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# Exposure Assessment of 3,3'-Dichlorobenzidine (DCB) at Two Chemical Plants

Matthew A. London,<sup>A</sup> James M. Boiano<sup>B</sup> and Steven A. Lee<sup>B</sup>

<sup>A</sup>New York State Department of Health, Bureau of Occupational Health, 2 University Place, Albany, New York 12203;

<sup>B</sup>Hazard Evaluations and Technical Assistance Branch, National Institute for Occupational Safety and Health, 4676 Columbia Parkway, Cincinnati, Ohio 45226

3,3'-Dichlorobenzidine (DCB), an analogue of benzidine, has been an Occupational Safety and Health Administration (OSHA)-regulated carcinogen since 1974. This article presents a limited case study evaluating worker exposure to DCB at two pigment manufacturing plants. In each plant, exposure to DCB was estimated by personal breathing-zone (PBZ) and general area (GA) air samples, by skin patch and surface wipe samples, and by analysis of urine collected before and after the DCB-charging operation.

Plant A performs the DCB-charging operation in a dedicated 12-ft × 10-ft enclosed room. Two workers perform the operation, each wearing full protective clothing and an air-supplied hood. After decontaminating the work area with a sodium hypochlorite bleach solution, the workers enter a "dirty" change room to undress, and then shower and change into clean work clothes in a "clean" change room. The levels of DCB found averaged 0.45 µg/m<sup>3</sup>, PBZ; 0.18 µg/m<sup>3</sup>, GA; and 0.04 µg/cm<sup>2</sup>, skin. Detectable levels of urinary DCB, averaging 10.5 µg/L or 5µg/g creatinine, were found in four of five post-charging urine samples from both workers.

Plant B performs the DCB-charging in an open area, bounded only by a suspended chain with a warning sign. The charging port is exhausted locally. One worker performs the operation, wearing a half-facepiece respirator with high efficiency particulate filter, protective gloves, and foot covers, but no protective coveralls. None of the DCB samples exceeded the limit of detection (LOD). These limits ranged from 0.03–1.7 µg/m<sup>3</sup>, PBZ; 0.02–0.09 µg/m<sup>3</sup>, GA; and 0.02 µg/cm<sup>2</sup>, skin. No urinary DCB was detected either (LOD = 10 µg/L). Because a limited number of air samples were collected and because many of the air samples were below the analytical limits of detection, statistical comparison of the environmental and biological data between the two plants was impractical. Nevertheless, the data suggest that DCB exposure is higher in Plant A where the level of protection afforded workers was considerably higher. These results were initially surprising. However, while Plant A uses approximately 1600 pounds of DCB in a drum charging operation which takes 30–45 minutes, Plant B uses only 250 pounds of DCB in a 5- to 15-minute charging operation. Other deficiencies existed in Plant A which may also explain the results. London, M.A.; Boiano, J.M.; Lee,

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## Background

3,3'-Dichlorobenzidine, or DCB, is an analogue of benzidine, a chemical which has been linked to bladder cancer in humans.<sup>(1,2)</sup> Clear evidence that DCB causes cancer in humans has not been found; however, DCB has exhibited carcinogenicity in animals.<sup>(3)</sup>

Pliss<sup>(4)</sup> observed a high incidence of adenomas and carcinomas of the zymbal gland and other organs, including two tumors of the bladder, in 12 of 50 rats fed 10–20 mg DCB six times per week for a year. He also found liver tumors in mice exposed to DCB. In a study by Stula *et al.*<sup>(5)</sup> of 44 male rats fed 1000 ppm DCB for 12 months, 9 developed leukemia and 8 developed zymbal gland tumors; mammary gland tumors were found in rats of both sexes. Sellakumar *et al.*<sup>(6)</sup> fed hamsters 0.3 percent DCB in the diet and produced transitional cell carcinomas of the bladder and some liver cell tumors.

