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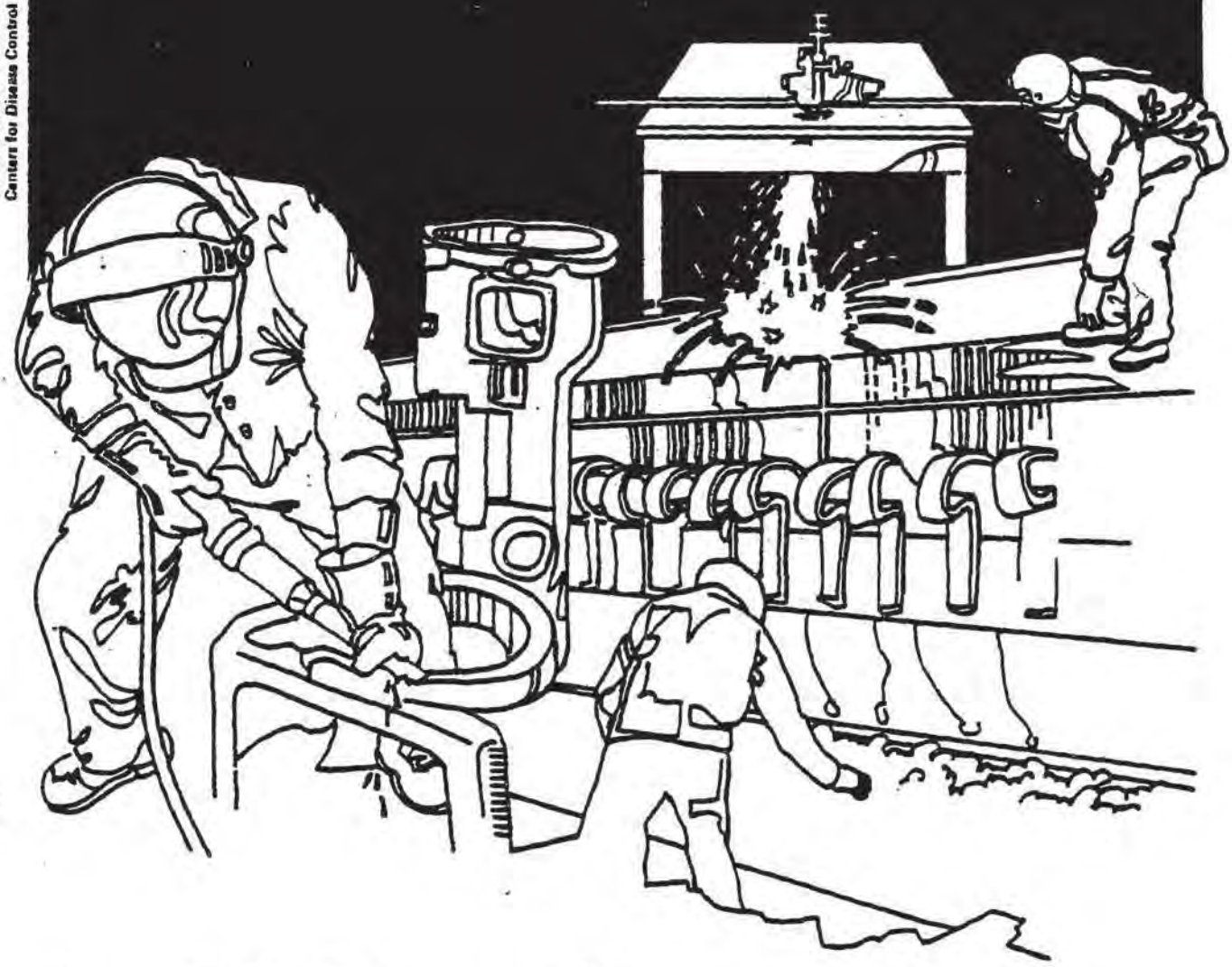

Health Hazard Evaluation Report

HETA 84-058-1700
HILTON-DAVIS CHEMICAL COMPANY
CINCINNATI, OHIO

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.

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

HETA 84-058-1700
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HILTON-DAVIS CHEMICAL COMPANY
CINCINNATI, OHIO

NIOSH INVESTIGATORS:
Matthew A. London, I.H.
James M. Boiano, I.H.

I. SUMMARY

In November 1983, the National Institute for Occupational Safety and Health (NIOSH) received a request from the International Chemical Workers Union (ICWU) for an evaluation of occupational exposures to suspect bladder carcinogens at Hilton-Davis Chemical Company, Cincinnati, Ohio. The Union requested that NIOSH assess current exposures to those chemicals and compile a list of former employees who had been potentially exposed.

An initial survey was conducted February 22-23, 1984, encompassing an opening conference and a walk-through of the plant areas in which 3,3'-dichlorobenzidine (DCB), ortho-dianisidine (ODA), and ortho-toluidine were used.

The compilation of the list of former employees potentially exposed to suspect bladder carcinogens was initiated May 31, 1984, and completed in May 1986.

On August 6-7, 1984, NIOSH investigators conducted an environmental and medical survey in the DCB charging area of the Pigments Department. Environmental sampling included the collection of: (1) personal breathing-zone (BZ) air samples inside a reusable air hood of a two-piece full body suit (shrouded hood and disposable Tyvek® coveralls), (2) area air samples from non-regulated areas adjacent to the dedicated charge room, (3) forearm gauze patch samples from underneath worker's coveralls, and (4) wipe samples from various surfaces, etc., routinely contacted by workers. All four personal BZ air samples and 3 of 4 area air samples contained low but detectable quantities of DCB (concentrations ranged from 0.16 to 0.60 micrograms per cubic meter (ug/M^3) or 0.015 to 0.058 parts per billion (ppb)). Seven of 8 skin gauze patch samples and 19 of 26 wipe samples contained measurable quantities of DCB, with concentrations ranging from 0.2 to 3.7 ug/25 cm^2 and from 0.4 to 2800 ug/100 cm^2, respectively. Twelve (46%) of the wipe samples exceeded Hilton-Davis' self-imposed limit of 10 ug/100 cm^2. These findings revealed deficiencies in the personal protective equipment and in the decontamination procedure.

