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RESIDUAL BENZIDINE IN IMPORTED AND DOMESTIC BENZIDINE DYES

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SUMMARY

Randomly selected imported and domestic dyes, derived from the carcinogenic intermediate, benzidine, were analyzed for unreacted benzidine amine and its salts. The imported dyes were found to contain slightly greater amounts of benzidine than those dyes produced in the United States but the difference was not statistically significant. Possible dye impurities present during the manufacture and use of all synthetic organic dyes should be considered when evaluating their hazard potential.

INTRODUCTION

Dyes utilizing benzidine as a base have been widely used in the leather, paper, and textile industries as well as by artists and craftsmen. Concern about the concentration of residual benzidine in the finished dye is due to the general recognition of benzidine and its salts as human carcinogens. Occupational exposure to them has been established as a cause of cancer of the bladder [1]. Recent increases in the importation of benzidine-based dyes, accompanying decreasing domestic production, is of concern especially in view of suspicion that levels of residual benzidine in imported dyes may be far higher than in the domestic products they replace [2].

Imports of benzidine dyes have increased substantially during recent years (Table I) [3, 4]. On the other hand, the quantity of domestically produced benzidine-derived dyes in 1973 was almost 12 million pounds [5] and decreased to about 3.5 million pounds by 1978 [6]. Intertwined in these data are complex issues including not only the minimization of occupational exposure to demonstrated human carcinogens in the United States, but also the ethics of even unintentional exportation of hazardous processes to less developed countries, where the contamination of the

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TABLE I
IMPORTS OF BENZIDINE-DERIVED DYES INTO THE U.S.

Year	Pounds[a]
1973	53537
1974	22730
1975	25748
1976	149338
1977	76351
1978	266915
1979	462421

[a]Reported imports by the U.S. International Trade Commission usually comprise 85–87% of all imported dyes for that year. In addition, during 1979, 38.7% of the reported direct dyes were not specified with a common identifying name, thus some of these dyes may also have been derived from benzidine.

environment and preservation of workers' health may be of lesser concern [7]. In the present situation, poorer quality control during foreign dye manufacture also may be resulting in the importation and use of more highly contaminated benzidine-based dyes in this country.

METHODS

The National Institute for Occupational Safety and Health (NIOSH), in cooperation with the United States Customs Service, has analyzed random samples of benzidine-based dyes recently imported into the United States. A representative portion of each imported dye was carefully extracted to retain the free benzidine (as both the base and salt) in the sample, and a sensitive technique of HPLC was used to detect the trace benzidine [8].

RESULTS

The data from 33 samples received from 8 countries (Table II) showed considerable variation in free benzidine, ranging from less than 1 ppm to 1254 ppm, with an average of 64 ppm, a medium of 6, and a standard deviation of 219. From these limited data, there appears to be no correlation between the residual benzidine found in the imported dyes and the exporting country or color.

During the same period of time, samples of benzidine-derived dyes produced by three United States companies were collected during industrial hygiene surveys of dye manufacturers and dye-using facilities.

For 26 randomly chosen domestic dyes, the free benzidine is seen to range from 1 to 270 ppm (25 dyes contained 20 ppm or less) with an average of 16 ppm, a median of 3.5, and a standard deviation of 52 (Table III). Although a statistical comparison using the nonparametric Wilcoxon Rank Sum Test does not indicate an overall

TABLE II
FREE BENZIDINE IN RECENTLY IMPORTED DIRECT DYES TO THE U.S.

Benzidine dye	Exporting country	Free benzidine ppm (w/w)
Direct Black 38	Egypt	53
Direct Black 38	Egypt	1,254
Direct Black 38	France	10
Direct Black 38	Holland	2
Direct Black 38	India	9
Direct Black 38	Poland	38
Direct Black 38	Poland	40
Direct Blue 2	Belgium	8
Direct Blue 2	Belgium	87.4
Direct Blue 2	Holland	24
Direct Blue 2	India	7
Direct Blue 2	Poland	Less than 1
Direct Blue 2	Poland	1
Direct Blue 2	Poland	2
Direct Blue 2	Romania	8
Direct Blue 6	Belgium	6.6
Direct Blue 6	India	10
Direct Brown 1/154	Poland	1
Direct Brown	Poland	1
Direct Brown 95	India	47.4
Direct Green 1	Holland	70
Direct Green 1	Poland	3
Direct Orange	India	143
Direct Red 1	Belgium	224
Direct Red 1	Poland	3
Direct Red 28	Belgium	2
Direct Red 28	India	6
Direct Red 28	Korea	Less Than 1
Direct Red 28	Poland	2
Direct Red 28	Poland	5
Direct Red 28	Poland	7
Direct Red 28	Romania	2
Direct Red 3	Holland	1

TABLE III
FREE BENZIDINE IN DIRECT DOMESTIC DYES

Benzidine dye	Manufacturer	Free benzidine ppm (w/w)
Direct Black 38	A	20
Direct Black 38	B	13
Direct Black 38	B	4
Direct Black 38	A	2
Direct Black 38	B	2
Direct Blue 2	A	1
Direct Blue 6	A	12
Direct Blue 6	B	14
Direct Blue 6	C	1
Direct Brown 2	A	1
Direct Brown 31	A	10
Direct Brown 31	A	3
Direct Brown 95	A	270
Direct Brown 95	A	19
Direct Brown 95	B	2
Direct Brown 154	A	15
Direct Brown 154	A	4
Direct Green 1	A	12
Direct Green 1	A	1
Direct Green 6	A	3
Direct Green 6	C	1
Direct Green 74	A	4
Direct Red 28	A	2
Direct Red 28	B	1

significant difference between the imported and domestically produced dyes, the imports in this sample do appear to contain more residual benzidine than their domestic counterparts.

DISCUSSION

The presence of carcinogenic aromatic amines would potentiate any health risk

during exposure to synthetic organic dyes if skin contact or volatilization of the unreacted amine during dyeing and heat processing were allowed to occur. It is important that these data support other reports that indicate synthetic organic dyes, as a whole, may often contain unintended impurities, some of which might present a carcinogenic hazard. Such carcinogenic impurities in dyes as the potent carcinogens, 4-aminobiphenyl and 2-napthylamine, have also been found [9–13].

The source of the free benzidine in these imported and domestically produced benzidine-based dyes was not determined. Free benzidine may have resulted from incomplete dye synthesis or through the breakdown of the dye after manufacture, since it is known that benzidine-based dyes are sensitive to temperature and light [14, 15]. Incomplete dye synthesis is probably the most likely source of the range of residual benzidine found, since at least one dye manufacturer was able to almost eliminate it at the initial stages of manufacture [16]. Dyestuff purification, however, appears to be the exception rather than the norm considering the range of residual benzidine found during this investigation.

This is the first instance we know where residual benzidine concentrations have been reported for a diverse number of these dyes obtained from a variety of sources. As a result of these data and a comprehensive review of the hazards of occupational exposure to benzidine-based dyes (including carcinogenic potential and metabolic conversion to benzidine in man), NIOSH has recently recommended that the production and use of all benzidine-based dyes be discontinued [17]. Substitution of noncarcinogenic dyes for those that are benzidine-based is advised. However, because few other dyes have been adequately tested for chronic toxicity, carcinogenicity, metabolism, or at least the presence of hazardous impurities, it would also be prudent to minimize worker exposure to these other dyes as well, until appropriate testing can be performed.

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