On the basis of the available evidence, OSHA began regulating DCB as a carcinogen in 1974.<sup>(7)</sup> The standard (29 CFR 1910.1007) specifies the requirements for engineering controls, decontamination, personal protective equipment, hygiene facilities and practices, employee education, posting of signs, medical surveillance, and recordkeeping concerning exposure to DCB.

The National Institute for Occupational Safety and Health (NIOSH)<sup>(8)</sup> and the American Conference of Governmental Industrial Hygienists (ACGIH)<sup>(9)</sup> consider DCB as a suspect human carcinogen. NIOSH policy regarding carcinogens is to minimize exposures to the lowest feasible level; it assumes that there probably is no safe level of exposure to carcinogens for elimination of all cancer risk.

This article discusses investigations conducted at two chemical plants that employ DCB in the production of organic pigments.<sup>(10,11)</sup> These evaluations were in response to separate requests for a Health Hazard Evaluation from the Health and Safety Department of the International Chemical Workers Union.

## Process Descriptions

The chemical process is similar at each plant, with the DCB used in the production of organic pigment. The DCB is purchased from suppliers as the dihydrochloride salt in sealed fiber drums. It contains about 30 percent water as a means of minimizing dust generation during manual drum unloading.

Plant A performs the DCB-charging operation once every other shift in a dedicated 12-ft × 10-ft enclosed room. The charging operation lasts 30 to 45 minutes and utilizes approximately 1600 lbs of DCB. Two workers perform the operation, each wearing Tyvek® coveralls, an air-supplied hood, polyethylene foot covers, nitrile rubber gloves, and safety glasses. After decontaminating the work area with a sodium hypochlorite bleach solution, the workers shower off their protective garb, enter a "dirty" change room to undress, and then shower and change into clean work clothes in a "clean" change room.

Plant B performs the DCB-charging once per shift in an open area, bounded only by a suspended chain with a warning sign. The charging operation lasts 5 to 15 minutes and utilizes approximately 250 lbs of DCB. The DCB vessel is exhausted so that the charging port acts as a local exhaust hood with an average face velocity of 120 feet per minute during charging. One worker performs the operation, wearing a long-sleeve cotton shirt, Survivair® half-facepiece respirator with high efficiency particulate filter, nitrile rubber gloves, and polyethylene foot covers. After completing the charging operation, the operator removes his protective equipment at the charging site and then showers in the common locker room.

## Methods

Similar study protocols were used for each plant. Exposure to DCB was assessed by personal breathing-zone (PBZ) and general area air samples, by skin patch samples, and by surface wipe samples. All air samples were collected at least for the duration of the charging operation on 37-mm binderless glass fiber filters (Gelman Type A/E) connected via flexible tubing to personal sampling pumps calibrated at 3 L/min. Sampling durations for Plant A samples ranged from 30–67 minutes, while those from Plant B ranged from 5–402 minutes. Pumps were calibrated before and after each use with a portable mass flow meter. Skin patch samples were collected by taping gauze patches (25 cm<sup>2</sup>) to the ventral surface of the workers forearm underneath the protective clothing.<sup>(12)</sup> The surface wipe samples were collected on Whatman filter paper moistened with methanol. All of these environmental samples were desorbed in methanol; the resulting solutions were sonicated, filtered, and analyzed via high-pressure liquid chromatography (HPLC) according to NIOSH Method P&CAM

246<sup>(13)</sup> with the following modifications:

Column:	Supelco Supelcosil C8; 250 × 4.6 μm
Mobile phase:	60/40 methanol/acetate buffer
Flow:	0.9 ml/min, isocratic
Detector:	amperometric, +0.8 volts at 5 nanoamperes full scale

Several blind quality assurance samples were prepared by spiking glass fiber filters with known amounts of DCB. These samples were analyzed with the field samples. Average recovery for these samples was 109 percent.