Both workers who performed the DCB-charging operation at this time had low, but measurable, concentrations of DCB in their urine. Subsequently, the company replaced the two-piece suit with a one-piece supplied air disposable Tyvek® total enclosure suit.

On August 26-27, 1985, NIOSH investigators conducted a follow-up environmental and medical survey in the DCB-charging area. This survey was intended largely to document the effectiveness of the company's recently implemented changes.

The environmental sampling protocol for this survey virtually duplicated that of our initial survey. Breathing-zone air samples collected from inside the new total enclosure suits showed no detectable DCB (less than 0.025 ug/M^3). Three of 7 area air samples contained detectable quantities of DCB (0.21 to 0.78 ug/M^3 or 0.020 to 0.076 ppb). The presence of airborne DCB in non-regulated areas outside of the charge room was probably due to the fact that the DCB charge room was not maintained under negative pressure. Six of 8 skin gauze patch samples contained measurable DCB, with concentrations somewhat lower than that measured during the initial survey (0.2 to 1.2 ug/25 cm^2). We suspect that these samples, as well as those obtained during the August 1984 survey, became contaminated not as a result of permeation of the Tyvek® material, but rather during donning/doffing of the suits. Surface wipe sampling results showed that DCB concentrations were lower than during the August 1984 survey, whereby only 4 of 23 (17%) samples exceeded the company's 10 ug/100 cm^2 guideline. This difference was due to the fact that the 1985 sampling was conducted immediately after the comprehensive monthly hypochlorite washing of work surfaces in and near the charge room.

Neither of the two workers who performed the DCB-charging operation at the time of the August 1985 survey had detectable concentrations of DCB in their urine.

On the basis of the data collected in this evaluation it was determined that a potential health hazard existed in August 1984 due to exposure to DCB. Control measures implemented prior to the follow-up survey in August 1985 resulted in reduced exposure. Recommendations are presented in Section VIII concerning improvements in the decontamination method, charge room ventilation, employee training, and environmental and medical monitoring.

Keywords: SIC 2865 (Cyclic (coal tar crudes), and Cyclic Intermediates, Dyes, and Organic Pigments) 3,3'-dichlorobenzidine (DCB), urinary DCB, bladder cancer.

II. INTRODUCTION

In November 1983, the National Institute for Occupational Safety and Health (NIOSH) received a request from the International Chemical Workers Union (ICWU) for a Health Hazard Evaluation (HHE) of possible exposures to suspect bladder carcinogens at Hilton-Davis Chemical Company in Cincinnati, Ohio. The Union requested that NIOSH assess current exposures to those chemicals, and that NIOSH also compile a list of former employees who had been potentially exposed.

An initial survey was conducted February 22-23, 1984, encompassing an opening conference and a walk-through of the plant areas in which 3,3'-dichlorobenzidine (DCB), ortho-dianisidine (ODA), and ortho-toluidine were used. It was determined that ODA and ortho-toluidine had formerly been used in small quantities, and had not been used at all at Hilton-Davis for many years. A second meeting was held May 10, 1984 to discuss the study protocol for the HHE.

The compilation of the list of former employees potentially exposed to suspect bladder carcinogens was initiated May 31, 1984, and completed in May 1986.

On August 6-7, 1984, NIOSH investigators conducted an environmental and biological monitoring survey in the DCB-charging area of the Pigments Department. On January 2, 1985, letters were sent to the study participants informing them of their individual biological monitoring test results. A meeting with company and union representatives was held February 1, 1985, to discuss the implications of the urinary DCB results. On March 5, 1985, a letter was sent informing the Union and Company of the group environmental and biological monitoring results. On May 14, 1985 another meeting was held to discuss in more detail, the study results and the implementation of NIOSH's recommendations.

On August 26-27, 1985, NIOSH investigators conducted a follow-up environmental and biological monitoring survey in the DCB-charging area. This survey was intended largely to document the effectiveness of the company's recently implemented changes. Notification letters were sent to the study participants November 1, 1985. The company and the union were then notified of the group results. On January 22, 1986, a letter was written to the Company and Union discussing the results in greater detail, and outlining some additional recommendations.

III. BACKGROUND

Hilton-Davis Chemical Company, Cincinnati, Ohio, division of Sterling Drug Incorporated, employs 560 hourly workers in the manufacture of inorganic and organic pigments, salicylic acid, and other chemicals. The plant, situated on 75 acres and housed in approximately 30

buildings, started production at the present site in 1926. The specific area of the plant involved in the study was in Pigments Department No. 10 of Building 12, where 3,3'-dichlorobenzidine (DCB) is used. At the time of the request, approximately 30 workers were assigned to this department, but only 4 were involved in the direct handling of the compound.

A. Process Description

Hilton-Davis uses DCB in the production of diarylide yellow pigment No. 12. This pigment is synthesized on a batch basis in a reaction vessel by initially acidifying the DCB with sulfuric acid, followed by treatment with excess sodium nitrite to form the tetrazonium salt. A coupling agent, acetoacetanilide, is then added to the aqueous tetrazonium solution to form the yellow pigment. Upon completion of the coupling reaction, the slurry is filtered and drummed.

DCB is purchased from suppliers as the dihydrochloride salt in sealed fiber drums and is handled by Hilton-Davis as a controlled substance, using procedures designed to comply with the OSHA Regulation 290 CFR 1910.1007[1] Each drum contains 280 lbs. of the wetted salt, 80 lbs. (approximately 30%) of the total weight consisting of water. The relatively high water content is intentional and serves to suppress dust generation during drum unloading. Whole drums are used in each batch to eliminate manual weighing. Two workers wearing protective equipment (described later) charge the DCB into a reactor chute which is maintained under negative pressure. The charging operation is conducted in a dedicated 12' X 10' enclosed room. It typically lasts no longer than 30-45 minutes and is done no more than once every 12 hours.

After the drums of DCB are charged into the reactor, they are rinsed with water, which is then emptied into the chute. After the chute is covered, the water-rinsed drums are sprayed with a 12% sodium hypochlorite bleach solution, then placed in polyethylene bags for subsequent disposal. The decontaminating solution, which according to the Company converts the DCB to a less toxic quinone-type compound, is then sprayed throughout the interior of the charge room, as well as on the workers themselves, followed by a water rinse. Subsequently, both workers enter a "dirty" change room where they remove the protective clothing (coveralls, etc.) prior to showering and changing into clean work clothes in a "clean" change room.

