center for Toxicological Research, including chronic toxicity, carcinogenicity, and metabolic behavior, should be available in the near future. Benzidine is being examined in the expanded EPA drinking water survey and is being studied for possible inclusion under the hazardous spill provisions of the Federal Water Pollution Control Act (14). The Mining Enforcement and Safety Administration has proposed a mandatory standard that would require storage and use of 16 toxic chemicals (including benzidine) only under strict laboratory conditions approved by a nationally recognized agency (16). Benzidine is also designated a priority pollutant under the Federal Water Pollution Control Act.

(16) Toxic Material News, 4(26):163, 1977.

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16. ABSTRACT

The properties, sources, production processes, and uses of benzidine are reviewed in the report. Benzidine is a proven human carcinogen, and its widespread use as a dye intermediate has led to the high recurrence of bladder cancer in that industry. OSHA has imposed stringent workplace standards. Further information is needed on benzidine production and use to better define necessary regulatory action.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Biphenyl, Diphenyl, Aromatic hydrocarbons, Aromatic polycyclic Hydrocarbons, Hydrocarbons, polyphenyl compounds, Polyphenyl hydrocarbons, unsaturated hydrocarbons	Benzidine, Dyes, Rubber	68A 68D 68G

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