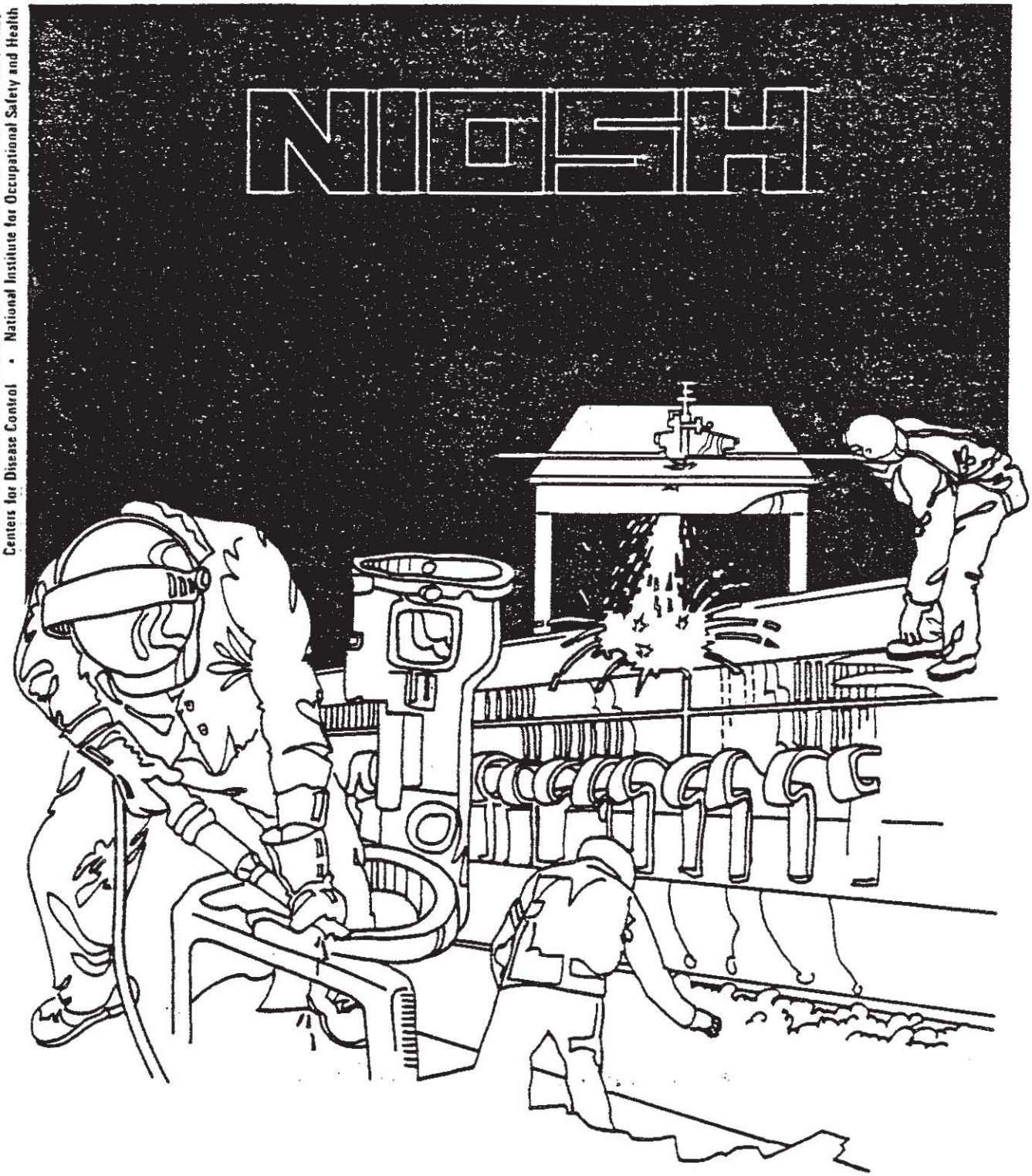
p Liddle Burgess

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES • Public Health Service
Centers for Disease Control • National Institute for Occupational Safety and Health

NIOSH



# Health Hazard Evaluation Report

80-082-773

## 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. 699(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.

HE 80-082-773
November 1980
PPG Industries/Natrium Plant
New Martinsville, West Virginia

NIOSH INVESTIGATORS:
William N. Albrecht, IH

## I. SUMMARY

On March 10, 1980, a request for a health hazard evaluation was received from Local 45, International Chemical Workers Union (ICWU), PPG Industries, New Martinsville, West Virginia. Hazards suspected to exist were restricted to the monochlorobenzene (MCB) manufacturing area of the Natrium Plant, and included exposure to benzene, para-dichloro-benzene (p-DCB), and polychlorinated biphenyls (PCBs).