B. Personal Protection Equipment

The two DCB workers were required to wear a two-piece full body outfit consisting of Tyvek® coveralls (one-piece up to the neck) and an (abrasive blasting type) air supplied hood during the

charging operation. Polyethylene foot covers, nitrile rubber gloves, and safety glasses were also worn.

Prior to our follow-up environmental and medical evaluation in August 1985, the company replaced the two-piece full body outfit with a one-piece supplied air disposable Tyvek® total enclosure suit. This change was made to better protect the workers from DCB exposure given that NIOSH had detected low levels of DCB inside the air hood during our August 1984 survey.

C. Housekeeping

Apart from the routine hypochlorite decontamination of the DCB charge room at the end of each charging operation, at the end of each month, this area as well as other areas adjacent to the charge room (i.e., change and shower rooms, reactor and storage areas) are decontaminated. Surface wipe sampling is then conducted to determine the effectiveness of the decontamination.

D. Company environmental and medical monitoring

Hilton-Davis employs a chemist and a technician to implement an environmental monitoring program at the plant. Since its inception in 1973, environmental monitoring for DCB has consisted almost exclusively of the collection of surface wipe samples, which is currently done on a quarterly basis. Although the company has been conducting this type of sampling since 1973, it was not until 1977 that the analysis was specific for DCB. Prior to 1977 the analysis was for total aromatic amines, since an analytical method specific for DCB was not available until this time. Wipe samples are currently collected on Whatman filters which are analyzed in-house according to NIOSH P&CAM 246.[2] The company has instituted an action limit of 10 micrograms per 100 square centimeters (ug/100 cm^2) of surface area for comparison of sampling results. Surfaces exceeding this value are decontaminated with the sodium hypochlorite solution.

Medical capabilities include an on-site dispensary staffed full-time with a physician and a nurse. Employees who are potentially exposed to DCB are given annual physicals including urinary cytology. Biological monitoring of urine for DCB has not been done by the company.

IV. EVALUATION METHODS AND MATERIALS

A. Environmental

During the initial (August 6-7, 1984) and follow-up (August 26-27, 1985) surveys, environmental sampling for DCB was conducted during first-shift charging operations. Sampling included the collection

of personal breathing-zone and general area air samples to assess inhalation exposure, skin gauze samples to assess potential skin exposure, and wipe samples to assess surface contamination. Samples collected during the follow-up survey virtually duplicated that of our initial survey. The primary intent of the latter survey was to evaluate the effectiveness of the new full body suit used by workers during the charging operation. A brief description of our sampling and analytical methodologies for each of the three types of environmental samples collected, is provided below.

Air samples - air samples were collected on 37 mm glass fiber filters using personal sampling pumps calibrated at 3.0 liters per minute (Lpm). This flow rate was selected because of the short sampling time and the anticipated low concentrations of DCB. The filters were placed inside the full body suit and attached to the collar so that an air sample representative of actual exposure could be obtained. These air samples were collected from both DCB workers on each day and ran only for the duration of the charging operation.

General area air samples were collected from selected locations in non-regulated areas outside the charge room (i.e. dirty change room, clean change room, and/or staging area). These samples were positioned at breathing zone level (approximately 5 ft above floor) and were collected within the same time period as the personal air samples.

Following collection, all of the air samples were desorbed in methanol and analyzed by high pressure liquid chromatography (HPLC) equipped with an electrochemical detector according to modified NIOSH Method P&CAM 246[2]. The limit of detection (LOD) for the analysis was 0.025 ug/sample.

Skin Samples - 2" x 2" (25 cm^2) gauze patches, with an impermeable aluminum foil backing, were taped to the ventral surface of each forearm (underneath the worker's coveralls and Tyvek® suit) to assess potential skin exposure to DCB. These samples were also collected during the same time period as the other samples. They were then desorbed in methanol and analyzed by HPLC equipped with a UV detector, according to modified NIOSH Method P&CAM 246[2]. The LOD for the analyses were 0.2 and 0.1 ug/sample for the initial and follow-up surveys, respectively.

Surface Wipe Samples - 11cm diameter filter papers (Whatman No. 1 ashless), moistened with methanol, were wiped over an area of approximately 100 cm^2 to assess surface contamination. Each filter was handled using a new pair of disposable gloves to avoid potential cross contamination of the samples. Wipe samples were collected from various locations at sites (such as door handles, drum rims, etc.) that are commonly contacted by workers during the

course of normal work activities. Locations included the dirty and clean change rooms, shower room, staging area, reactor area, charge room, exterior surfaces of unopened DCB drums and from opened DCB drums which had been decontaminated. Samples were also collected from interior surfaces of selected articles of personal protective equipment (airhoods, shoes), but only during the August 1984 survey.

Wipe samples collected during the August 1985 survey were obtained from most of the same locations sampled during the August 1984 survey. On August 26, 1985, wipe samples were collected prior to the charging operation and were used to assess the relative effectiveness of the monthly decontamination effort, given that the charging operation on this date was the first since the monthly decontamination effort. The wipe samples collected the following day were obtained after the charging operation and were used to assess the relative effectiveness of daily post-charge decontamination efforts.

All surface wipe samples were desorbed in methanol and analyzed by HPLC (UV detector) according to NIOSH Method P&CAM 246, with modifications [2]. The LOD for samples analyzed during the initial survey ranged between 0.2 and 4.0 ug/sample. The LOD was 0.06 ug/sample for samples analyzed from the follow-up survey.

B. Medical

At the onset of NIOSH's August 1984 survey, two workers were identified by the company as being assigned to the DCB charging operation during the course of our visit.

A urine sample was obtained from each of the two workers on Monday morning, August 6, before the workers entered the plant to begin the work shift. As DCB has a half-life in the body estimated at 5-6 hours[13], and the workers had been unexposed for at least 60 hours, these samples served to provide baseline measurements of urinary DCB.

