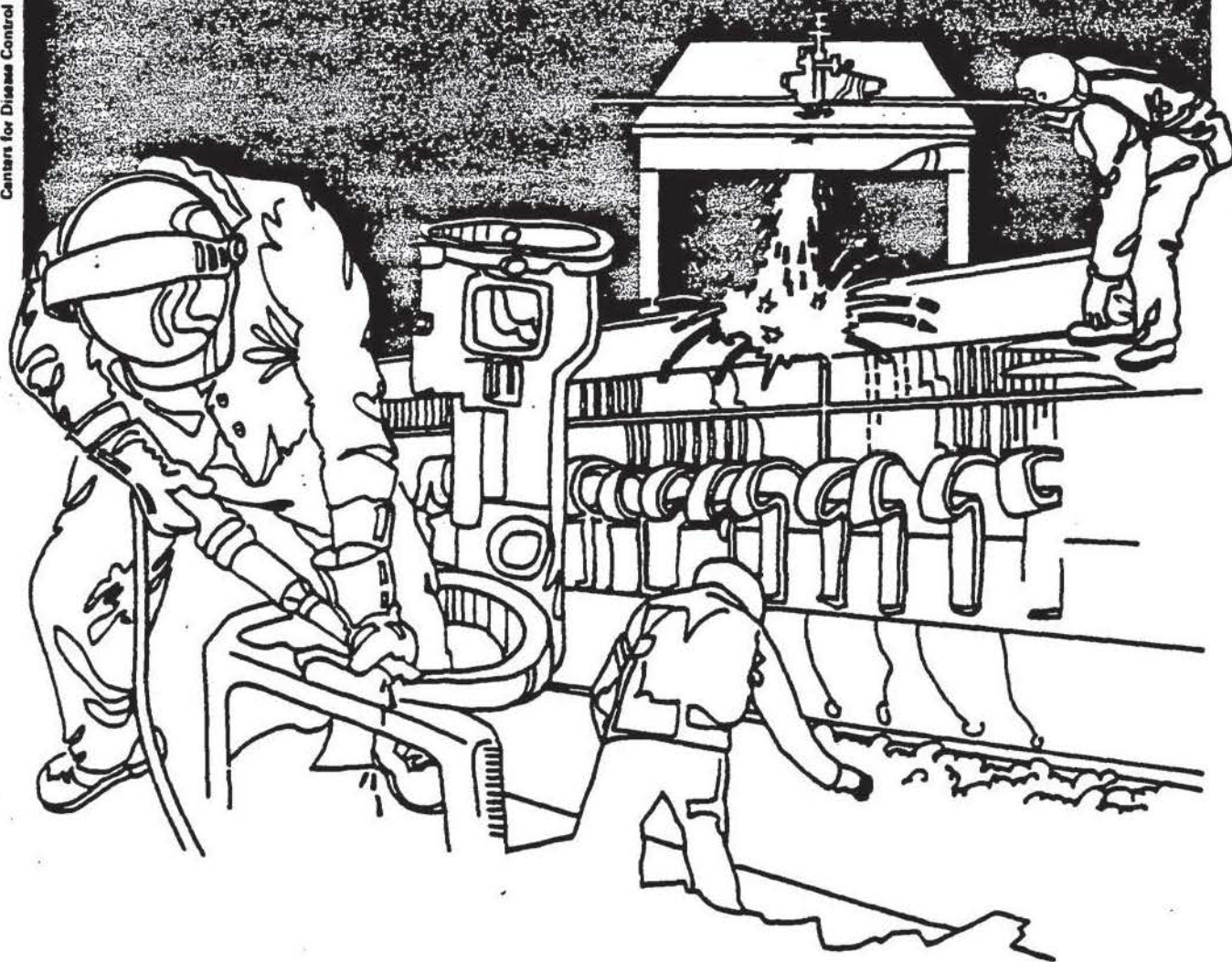


# NIOSH



## Health Hazard Evaluation Report

HETA 84-123-1601  
HARSHAW/FILTROL  
LOUISVILLE, KENTUCKY

## PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.



HETA 84-128-1601  
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LOUISVILLE, KENTUCKY

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## I. SUMMARY

In January, 1984, the National Institute for Occupational Safety and Health (NIOSH) received a request from the International Chemical Workers Union (ICWU) to evaluate occupational exposures to two suspect bladder carcinogens, 3,3'-dichlorobenzidine (DCB) and ortho-dianisidine (ODA), at Harshaw/Filtrol, Louisville, Kentucky. The plant employs approximately 125 workers in the production of inorganic and organic pigments.