The MCB area makes chlorinated benzene derivatives from benzene and chlorine gas. PCBs are formed as an impurity in the process. Fifty maintenance and production personnel on three shifts are responsible for the area, although only two were involved in processes of interest.

Personnel and area sampling was performed on July 11, 1980 to evaluate exposures at the para-dichlorobenzene drumming operation and during the removal of reaction residues, where PCB exposure was suspected.

The worker at the p-DCB drumming operation was exposed to an approximate level of 32.5 mg/M$^3$ of para-dichlorobenzene. An acceptible level as determined by the American Conference of Governmental Industrial Hygienists is 450 mg/M$^3$. The employee responsible for residue drumming was shown to have no measureable exposure to PCB during the course of his job. Area sampling confirmed the potential for airborne exposure to PCBs. Bulk material analysis showed no unreacted benzene in any of the products.

On the basis of the data obtained in this investigation, NIOSH determined that a hazard from exposure to para-dichlorobenzene and polychlorinated biphenyls did not exist at the time of the survey. Recommendations for reduction of para-dichlorobenzene exposure by engineering and personal protective methods are included in this report.

KEYWORDS: SIC 2869 (industrial organic chemicals), para-dichlorobenzene, polychlorinated biphenyls.

## II. INTRODUCTION

On March 10, 1980, a request for a health hazard evaluation was received from authorized representatives of Local 45, International Chemical Workers Union (ICWU), PPG Industries, New Martinsville, West Virginia. Hazards suspected to exist were restricted to the monochlorobenzene area of the Natrium Plant. Specifically, the substances and situations were; exposure to benzene in the general area, exposure to para-dichlorobenzene in the drumming area, and exposure to polychlorinated biphenyls during the dopp kettle blowdown. An interim report was issued in May 1980 describing the activities up to that date.

## III. BACKGROUND

Products made in the monochlorobenzene area are chlorinated derivatives of benzene viz. monochlorobenzene (MCB); the ortho and para isomers of dichlorobenzene (DCB); and the 1,2,3/1,2,4/1,3,4 isomers of trichlorobenzene (TCB).

Benzene is received in barge quantities (200-400 X $10^3$ gal./775-1550 X $10^3$l.); then transferred to storage tanks at the river terminus. The tank field is fenced, locked, and displays warnings denoting the benzene hazard. Workers are required to wear respiratory protection when engaged in measuring tank volume and other associated tasks. Benzene is piped to the manufacturing site where it is catalytically reacted with chlorine gas at elevated temperature and pressure. These variables are manipulated during the several stages of the reaction, thereby achieving the desired benzene-chlorine product. It is an enclosed system; entirely outdoors, except for the control room where the operators manage the process.

Various grades or mesh of p-DCB are drummed. Usually two employees are engaged in the procedure, although due to a decrease in production, only one was present during sampling. About six tons of material per shift are packaged. Responsibilities of the drum-man include: leveling of the p-DCB in the drums, transferring them to a scale for weight check, stencilling, and palletizing the containers. A moderate proportion of the workers time is spent within an enclosed booth.

PPG Industries modified their DCB process in an effort to maximize the ratio of para to ortho isomer recovered. Later, they discovered that this change also increased the levels of polychlorinated biphenyl (PCB), an impurity generated in the MCB scheme. Levels of contaminant present in the final species of the reaction series, TCB, were in excess of allowable market standards. Correspondingly, greater levels appeared in the residues generated by the MCB process.

The removal from the system of this sludge or residue is a procedure called "dopp kettle dropping" (DKD).

"Dopp kettle dropping" or "blowdown" is a maneuver which empties the contents of a steam jacketed vessel which has collected spent catalyst, and tarry residuals of the MCB process. During dopp kettle dropping, employees are required to wear appropriate air purifying respirators, neoprene gloves, and plasticized disposable suits. No superfluous personnel are allowed in the general area. The job is rotated among the area's workers and each man performs the DKD task about once per month. The collecting of the residue takes from 1 1/2 to 2 hours, while the emptying (DKD) ranges from 30-90 minutes in duration. It is customarily performed on Saturday morning.

Residue is piped at a moderate rate (to prevent splashing) into 55 gallon drums which are on a pallet. A pipe is used as a spigot. The operator remains about six feet from the drums while they are filling, but occasionally walks over to check the level. Once full, the drums are allowed to cool to prevent collapsing. They are then removed with a lift truck. As of March 1980, they are placed in a labeled, diked and fenced storage area.