Urine was collected from the time the worker completed the DCB charging operation until the end of that work shift. DCB values were determined utilizing sample collection, storage, and analytical procedures outlined in NIOSH Method #8306[4] and in Nony and Bowman[5]. Urine creatinine values were determined as well. Samples were collected from both workers on both August 6 and August 7.

The same protocol for collecting and analyzing urine for the presence of DCB was employed in NIOSH's follow-up survey of August 26-27, 1985. Again, two workers were involved, one of whom had been a participant in the August 1984 survey.

Urinary DCB results are reported as ug DCB per gram of creatinine. This is done as a means of normalizing (standardizing) the data. The analytical limit of detection for the samples was 10 ug DCB/liter of urine.

C. List of Former DCB Workers

The following methodology has been used to compile the list of former Hilton-Davis employees who, as could best be determined, ever worked with DCB.

In meetings held February 22-23 and May 10, 1984, with representatives of the Company and ICWU Local 342, it was learned that DCB has been used at Hilton-Davis since shortly after World War II. The department in which it has been used has been known by a number of names -- Pigment Department, Department 10, Blue-Green, Chrome Yellow, or Red 4.

Job history records ("history cards") for former Hilton-Davis employees are housed in a downtown Cincinnati warehouse. We were told that the employee records include information only as detailed as the department worked, and dates worked therein. No information as to specific job(s) worked was reportedly included on the history cards. There were an estimated 5000 cards to be reviewed.

A total of 91 cartons contained history cards of Hilton-Davis employees. Each carton contained an average of 60 files. NIOSH randomly selected 53 cartons, from which the history cards of 120 former employees were chosen. For each of the 120 people, we extracted their name, social security number, whether they had worked in the Pigment Department or any of its synonyms, and if so, during which years. After this information was transcribed, the file was immediately replaced in its carton.

During the next few months, the Company reviewed the contents of all 91 cartons. On January 2, 1985, we received from Hilton-Davis a list of all people who, the company stated, had worked in the Pigment Department. This list included each individual's name, social security number, last known address and phone number, and the years worked in the department. The list included 261 people. Anyone not on the list was assumed to have not worked in the department (according to the Company).

Comparing NIOSH's determination of Pigment Department status with the Company's, there was agreement on 117 of the 120 people (97.5%). For the three discrepant observations, NIOSH and the company jointly reviewed their history cards. Two persons had been mistakenly excluded by NIOSH and one person had been mistakenly excluded by Hilton-Davis. Therefore, Hilton-Davis had correctly

classified 119/120 (99.2%) of the files. The person misclassified by them was added to the list, making a total of 262 individuals.

On the basis of this level of accuracy, NIOSH decided to accept the validity of Hilton-Davis' assessment of the job history cards for all former employees.

The social security numbers for the 262 people were then submitted to the Internal Revenue Service to obtain the most recent address of each person.

Subsequently, on August 16, 1985, NIOSH sent a letter to each of the 262 people identified as having worked in the Pigment Department. This letter inquired as to whether they had ever worked with DCB and, if so, during which years.

A total of 163 people returned their questionnaire to NIOSH, or were contacted by telephone, or were lost to follow-up if their letter had been returned by the Post Office. On January 27, 1986, letters were sent to the remaining 99 people.

Simultaneous with the release of this HHE final report, a list of former employees who stated that they remembered working with DCB at Hilton-Davis will be sent to the company. Company representatives, at the February 22, 1984 meeting, and subsequently as well, stated that they would then make the list available to the Union. It is our understanding that the Union intends to design and implement a medical screening program for these workers.

V. EVALUATION CRITERIA

A. Environmental Criteria

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy).

In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health

effects even if the occupational exposures are controlled at the level set by the evaluation criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

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. The OSHA standards also may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH-recommended standards, by contrast, are based primarily on concerns relating to the prevention of occupational disease. In evaluating the exposure levels and the recommendations for reducing these levels found in this report, it should be noted that industry is legally required to meet those levels specified by an OSHA standard.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended short-term exposure limits or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high short-term exposures.

B. 3,3'-Dichlorobenzidine (DCB)

3,3'-Dichlorobenzidine (DCB) is an analogue of benzidine, a chemical which has been linked to bladder cancer in humans [6,7].

Clear evidence that DCB causes cancer in humans has not been found. However, DCB has demonstrated carcinogenicity in animals. Pliss[8] observed a high incidence of adenomas and carcinomas of the zymbal gland and other organs, including 2 tumors of the bladder, in 12 of 50 rats fed 10-20 mg DCB six times per week for a year.

In another study, of 44 male rats fed 1000 ppm DCB for 12 months, 9 developed granulocytic leukemia, and 8 developed zymbal gland tumors; mammary gland tumors were found in rats of both sexes.[9]

In hamsters, 0.3% DCB in the diet produced transitional cell carcinomas of the bladder and some liver cell tumors.[10] Liver tumors were also found in mice exposed to DCB.[8]

On the basis of the available evidence, OSHA began regulating DCB as a carcinogen in 1974.[1] 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.

NIOSH and the American Conference of Governmental Industrial Hygienists (ACGIH) consider DCB as a suspect human carcinogen.[11,12] NIOSH policy regarding carcinogens is to minimize exposures to the lowest feasible level, given that there probably is no safe level of exposure to DCB for elimination of all cancer risk.

VI. RESULTS

A. Environmental

Air samples -- Personal breathing-zone air sampling results from the August 1984 survey revealed that both DCB workers were exposed to low levels of DCB while wearing the two-piece full body suit (shrouded supplied air hood and Tyvek® coveralls) during the charging operation. DCB was detected in all four air samples with levels ranging from 0.34 to 0.60 micrograms per cubic meter of air (ug/M^3), equivalent to 0.033 to 0.058 parts per billion (ppb) (Table 1).

During the follow-up survey when workers were wearing a new one-piece air supplied full body suit, air samples taken inside the suit showed no detectable DCB, i.e., levels were below the analytical detection limit of 0.025 micrograms per sample (see Table 2).