On August 20-21, 1984, NIOSH investigators conducted an environmental and medical survey in the Colormaking Area of the Organic Pigments Department. Four personal breathing-zone samples were collected to measure exposure to DCB and ODA during charging of these compounds. Wipe samples for determination of DCB were collected from various surfaces near the work area and skin gauze samples were collected from the DCB charging operator. Four workers potentially exposed to DCB and ODA gave urine samples for determination of urinary levels of the two compounds.

All of the air, urine, and skin exposure samples for DCB were below the limits of detection. DCB surface contamination up to  $1.4 \text{ ug/cm}^2$  was found in the DCB work area while DCB surface concentrations ranged from  $0.01$  to  $0.03 \text{ ug/cm}^2$  in the locker room. An ODA worker was exposed to an airborne ODA concentration of  $2 \text{ ug/M}^3$  on August 20, and  $16 \text{ ug/M}^3$  on August 21. One worker provided two samples which had measurable levels of urinary ODA; while no worker exhibited detectable levels of urinary DCB.

On the basis of the data collected in this evaluation, it was determined that a potential health hazard existed due to exposure to ODA. No current health hazard existed due to exposure to DCB, although it was determined that improved housekeeping and process isolation procedures should be used to provide a greater margin of safety when handling DCB. Recommendations are presented in Section VII.

KEYWORDS: SIC 286 (Industrial organic chemicals)  
3,3'-dichlorobenzidine, DCB, ortho-dianisidine, ODA, bladder cancer.

## II. INTRODUCTION

In January, 1984, the National Institute for Occupational Safety and Health (NIOSH) received a request from the International Chemical Workers Union (ICWU) for a Health Hazard Evaluation of possible exposures to suspect bladder carcinogens at Harshaw/Filtrol in Louisville, Kentucky. The plant employs approximately 125 workers in the production of pigments, both inorganic and organic.

An initial survey was conducted on May 1, 1984, encompassing an opening conference and a walk-through of the plant areas in which 3,3'-dichlorobenzidine (DCB) and ortho-dianisidine (ODA) are used.

Subsequently, on August 20-21, 1984, NIOSH investigators conducted environmental and medical surveys in the Colormaking Area of the Organic Pigments Department.

A letter summarizing the latter survey was distributed August 31, 1984. Notification letters of individual urinary DCB levels and urinary ODA levels were sent to the four potentially exposed workers on January 3, 1985.

## III. BACKGROUND

This plant employs approximately 125 hourly workers in the production of pigments, both inorganic and organic. Three people were assigned to the area of interest, the Colormaking Area of the Organic Pigments Department, during our survey. Harshaw/Filtrol currently uses two suspect bladder carcinogens, DCB and ODA, both in the Colormaking Area.

Both chemicals are intermediaries in the production of pigments. They are dry powders that are dumped into the charging ports of mixing vessels. Once all ingredients are thoroughly mixed, they chemically react and no longer exist in their original form. These vessels are located on an open floor among a number of other mixing vessels. There are no physical dividers between regulated and unregulated work areas. The DCB vessel, but not the ODA vessel, has a plenum on top of the charging port. During charging, negative pressure is applied to the vessel creating air flow into the vessel. No special precautions are used when handling ODA.

Harshaw bought this plant from Kentucky Color and Chemical Company in 1958, and built the organic pigments building in 1964. 3,3'-Dichlorobenzidine (DCB) and o-dianisidine (ODA) are currently used as raw materials for manufacturing organic pigments. The processes for each are such that they are reacted to form diazo compounds that are combined by azo couplings with other organic compounds to form insoluble pigments.

One or two workers per shift handle DCB and ODA which are stored in powder form in 100 or 200 pound drums. These drums are dumped into the charging ports of mixing vessels located on an open floor among

numerous other mixing vessels with no physical dividers between them. The vicinity around the DCB vessel is designated as a regulated work area by roping off the area during DCB charging. In addition, the DCB vessel is exhausted to keep it under negative pressure and create air flow into the vessel during charging. These controls and precautions are not used when handling ODA. There is usually one batch of each compound used per shift, with less than 30 minutes required for charging each batch.