Employees of the MCB production area were informed of proper work practices relative to the potential hazard of PCB exposure during the period February 12-16, 1980. The company has outlined safety measures, good work practices, and spill clean-up procedures for PCB.

## IV. METHODS AND MATERIALS

Bulk samples of each product in the MCB area and the residue were collected during the March 19, 1980 visit. The contents were given as MCB for Bulk #1, isomers of TCB for Bulk #2, o-DCB for Bulk #3, and p-DCB for Bulk #4. Only a confirmation of each solvent was requested. Bulk #5, dopp kettle residue was submitted for qualitative analysis of organics, in particular benzene, PCB, and chlorinated naphthenes.

All of the samples were analyzed by gas chromatography (FID) using a 20',10% SP-1000 column. No dilution of bulk liquids (#1, #2, #3) was necessary; however Bulk #4, a white granular substance was dissolved in $CS_2$ prior to analysis. A portion of the liquid from Bulk #5 was also diluted with $CS_2$ before analysis. Standards were analyzed under the same conditions as the samples and the retention times compared as a means of tenative identification. This was followed by mass spectrographic (MS) analysis for positive identification of each sample. Bulk #5 was sent to NIOSH's contract laboratory (UBTL) for quantitative analysis of PCB. Analytical difficulties encountered by UBTL with the quantitative analysis of PCB were clarified with the assistance of PPG Industries.

During the return visit on July 10-11, 1980, personal and area sampling was conducted in the p-DCB drumming area and during the DKD. SKC pumps were used at the p-DCB area at 50 mℓ/min. The sampling media was a 0.8μ MCE filter with a charcoal tube as a back-up. Each of the sample filters were desorbed in four mℓ. $CS_2$ containing one μℓ per mℓ. ethylbenzene as an internal standard and placed in an Ultrasonic bath for 30 minutes to complete the desorption. Samples were analyzed by gas chromatography following a modification of NIOSH Method S-281[1] using a Hewlett-Packard 5731A gas chromatograph. It should be noted that this method recommends sample collection on charcoal tubes, but is easily modified to include filters. A 6' X 1/8" stainless steel column packed with 20% SP-2100 on 100/120 Supelcoport was used with an oven temperature of 140°C. A and B sections of the corresponding back-up charcoal tubes were desorbed in one mℓ. $CS_2$ with one μℓ n-octane per mℓ as an internal standard. The fractions were analyzed like the filters, although an oven temperature of 180°C was used. Limits of detection were 0.02 mg pDCB/sample for the filters and 0.01 mg/sample for the charcoal tubes.

Personal and area samples were collected at the DKD. Dupont P-4000 pumps pulling 1.5 ℓ/min through Florisil tubes were used. Front and back sections of the Florisil tubes were desorbed separately in 1 mℓ benzene and analyzed by GC/MS. A blank Florisil tube and a spiked blank were also analyzed. Another bulk sample was taken and analyzed. It was suspended in enough benzene to make 100 mℓ. After the sediment settled, 1 mℓ was chromatographed on a Florisil column, shaken with sulfuric acid, and passed through a Florisil column again. The eluate was analyzed by GC/MS. A blank was also treated with the same clean-up procedure. The GC used a 28" X 1/8" glass column packed with 3% OV-101 on 100/120 mesh Ultrabond 20M. Oven temperature was $60^0$C for 1 minute, heating to $220^0$C at $8^0$C/min. carrier gas was helium at 34 cc/min. MS was operated in the impact mode.

## V. EVALUATION CRITERIA

p-dichlorobenzene vapor is an irritant of the eyes and upper respiratory tract. It is toxic to the liver. Solid particles in the eye cause pain. The solid material produces a burning sensation when held in contact with the skin, but the resulting irritation is slight. Warm fumes may irritate intact skin slightly on prolonged or repeated contact.[2] The current Threshold Limit Value (TLV)[3] as recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) is 450 mg/M$^3$ or 75 ppm.

In general, PCBs are eye irritants, hepatotoxins, and may cause chloracne. NIOSH recommends that no worker be exposed to a concentration greater than 1.0 microgram total PCBs per cubic meter of air (1.0 µg/M$^3$) determined as a time weighted average for up to a 10 hour workday, 40 hour workweek.[4]

## VI. RESULTS

The only GC peak in Bulk #1 was MCB. Major peaks in Bulk #2 were the three isomers of TCB; however it also contained other minor peaks identified as DCB isomers, bromochlorobenzenes, a dichlorobromobenzene isomer, and tetrachlorobenzenes. Bulk #3 was primarily o-DCB with a trace of other DCB's present. Only p-DCB was identified in Bulk #4. Bulk #5 was analyzed, but the results were discounted because of the previously mentioned analytical difficulties.