Detectable levels of DCB were measured in air samples obtained from the clean change room and the staging area during the initial survey. Two samples from the former area revealed air concentrations of 0.27 and 0.24 ug/M^3 (0.023, 0.026 ppb). Two air samples from the latter area were somewhat lower; one was non-detectable (ND) while the other measured 0.16 ug/M^3 (0.015 ppb).

During the follow-up survey, area air samples were collected from four areas. These included the same two areas sampled during the initial survey (clean change room and staging area) and two other areas; the dirty change room and the area east of the change room (above the ice chute). Results show that DCB was only detected in

two of these areas, the dirty and clean change rooms. Of these two areas, airborne DCB levels were higher in the dirty change room. Two air samples collected from this area revealed levels of 0.78 ug/M^3 (0.076 ppb) and 0.57 ug/M^3 (0.055 ppb) compared to 0.21 ug/M^3 (0.020 ppb) for the clean change room.

Skin Gauze Patch Samples -- Forearm skin exposure sampling results for the initial and follow-up surveys are presented in Tables 3 and 4, respectively. Seven of eight samples collected during the initial survey contained detectable quantities of DCB, with levels ranging from 0.2 to 3.7 ug/25 cm^2 (mean: 1.1 ug/25 cm^2).

Similar sampling conducted during the follow-up survey revealed somewhat lower levels. Six of eight gauze patch samples contained detectable quantities of DCB. Levels ranged from 0.2 to 1.2 ug/25 cm^2 (mean: 0.5 ug/25 cm^2).

Surface Wipe Samples -- Surface wipe sampling results from the initial and follow-up surveys are presented in Tables 5 and 6, respectively. Of the 26 samples collected during the initial survey, 19 (73%) contained detectable quantities of DCB while 12 (46%) exceeded the company's self-imposed limit of 10 ug/100 cm^2. The highest DCB levels were measured in samples obtained from the used, decontaminated DCB drums, with surface concentrations ranging from 32 to 2800 ug/100 cm^2. Two samples from unopened drums, by comparison, measured 2.3 and 7.5 ug/100 cm^2. Apart from the DCB drums, detectable levels of DCB were found in samples obtained from the interior surfaces of both supplied air hoods (1.2 and 4.9 ug/100 cm^2) and on surfaces in the clean change room (ND and 27 ug/100 cm^2, shower room (0.4 and 1.4 ug/100 cm^2), dirty change room (30 and 160 ug/100 cm^2), staging area (21 ug/100 cm^2), and reactor area (ND and 2.4 ug/100 cm^2). No DCB was detected in the work shoes of either worker nor was any found on the north and east exterior walls of the change room, wash sink, or the manhole cover to the DCB reactor.

Twenty-nine surface wipe samples were collected during the follow-up survey. Twenty-three of the 29 wipe samples were collected from the same area as for the initial survey. Comparison of these similar samples revealed that DCB surface contamination levels were lower during the follow-up survey. Only 17% (4 of 23) of the wipe samples exceeded Hilton-Davis' guideline of 10 ug/100 cm^2 as compared to 46% of the samples collected during the initial survey. One of the reasons for the relatively lower levels was that the August 1985 sampling was conducted the first two working days following the comprehensive "monthly" washing with hypochlorite bleach solution.

Six of seven samples collected on August 26, the first workday following the monthly decontamination effort, contained detectable quantities of DCB. Levels were highest in the change room (90 to 2400 ug/100 cm^2) and especially on a spatula used by workers to direct DCB down the chute. Progressively lower levels of DCB were measured on surfaces in the dirty change room (30 ug/100 cm^2), clean change room (8.0 ug/100 cm^2), and staging area (0.5 ug/100 cm^2) with the exception of the shower room where no DCB was detected.

Wipe samples collected on August 27 in the same areas sampled above showed that the relative degree of contamination in the various work areas was roughly the same.

Results of the surface wipe samples obtained from the DCB drums (follow-up survey) revealed that the level of DCB contamination on the exterior surfaces was virtually no different between used, decontaminated drums and those which were unopened. DCB levels measured from the used DCB drums ranged from 5 to 25 ug/100 cm^2, whereas levels from their unopened counterparts ranged from 0.2 to 31 ug/100 cm^2. These levels, particularly for the used "decontaminated" drums, were considerably lower than those measured during our initial survey in August 1984.

B. Medical

A total of seven urine samples were collected from the two workers during the August 1984 survey. Two of the samples (one for each worker) were pre-shift baseline samples. Neither of them had detectable levels of DCB. Three samples were collected post-DCB charge on that same day. Detectable levels of DCB (4 ug/g Cre and 8 ug/g Cre) were found in two of the samples, one from each worker. Two samples were obtained post-DCB charge the following day (August 7, 1984). Both samples (one from each worker) had measurable levels of DCB (4 ug/g Cre and 5 ug/g Cre) (Table 7).

During the follow-up visit, a total of seven urine samples were again collected. Two were pre-shift samples collected August 26, 1985. Three post-DCB charge samples were collected that same day. Two post-DCB charge samples were collected the following day. None of the seven samples had detectable levels of urinary DCB (Table 8).

C. List of Former DCB Workers

The mailing of August 16, 1985 resulted in the return of 163 of the 262 (62.2%) questionnaires. Subsequently, on January 27, 1985, another mailing was sent to those 99 people whose questionnaires had not been returned. Thirty-six (36.4%) questionnaires from this second mailing were received.

Overall, 199 of 262 (76.0%) questionnaires were returned. Ninety-five people (36.3%) stated that they thought they had worked with DCB at Hilton-Davis. Forty people (15.3%) responded that they did not remember working with DCB. Ten people (3.8%) were unsure whether they had worked with DCB. Twelve people (4.6%) were reported to be deceased. The remaining 42 people (16.0%) were lost to follow-up. This classification included people for whom no current address or telephone number could be found (Table 9).

VII. DISCUSSION

A. Environmental

Of the 42 environmental (air, skin, work surface) samples collected during the August 1984 survey, 33 (78%) contained detectable levels of DCB. DCB was detected in all three types of environmental samples, which demonstrated that despite the use of personal protective equipment and decontamination with hypochlorite bleach solution, workers were exposed to DCB at low levels, and work surfaces outside of the charge room and personal protective equipment were contaminated with DCB.