Absorbed dose for each worker was estimated as well. DCB, which is largely unmetabolized in the body,<sup>(14)</sup> was measured as urinary DCB according to NIOSH Method 8306.<sup>(15)</sup> Urine was collected before the first work shift of the week, providing a baseline measure of DCB. Samples were subsequently collected on each day of charging from the end of the charging operation until the end of that work shift. If a worker provided more than one urine sample on a given day, those samples were analyzed separately. Urinary DCB levels were standardized by reporting the results in μg/g creatinine, in addition to μg/L.

In both plants, sampling took place for two days in 1984. In plant A, however, after finding measurable levels of DCB, the plant replaced the two-piece full-body outfit with a one-piece, supplied-air, disposable Tyvek® total enclosure suit. NIOSH investigators repeated the environmental and biological monitoring for two days in 1985.

## Results

In Plant A, the PBZ samples in 1984 for two workers had a mean DCB level of 0.45 μg/m<sup>3</sup>, four area samples averaged 0.18 μg/m<sup>3</sup>, and eight skin patch samples averaged 0.04 μg/cm<sup>2</sup>. Twenty-six wipe samples were taken from locations including inside the respiratory air hood, outside the clean and dirty change rooms, and the rim of a used, decontaminated DCB drum. It was the latter location which provided the highest level, 28 μg DCB/cm<sup>2</sup> (Table I).

In 1985, all PBZ samples taken at Plant A were below the limit of detection for DCB, two of the three area samples were below the limit of detection, and eight skin patch samples averaged 0.02 μg/cm<sup>2</sup>. Two were below the limit of detection. Twenty-nine wipe samples were taken from locations similar, but not identical, to 1984. The highest concentration, 24 μg DCB/cm<sup>2</sup>, was obtained from the spatula blade used in the charging operation (Table I).

In Plant B, both PBZ samples taken in 1984 were below the limit of detection, as were all six area air samples and both skin patch samples. Nine surface wipe samples were taken from lo-

TABLE I. DCB Environmental Sampling Results

Sample Type (Units)	PLANT A						PLANT B		
	1984			1985			1984		
	N	Mean <sup>a</sup>	(range)	N	Mean <sup>a</sup>	(range)	N	Mean <sup>a</sup>	(range)
PBZ (μg/m <sup>3</sup> )	4	0.45	(0.34–0.60)	4	0.13	(ND: 0.20–0.27) <sup>b</sup>	2	0.43	(ND: 0.03, 1.7) <sup>b</sup>
GA (μg/m <sup>3</sup> )	4	0.18	(ND–0.27)	3	0.11	(ND–0.21)	6	0.02	(ND: 0.02–0.09) <sup>b</sup>
Skin (μg/cm <sup>2</sup> )	8	0.04	(ND–0.15)	8	0.02	(ND–0.05)	2	0.01	(ND: 0.02) <sup>c</sup>
Wipe (μg/cm <sup>2</sup> )	26	—	(ND–28)	29	—	(ND–24)	9	—	(ND–1.4)

<sup>a</sup>Means were calculated using half of the environmental limit of detection (ELOD) for samples which are nondetectable (ND). The ELOD was calculated by dividing the laboratory limit of detection (LOD), in μg, by the sample air volume, in m<sup>3</sup>. Means are not reported for the surface wipe samples.

<sup>b</sup>The ELOD range is reported, since every sample was ND.

<sup>c</sup>The LOD is reported and is the same for both ND samples.