#### IV. EVALUATION DESIGN AND METHODS

##### A. Environmental

Two personal breathing-zone air samples each, were collected for DCB and ODA during the two batches of each compound that were run during the NIOSH survey. Also, six area air samples were collected for DCB near the mixing vessel.

ODA air samples were collected on teflon filters at a flow rate of 3 liters per minute and analyzed by high pressure liquid chromatography (HPLC) according to NIOSH Method 5013. DCB air samples were collected on glass-fiber filters at a flow rate of 3 liters per minute and analyzed by HPLC according to NIOSH Method P&CAM 246.

Wipe samples for DCB were collected from various surfaces (approximately 100 cm<sup>2</sup> each) near the DCB work area, hand tools, locker room, and a worker's hand. The samples were collected on gauze pads moistened with isopropanol. During DCB charging, skin exposure to airborne DCB was sampled with gauze patches attached to the ventral surface of the worker's forearm inside the shirt sleeve. These patches had 25 square centimeters of exposed surface area and an aluminum foil backing. All gauze samples were desorbed with methanol and analyzed by HPLC.

The velocity of air through the DCB charging port was measured with a Sierra Model 441®.

##### B. Medical

At the onset of NIOSH's survey, four workers were identified by the company as being potentially involved in the handling of 3,3'-dichlorobenzidine (DCB) and/or ortho-dianisidine (ODA) during the course of our visit.

A urine sample was obtained from each of the four workers on Monday morning, August 20, before the workers entered the plant to begin the work shift. As these two substances each have a half life in the body estimated at 5-6 hours, and the workers had been unexposed for at least 60 hours, these samples should provide valid baseline measurements.

Subsequently, three of the four workers were actually assigned to the Colormaking Area during at least part of the two days of the survey.

Urine was collected from the time the worker entered the Colormaking Area until the end of that work shift. DCB and ODA values were determined utilizing sample collection, storage, and analytical procedures outlined in NIOSH Method #8306<sup>1</sup> and in Nony and Bowman<sup>2</sup>. Urine creatinine values were determined as well. A total of 12 samples were collected from the four workers.

## V. EVALUATION CRITERIA

### A. Environmental

The primary sources of environmental evaluation criteria for the workplace are: 1) NIOSH Criteria Documents and recommendations, 2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLV's), and 3) the U.S. Department of Labor (OSHA) occupational health standards. Often, the NIOSH recommendations and ACGIH TLV's are lower than the corresponding OSHA standards. Both NIOSH recommendations and ACGIH TLV's usually are based on more recent information than are the OSHA standards. OSHA is empowered to set and enforce exposure limits for the workplace while NIOSH's mandate is to conduct research and forward recommendations to all concerned parties.

### B. DCB and ODA

Both 3,3'-dichlorobenzidine (DCB) and o-dianisidine (ODA) are analogues of benzidine, a chemical which has been linked to bladder cancer in humans<sup>3,4</sup>.

Clear evidence that DCB causes cancer in humans has not been found. However, DCB has demonstrated potent carcinogenicity in animals. Of 111 rats given 20 mg DCB by injection or gastric intubation six days/week for 10 to 20 months, 17 had tumors of the zymbal gland, 13 had mammary tumors, eight had skin tumors, five had malignant lymphomas, three had urinary bladder tumors, and two had intestinal tumors. No tumors were found in 130 control rats.<sup>5</sup>

In another study, of 44 male rats fed 1000 ppm DCB for 12 months, nine developed granulocytic leukemia, and eight developed zymbal gland tumors; mammary gland tumors were found in rats of both sexes.<sup>6</sup>

In hamsters, 0.3% DCB in the diet produced transitional cell carcinomas of the bladder and some liver cell tumors.<sup>7</sup> Liver tumors were also found in mice exposed to DCB.<sup>5</sup>

On the basis of the available evidence, OSHA began regulating DCB as a carcinogen in 1974.<sup>8</sup> 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 record keeping concerning exposure to DCB. In addition, the American Conference of Governmental Industrial Hygienists recommends that human exposure by any route be avoided.<sup>9</sup> As with all suspected human carcinogens, NIOSH recommends that exposure be kept as low as possible.