The presence of DCB in the personal breathing-zone air samples indicated that deficiencies existed in the respirator protection program. Based on our observations of work practices and discusssion with workers, these deficiencies could have been related to a combination of factors including, but not limited to, improper storage, decontamination, and maintenance of the supplied air hoods. We observed that both air hoods were stored unprotected in the dirty change room, an area shown to be contaminated with DCB, which may explain its presence on interior surfaces of the air hood. However, the air hoods may also have become contaminated while they were being decontaminated with the bleach solution, since the solution is sponged on both the exterior and interior surfaces.

Maintenance-related problems were noted which may have compromised the effectiveness of the air hoods. We observed that the air hose to one of the air hoods became disconnected at least once on both days of the initial survey. This situation, although brief, produced a temporary loss of positive air pressure inside the hood which may have resulted in exposure to DCB from the ambient environment.

The extent to which each of these deficiencies contributed to the overall breathing-zone exposures is unclear. The fact that they existed prompted the company to replace the existing air hoods with

a disposable, air-supplied total enclosure suit. These suits were shown to provide good protection, based on the results of the personal breathing-zone air samples obtained during the follow-up survey.

Stationary air sampling results showed that DCB was detected at low levels in areas outside the charge room during both surveys. Levels were highest in the dirty change room and were progressively lower in the clean change room and staging areas. The presence of airborne DCB in these areas is noteworthy because workers are typically unprotected when present in these rooms/areas. Based on our observations, we feel that the presence of airborne DCB in the change room was probably associated with the fact that there was no provision for maintaining the charge room under negative pressure. Furthermore, the charge room was not completely sealed from the dirty change room. An air vent was situated in the wall separating the charge room from the dirty change room, which allowed air movement between these two areas.

The results of the skin gauze samples show that workers were potentially exposed dermally to low levels of DCB while wearing the Tyvek® coveralls (initial survey) and the Tyvek® total enclosure suit (follow-up survey). It is unclear why these samples contained DCB, especially considering that both suits were made of impervious Tyvek® material. We suspect that these samples became contaminated not as a result of permeation of the Tyvek® but, rather, during donning/doffing of the coveralls or full body suit.

The presence of measurable quantities of DCB on surfaces treated with sodium hypochlorite bleach solution suggests that this method is only partially effective in removing DCB. Inability to effectively decontaminate or remove DCB from the charge room has resulted in low level contamination of other areas, such as the dirty and clean change rooms and the staging area. Whether the partial ineffectiveness of the bleach decontaminating solution was attributable to insufficient contact time of the bleach solution with DCB or to incomplete conversion of the DCB to quinone-type compounds, is unclear. Work conducted by Borden, Inc., indicates that the hypochlorite treatment does not provide for complete conversion (oxidation) of the DCB.[3] As an alternative, they found that an aqueous solution of 10% sodium ethyl hexyl sulfate and 5% tetrapotassium pyrophosphate, when blended in a jet sprayer, did an effective job of removing DCB from contaminated work surfaces, with reduction of 90-99%. Since DCB is not chemically altered by this solution, the washings must be collected and chemically treated (by diazotization) in order to eliminate DCB.

B. Medical

The amounts of DCB found in the urine of the workers during the August 1984 survey were low, barely above the limit of detection. However, because DCB is a suspect bladder carcinogen, exposures should be limited to the lowest feasible level.

The fact that no urinary DCB was detected in the 1985 follow-up survey indicates that the changes implemented by Hilton-Davis were somewhat effective in reducing exposures.

The Company's present policy is to perform annual urinary cytology screening for potentially-exposed current employees. 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 Hilton-Davis. The Company does not currently debrief persons leaving employment as to the necessity of receiving such testing. The Company, Union, and individual workers should develop a mechanism for arranging such a debriefing and screening program.

In addition to the urinary cytology screening which currently is performed, periodic sampling for urinary DCB should be instituted, to be conducted simultaneously with environmental sampling on those workers with potential exposure at that time. As a suspect carcinogen, levels of DCB in the urine should be kept at the lowest feasible level (below the current analytical limit of detection, in this case).

The appearance of detectable levels of DCB should be a signal that some changes, or tightening of work practices, are 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.

VIII. RECOMMENDATIONS

1. Based on the finding that airborne DCB was present in areas outside of the charge room (i.e., dirty and clean change rooms), appropriate ventilation should be installed to ensure that the charge room is maintained, at all times, under negative pressure, relative to adjacent areas. In the meantime, the passive air vent in the wall separating the charge room should be covered to eliminate the potential for air movement into the dirty change room.

2. The Company should determine whether providing longer contact time between the hypochlorite solution and DCB-contaminated surfaces

would consistently reduce DCB surface levels to below 10 mg/100 cm^2 for all surfaces treated in this manner. If this modification is shown to be ineffective, the Borden decontamination method[3] should be considered.

3. Workers should continue to receive instruction relating to the importance of proper decontamination and should be provided with sufficient time to ensure that the decontamination solution is applied thoroughly to all work surfaces.

4. The Company should institute periodic sampling for urinary DCB, to be conducted simultaneously with environmental sampling on those workers potentially exposed to DCB at that time. Samples should be analyzed using the most sensitive method available. Workers should be informed of their results.

5. The Company's present policy of performing urinary cytology screening should be continued. In addition, the Company should debrief departing employees of the need for continued medical monitoring for bladder cancer. Such monitoring should be continued for the rest of the employee's life. A program to make this screening available to employees once they leave employment at Hilton-Davis should be instituted.