**TABLE II. Urinary DCB Results ( $\mu\text{g}$  DCB/g creatinine)**

Worker	Plant A		Plant B
	1984	1985	1984
A1—Day 1 pre-shift	ND	ND	
Day 1 during shift	4 (11) <sup>A</sup>	ND	
Day 1 post-shift	ND	ND	
Day 2 post-shift	4 (10)	ND	
A2—Day 1 pre-shift	ND		
Day 1 post-shift	8 (11)		
Day 2 post-shift	5 (10)		
A3—Day 1 pre-shift		ND	
Day 1 during shift		ND	
Day 2 during shift		ND	
B1—Day 1 pre-shift			ND
Day 1 during shift			ND
Day 1 post-shift			ND
Day 2 during shift			ND
Day 2 post-shift			ND

A: the values in parenthesis represent the urinary DCB concentration in  $\mu\text{g}/\text{L}$ .  
 ND: nondetectable levels; less than 10  $\mu\text{g}/\text{L}$  of urine, the analytical limit of detection.

cations including inside the locker room, from the handle of a shovel used in the process, and the top of a used, decontaminated DCB drum. The shovel handle provided the sample with the highest DCB concentration, 1.4  $\mu\text{g}/\text{cm}^2$  (Table I).

Detectable levels of urinary DCB, averaging 10.5  $\mu\text{g}/\text{L}$  or 5  $\mu\text{g}/\text{g}$  creatinine, were found in a total of four of five post-charging urine samples from both workers in Plant A in 1984. In 1985, two workers were also sampled, one of whom was called Worker A1 in 1984. None of the samples had detectable urinary DCB (Table II).

In Plant B, only one worker performed the DCB-charging operation. None of his urine samples had detectable DCB (Table II).

## Discussion and Conclusions

This article presents a limited case study of worker exposure to DCB at two pigment manufacturing plants. A fairly small number of environmental and biological samples were collected, many of which were nondetectable, thus precluding meaningful statistical comparison of data between the two plants. For each air sample taken, the level reported represents the average concentration for the time period of that particular sample. For the longer samples, opportunity for direct exposure (i.e., during the charging operation) existed for only a small fraction of the time during which the sample was taken. This shortcoming, which makes interpretation of the air sampling results more problematic, pertains to both the PBZ and the general area samples. Nevertheless, the sampling results show that the exposures in Plant A were potentially higher than in Plant B. This was initially surprising given the apparent difference in the levels of protection offered in the two plants. However, it is important to note that Plant A uses approximately 1600 pounds of DCB in an operation that takes 30–45 minutes, while Plant B uses approximately 250 pounds of DCB in a 5–15 minute operation. Additionally, the level of protection provided at Plant A appears to have been compromised by a number of factors. The two-piece, full-body suit employed in 1984 allowed for the possibility that contaminants could pass between the shroud and the suit. In fact, workers reported occasionally smelling the DCB while performing the operation. This was rectified by switching to the one-piece, supplied-air, disposable suit. An added benefit of this switch

was that it eliminated the possibility that the reusable suit was not being thoroughly decontaminated. Finally, a passive air vent was found to exist in the wall between the charge room and the dirty change room, possibly contaminating all surfaces of the change room.

## Recommendations

In both plants described here, the following recommendations were made regarding control of exposure and medical monitoring of workers:

- Based upon the presence of DCB outside the charging area in Plant A, it was recommended that the charge room be under negative pressure.
- Separate shower and locker room facilities were recommended for DCB workers in Plant B. Given that none of the personal breathing zone, skin, or urinary samples showed detectable levels, other recommendations regarding engineering controls and personal protective equipment were conditional upon increased use of DCB.
- Based upon the wipe samples, recommendations to improve decontamination procedures were made at both plants.
- Plant A, as a result of our initial survey, changed to the one-piece Tyvek total enclosure suit.
- Both plants were encouraged to educate their workers more fully about DCB and possible routes of exposure, and to involve them in suggesting improvements in work practices.
- Both plants were urged to monitor periodically for urinary DCB as a means of estimating absorbed dose.
- Both plants currently perform urine cytology screening for current employees who are potentially exposed to DCB. In neither plant is this screening offered to workers who retire or otherwise terminate their employment. Given the 10- to 40-year latency period of bladder cancer, it was recommended that some mechanism be developed to offer this screening to former workers as well as current workers.

## Acknowledgments

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## Disclaimer

Mention of any manufacturer or product name does not constitute endorsement by NIOSH.

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