O-Dianisidine (synonymous with ODA or 3,3'-Dimethoxybenzidine) also has not demonstrated clear evidence of human carcinogenicity. As with DCB, however, a number of positive animal tests have been found.

Both Pliss<sup>10,11</sup> and Hadidian, et al.<sup>12</sup> observed a carcinogenic effect in rats following oral administration of ODA. Saffiotti et al.<sup>13</sup> and Sellakumar<sup>7</sup> observed the same effect in hamsters.

Subsequently, the International Agency for Research on Cancer considered ODA for its carcinogenic potential.<sup>14</sup>

On the basis of available information, ODA should be handled as a suspect carcinogen. Human exposure by any route should therefore be avoided.<sup>15</sup>

## VI. RESULTS

### A. Environmental

All air and skin exposure samples for DCB were below the limits of detection (Tables I and II). However, DCB surface contamination was detected in the DCB work area and in the locker room (Table II). The highest levels were found on the handle of a shovel used for putting ice in the DCB mixing vessel [1.4 micrograms per square centimeter ( $\mu\text{g}/\text{cm}^2$ )] and on the control handle of a cart used for lifting and moving DCB drums ( $0.9 \mu\text{g}/\text{cm}^2$ ). Door knobs and locker handles had DCB surface concentrations ranging from 0.01 to  $0.03 \mu\text{g}/\text{cm}^2$ .

Personal breathing-zone concentrations of ODA were  $2.0 \mu\text{g}/\text{m}^3$  on August 20 and  $16 \mu\text{g}/\text{m}^3$  on August 21 (Table I).

Personal protective equipment worn by the operator during DCB charging includes a Survivair® half-face piece respirator with a high efficiency particulate filter, a long-sleeve cotton shirt,



rubber gloves, and disposable plastic boot covers. After charging, the empty DCB drums are decontaminated with a sodium hypochlorite solution.

Special precautions are not currently required by management for handling ODA, although the worker usually wears a respirator during charging in order to avoid upper respiratory irritation caused by ODA dust. Nose and throat irritation and coughing were experienced by the NIOSH investigators and by the company industrial hygienist about 20 feet from the ODA mixing vessel during charging.

Ventilation measurements showed an average face velocity of 120 feet per minute at the charging port of the DCB mixing vessel.

#### B. Medical

Twelve urine samples were collected from the four employees of the Colormaking Area. Four of these samples were intended as baseline measurements, having been collected Monday morning August 20, 1984, before having entered the plant. Each of the twelve samples were analyzed for urinary DCB and urinary ODA, and had the amount of creatinine measured to allow for standardization.

All 12 of the samples had levels of urinary DCB less than the limit of detection (<10 ng/ml). Ten of the samples also had non-detectable levels of ODA (<10 ng/ml). Two urine samples (contributed by one worker) did show measurable levels of ODA. Upon standardization, these levels were 10 ug/g Cre and 22 ug/g Cre, respectively (Table III).

### VII. DISCUSSION, CONCLUSIONS, AND RECOMMENDATIONS

DCB exposure appears to be low as evidenced by the lack of DCB found in the air, skin, and urine samples collected during the NIOSH survey. However, these results are more likely due to the small batch processes and short durations of exposure, rather than exceptional control measures.

The surface wipe results indicate that improvements could be made in housekeeping and decontamination procedures for DCB. It would also be best if tools used for DCB-charging, such as ice shovels and drum carts, be kept in the DCB area and used only for DCB, in order to prevent the spread of contamination. DCB workers should have separate shower and locker facilities.

If future plans call for increased production of DCB-based pigments at Harshaw, it would probably be necessary to employ stricter controls, such as:



- (1) an enclosed DCB-charging room exhausted such that the room is kept under negative pressure
- (2) impervious full-body suits and positive-pressure supplied-air respirators for DCB charging
- (3) showers directly adjacent to the DCB-charging room to be used immediately after DCB charging

Harshaw should handle ODA as a suspect carcinogen, as well. The engineering controls and personal protective equipment that are currently used for DCB should also be used when handling ODA (both charging and weighing) in order to reduce the levels of ODA exposure found by NIOSH. These exposures should be reduced to as low a level as possible.