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X. AUTHORSHIP AND ACKNOWLEDGEMENTS

Report Prepared by:	Matthew A. London, M.S. Industrial Hygienist
	James M. Boiano, M.S. Industrial Hygienist
Industrial Hygiene Assistance	Steven A. Lee, M.S., C.I.H.
Originating Office:	Hazard Evaluations and Technical Assistance Branch Division of Surveillance, Hazard Evaluations, and Field Studies
Analytical Assistance	Anthony W. Smallwood Clinical and Biochemical Support Section Division of Biological and Behavioral Sciences
	Charles Neumeister Measurements Development Section Division of Physical Sciences and Engineering
Report Typed By:	Toni Frey

XI. DISTRIBUTION AND AVAILABILITY OF REPORT

Copies of this report are currently available upon request from NIOSH, Division of Standards Development and Technology Transfer, Publications Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), 5285 Port Royal, Springfield, Virginia 22161. Information regarding its availability through NTIS can be obtained from NIOSH Publications Office at the Cincinnati address. Copies of this report have been sent to:

1. Hilton-Davis Chemical Company
2. International Chemical Workers Union, Health & Safety Dept.
3. International Chemical Workers Union, Local 342
4. NIOSH, Region V
5. OSHA, Region V

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 1
Air Samples for 3,3'-Dichlorobenzidine

Hilton-Davis Chemical Company
Cincinnati, Ohio
HETA 84-058
August 6-7, 1984

Date	Sample Description	Sample Time (min)	Sample Volume (liters)	3,3'-Dichlorobenzidine Concentration (ug/M^3)	(ppb)
8-6-84	Operator 1	47	141	0.43	0.041
8-6-84	Operator 2	44	132	0.45	0.043
8-7-84	Operator 1	67	201	0.60	0.058
8-7-84	Operator 2	67	201	0.34	0.033
8-6-84	Area Sample, Clean Change Room	60	180	0.27	0.026
8-7-84	Area Sample, Clean Change Room	63	189	0.24	0.023
8-6-84	Area Sample, Staging Area	57	171	0.16	0.015
8-7-84	Area Sample, Staging Area	62	186	ND	ND

Limit of Detection - 0.025 ug/sample
Evaluation Criteria: DCB has been identified as a carcinogen. Because it is not possible to establish a safe exposure level for a carcinogen, NIOSH recommends restricting exposure to below levels that can still be reliably measured in the workplace.
ug/M^3 = micrograms DCB per cubic meter of air
ppb = parts DCB per billion parts air.
ND = nondetectable; DCB, if present, would be below 0.13 ug/m^3 or 0.012 ppb

Table 2
Personal and General Air Samples for 3,3' Dichlorobenzidine

Hilton-Davis Chemical Company
Cincinnati, Ohio
HETA 84-058
August 26-27, 1984

Date	Sample Description	Sample Time (min)	Sample Volume (liters)	3,3'-Dichlorobenzidine Concentration (ug/M^3)	(ppb)
8-26-85	Operator 1	34	102	ND	ND
8-27-85	Operator 1	37	111	ND	ND
8-26-85	Operator 2	30	90	ND	ND
8-27-85	Operator 2	33	99	ND	ND
8-26-84	Area Sample, Dirty Change Room	85	255	0.78	0.076
8-27-84	Area Sample, Dirty Change Room	64	192	0.57	0.055
8-26-84	Area Sample, Clean Change Room	84	252	0.21	0.020
8-27-84	Area Sample, Clean Change Room	64	192	Lost in Analysis	
8-26-85	Area Sample, Staging Area	86	258	ND	ND
8-27-85	Area Sample, Staging Area	65	195	ND	ND
8-26-85	Area Sample, Above Ice Chute	84	252	ND	ND
8-27-85	Area Sample, Above Ice Chute	66	198	ND	ND

Limit of Detection - 0.025 ug/sample
Evaluation Criteria: DCB has been identified as a carcinogen. Because it is not possible to establish a safe exposure level for a carcinogen, NIOSH recommends restricting exposure to below levels that can still be reliably measured in the workplace.
ug/M^3 = micrograms DCB per cubic meter of air
ppb = parts DCB per billion parts air.
ND = nondetectable; DCB, if present, would be no higher than an airborne concentration (in ug/M^3) determined by dividing the limit of detection (0.025ug) by the air volume in cubic meters.

Table 3

Skin Gauze Patch Sample Results for 3,3'-Dichlorobenzidine

Hilton-Davis Chemical Company
Cincinnati, Ohio
HETA 84-058
August 6-7, 1984

Date	Sample Description	3,3'-Dichlorobenzidine concentration (ug/25 cm^2)
8-6-84	Operator 1, right forearm	ND
8-6-84	Operator 1, left forearm	0.4
8-6-84	Operator 2, right forearm	0.2
8-6-84	Operator 2, left forearm	3.7
8-7-84	Operator 1, right forearm	0.3
8-7-84	Operator 1, left forearm	0.3
8-7-84	Operator 2, right forearm	1.7
8-7-84	Operator 2, left forearm	1.1

Limit of Detection - 0.2 ug/sample
Evaluation Criteria: DCB has been identified as a carcinogen. Because it is not possible to establish a safe exposure level for a carcinogen, NIOSH recommends restricting exposure to below levels that can still be reliably measured in the work place.
ND = nondetectable, less than 0.2 ug/sample

Table 4

Skin Gauze Patch Sample Results for 3,3'-Dichlorobenzidine

Hilton-Davis Chemical Company
Cincinnati, Ohio
HETA 84-058

August 26-27, 1985

Date	Sample Description	3,3'-dichlorobenzidine concentration (ug/25 cm^2)
8-26-85	Operator 1, right forearm	0.2
8-26-85	Operator 1, left forearm	0.2
8-26-85	Operator 2, right forearm	1.2
8-26-85	Operator 2, left forearm	ND
8-27-85	Operator 1, right forearm	ND
8-27-85	Operator 1, left forearm	0.2
8-27-85	Operator 2, right forearm	0.9
8-27-85	Operator 2, left forearm	0.3

Limit of Detection - 0.1 ug/sample
Evaluation Criteria: DCB has been identified as a carcinogen. Because it is not possible to establish a safe exposure level for a carcinogen, NIOSH recommends restricting exposure to below levels that can still be reliably measured in the work place.
ND = nondetectable, less than 0.1 ug/sample