The company's present policy of performing periodic urinary cytology screening for potentially-exposed individuals is to be commended. However, given the fact that bladder cancers usually exhibit a latency period of 10-40 years, it is important that each exposed worker continue to receive periodic urinary cytology screening even after leaving the employment of Harshaw/Filtrol. The company, union, and individual workers should develop a mechanism for doing this.

In addition to the urinary cytology screening which currently is performed, periodic sampling for urinary DCB and ODA should be instituted, to be conducted simultaneous to environmental sampling on those workers with potential exposure at that time. As suspect carcinogen, levels of both DCB and ODA in the urine should be kept below the limit of detection.

The appearance of detectable levels of either DCB or ODA should be a signal that some changes, or tightening of work practices is required in the handling of that chemical. Should that occur, it is recommended that the company, union, and affected worker (s) be involved in resolving the problem.

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X. DISTRIBUTION AND AVAILABILITY OF REPORT

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1. Harshaw/Filtrol
2. International Chemical Workers Union, Local 663
3. ICWU, Health & Safety Department
4. NIOSH, Region IV
5. OSHA, Region IV

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

TABLE I

## Air Sampling Results for DCB and ODA

Harshaw/Filtrol Partnership  
Louisville, Kentucky

HETA 84-128

August 20-21, 1984

Job/Location	Sampling Period	DCB Concentration (ug/m <sup>3</sup> )	ODA Concentration (ug/m <sup>3</sup> )
Charging DCB - personal breathing zone	(8/20) 0812-0817	N.D.*(<1.7)	-
Charging ODA - personal breathing zone	(8/20) 0737-0747	-	2.0
Charging DCB - personal breathing zone	(8/21) 0840-1404	N.D.(<0.03)	-
Charging ODA - personal breathing zone	(8/21) 0738-0827	-	16.0
Top of DCB-charging port	(8/20) 0755-0925	N.D.(<0.09)	-
Top of DCB-charging port	(8/20) 0755-0925	N.D.(<0.09)	-
Top of DCB-charging port	(8/20) 0925-1415	N.D.(<0.03)	-
Top of DCB-charging port	(8/20) 0925-1415	N.D.(<0.03)	-
35 ft.from DCB mixing tank	(8/21) 0718-1400	N.D.(<0.02)	-
35 ft.from DCB mixing tank	(8/21) 0723-1400	N.D.(<0.02)	-

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\*N.D. = none detected



TABLE II

## DCB Skin Exposure and Surface Contamination

Harshaw/Filtrol Partnership  
Louisville, Kentucky

HETA 84-128

August 20-21, 1984

Location	DCB Concentration (ug/cm <sup>2</sup> )
forearm gauze patch - during DCB charging (8/20)	*N.D. (<0.02)
forearm gauze patch - during DCB charging (8/21)	N.D. (<0.02)
wipe sample of worker's hand - after DCB charging (8/20)	N.D. (<0.003)
wipe - door knob to supervisor's office	0.01
wipe - top of "decontaminated" drum	0.2
wipe - desk near DCB charging area	0.01
wipe - shovel handle	1.4
wipe - drum cart, control handles	0.9
wipe - locker room bench	0.01
wipe - 5 locker handles, east side	0.02
wipe - 10 locker handles, west side	0.03

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\*N.D. = none detected

TABLE III

## Urine DCB, ODA, and Creatinine Values of Colormaking Employees

Harshaw/Filtrol  
Louisville, Kentucky

HETA 84-128

August 20-21, 1984

<u>Sample Number</u>	<u>Creatinine (g/L)</u>	<u>DCB (ng/ml)</u>	<u>DCB (ng/g Cre)</u>	<u>ODA (ng/ml)</u>	<u>ODA (ug/g Cre)</u>
1	1.42	ND*	-	ND	-
2	3.44	ND	-	ND	-
3	1.74	ND	-	ND	-
4	1.33	ND	-	ND	-
5	2.88	ND	-	ND	-
6	2.54	ND	-	ND	-
7	2.10	ND	-	20	10
8	2.48	ND	-	ND	-
9	2.42	ND	-	ND	-
10	2.45	ND	-	ND	-
11	2.72	ND	-	ND	-
12	2.24	ND	-	50	22

\*ND = less than 10 ng/ml, the analytical limit of detection

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