Table 5

Surface Wipe Sample Results for 3,3'-Dichlorobenzidine

Hilton-Davis Chemical Company
Cincinnati, Ohio
HETA 84-058
August 6-7, 1984

Date	Sample Location/Description	3,3'-dichlorobenzidine concentration (ug/100 cm^2)
8-6-84	Inside Respiratory Airhood #1	4.9
8-6-84	Inside Respiratory Airhood #2	1.2
8-7-84	Inside work shoe	ND (<0.2)
8-7-84	Inside work shoe	ND (<0.2)
8-6-84	Bench Inside Clean Change Room	ND (<3.8)
8-6-84	Floor Inside Clean Change Room	27
8-6-84	Handle of Locker in Clean Change Room	5.7
8-6-84	West Shower Head and Valve, Shower Room	0.4
8-6-84	Handle of South Shower Room Door, Shower Room Side	1.4
8-6-84	Handle of North Shower Room Door, Dirty Change Room Side	30
8-6-84	Handle of West Charge Room Door, Dirty Change Rood Side	160
8-7-84	East Exterior Wall of DCB Charge Room, Above Charge Chute	ND (<0.2)
8-7-84	North Exterior Wall of DCB Charge Room	ND (<0.2)
8-7-84	Floor, Exterior North Side of DCB Charge Room	0.4
8-7-84	Exterior Handle of South Sliding Door to DCB Charge Room (Staging Area)	21
8-7-84	Wash Sink, East of DCB Charge Room	ND (<4.0)
8-6-84	Manhole Cover, DCB Reactor (#2)	ND (<2.0)
8-6-84	Top of Guardrail, West of DCB Reactor (#2)	2.4
8-6-84	Exterior Wall of Unopened Drum Containing DCB	2.3
8-6-84	Lid of Unopened Drum Containing DCB	7.5
8-7-84	Bottom Rim of Used, "Decontaminated" DCB Drum	830
8-7-84	Bottom Rim of Used, "Decontaminated" DCB Drum	2800
8-7-84	Exterior Wall of Used, "Decontaminated" DCB Drum	45
8-7-84	Exterior Wall of Used, "Decontaminated" DCB Drum	32
8-7-84	Lid of Used, "Decontaminated" DCB Drum	49
8-7-84	Lid of Used, "Decontaminated" DCB Drum	62

Hilton-Davis guideline - 10 ug/100cm^2
ND - Nondetectable; the limit of detection (LOD) ranged between 0.2 and 4.0 ug/sample.
Levels of DCB, if present, were below the levels reported in parentheses. The variability in LOD was probably due to the presence of foreign material in the sample.

TABLE 6

Surfaces Wipe Sample Results for 3,3'-Dichlorobenzidine

Hilton-Davis Chemical Company
Cincinnati, Ohio
HETA 84-058

August 26-27, 1985

Date	Sample Location/Description	3,3' dichlorobenzidine concentration (ug/100cm^2)
8-26-85	Staging area, door handle to charge room	0.46
8-26-85	Clean change room, floor	8.0
8-26-85	Shower water valve, west	ND
8-26-85	Dirty change room, door handle to charge room	30
8-26-85	Charge room, door to dirty change room	90
8-26-85	Charge room, handle of chute cover	830
8-26-85	Charge room, spatula blade	2400
8-27-85	Staging area, door handle to charge room	1.1
8-27-85	Clean change room, floor	2.6
8-27-85	Shower water valve, west	ND
8-27-85	Shower door handle, south	ND
8-27-85	Dirty change room, door handle to charge room	2.5
8-27-85	Dirty change room, floor	24
8-27-85	Dirty change room, door handle to shower	0.21
8-27-85	Dirty change room, air vent to charge room	0.31
8-27-85	Charge room, door to dirty change room	ND
8-27-85	Charge room, handle of chute cover	11
8-27-85	Charge room, spatula blade	1800
8-27-85	Charge room, east exterior wall above ice chute	0.11
8-27-85	Charge room, north exterior wall	0.90
8-27-85	Charge room, north exterior floor	1.00
8-27-85	DCB reactor (#2), manhole cover	0.24
8-27-85	DCB reactor (#2), top of west guardrail	0.12
8-27-85	Top rim of used "decontaminated" DCB drum	25
8-27-85	Exterior wall of used, "decontaminated" DCB drum	5.8
8-27-85	Bottom rim of used, "decontaminated" DCB drum	6.2
8-27-85	Top rim of unopened DCB drum	7.5
8-27-85	Exterior wall of unopened DCB drum	0.17
8-27-85	Bottom rim of unopened DCB drum	31

Hilton-Davis guideline - 10ug/100cm^2
ND - nondetectable, less than 0.060 micrograms (ug) per sample.

NOTE: 8/26/85 samples were collected before the DCB charging operation, in an attempt to assess the effectiveness of the monthly decontamination effort performed on 8/23/85. Samples collected on 8/27/85 were obtained after the charging operation.

TABLE 7

Urinary DCB Results

Hilton-Davis Chemical Company
Cincinnati, Ohio
HETA 84-058

August 6-7, 1984

Worker	Date	Time of Day	DCB (ug/g Creatinine)
1	8/6/84	7:30 a	none detected
1	8/6/84	12:25 p	4 ug/g Cre
1	8/6/84	2:35 p	none detected
2	8/6/84	7:30 a	none detected
2	8/6/84	2:30 p	8 ug/g Cre
1	8/7/84	2:45 p	4 ug/g Cre
2	8/7/84	2:45 p	5 ug/g Cre

Limit of detection is 10 ug DCB/Liter of urine

Table 8

Urinary DCB Results

Hilton-Davis Chemical Company
Cincinnati, Ohio
HETA 84-058

August 26-27, 1985

Worker	Date	Time of Day	DCB (ug/g Creatinine
1	8/26/84	6:50 a	none detected
1	8/26/85	12:45 p	none detected
1	8/26/85	3:12 p	none detected
2	8/26/85	7:05 a	none detected
2	8/26/85	12:45 p	none detected
1	8/27/85	3:05 p	none detected
2	8/27/85	12:00 p	none detected

Limit of detection is 10 ug DCB/Liter of Urine

Table 9

Results of DCB-status Questionnaire
Former Pigment Department Employees

Hilton-Davis Chemical Company
Cincinnati, Ohio
HETA 84-058

Response	Number of Respondents	
Remembered working with DCB	95	(36.3%)
Did not remember working with DCB	40	(15.3%)
Unsure whether worked with DCB	10	(3.8%)
Deceased	12	(4.6%)
Lost to follow-up	42	(16.0%)
Did not respond	63	(24.0%)
TOTAL	262	(100.0%)