The combined masses collected on the filter-charcoal tube arrangement yield the following values for ambient concentrations of p-DCB in the drumming area:

| Sample Type | Location/Job | Concentration |
|---|---|---|
| Area-1 | Scales | 52.1 mg/M$^3$ |
| Area-2 | In front of filling toward booth | 30.7 mg/M$^3$ |
| Personal-1 | Extra operator-loader | 32.5 mg/M$^3$ |

Analysis of Florisil collection media determined these PCB concentrations at the DKD:

| | | |
|---|---|---|
| Area-1 | On top of drum adjacent to drum being filled | 49.3 ug/M$^3$ |
| Personal-1 | DKD operator | none detected |

There were no PCBs in the blanks. Average desorption efficiency of PCBs on Florisil was 104%. Dichlorobiphenyl, trichlorobiphenyl, and tetra chlorobiphenyl were seen in the Florisil samples. No monochloro- or pentachlorobiphenyl molecular ions were seen in the Florisil samples. Of the 1.7 µg collected during the sampling period, 0.4 µg (23%) were dichlorobiphenyls, 1.1 ug (65%) were trichlorobiphenyls, and 0.2 µg (12%) were tetrachlorobiphenyls. In the bulk, the PCBs detected were dicnloro-, trichloro-, tetrachloro-, and pentachlorobiphenyls. Other abundant chlorinated aromatic compounds were trichloro- and tetrachlorobenzenes (in great abundance) plus polychlorinated alkyl benzene, polychlorinated alkyl biphenyls, and polychlorinated alkyl terphenyls.

## VII. DISCUSSION AND CONCLUSIONS

Workers responsible for p-DCB drumming and DKD were not exposed at the time of the survey to concentrations of agents which may be considered detrimental to their health and well-being.

In contrast to aliphatic halogenated hydrocarbons, the toxicity of chlorinated benzenes generally decreases as the number of substituted chlorine atoms increases. Also, despite a structural similarity to benzene, blood dyscrasias and other sequallae are absent. The mono- and di- substituted chlorobenzenes accordingly have high TLVs. Exposure to p-DCB was determined to be less than 1/10 the recommended level.

PCBs in general have low volatility and high viscosity. While their toxicity is appreciable, the reluctance of PCBs to enter the vapor phase reduces their hazard potential, especially in an outdoor situation. During the short sampling period, no personal exposure was measured. The personal protective measures enacted by PPG are additional and necessary precautions when handling PCBs. The handling of the DKD was a well-managed and effective disposal procedure during the NIOSH visit.

## VIII. RECOMMENDATIONS

Although worker exposure at the p-DCB drumming operation is small, improvement in the ventilation would reduce levels even further. The local exhaust ventilation intake could be greatly improved by the addition of a circular flange on the duct. If drastic improvement were indicated, an arrangement modeling #4 in Figure 1 (VS-303) is suggested.[5] Gloves should be worn when workers level p-DCB in the drums with their hands. Disposable plastic gloves would be satisfactory for this purpose.

## IX. REFERENCES

1. NIOSH Manual of Analytical Methods 2nd ed. Vol. 3 S-281, p-dichlorobenzene. NIOSH No. 77-157-C (1977).

2. Proctor, N.H. and J.P. Hughes. Chemical Hazards of the Workplace. Lippincott Company, Philadelphia (1978).

3. TLVs® - Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1980, American Conference of Governmental Industrial Hygienists (1980).

4. NIOSH. Occupational Exposure to Polychlorinated Biphenyls (PCBs), NIOSH No. 77-225 (1977).

5. Industrial Ventilation 16th ed. ACGIH (1980).

## X. AUTHORSHIP AND ACKNOWLEDGEMENTS

| | |
|---|---|
| Evaluation Conducted and Report Prepared by: | William N. Albrecht<br>Industrial Hygienist<br>Industrial Hygiene Section |
| Laboratory Analysis by: | Measurements Support Branch<br>Division of Physical Sciences and Engineering<br>Cincinnati, Ohio<br><br>Utah Biomedical Technology Lab<br>Salt Lake City, Utah |
| Originating Office: | Hazard Evaluations and Technical Assistance Branch<br>Division of Surveillance, Hazard Evaluations and Field Studies<br>Cincinnati, Ohio |
| Report Typed by: | Jackie Woodruff<br>Clerk/Typist<br>Industrial Hygiene Section |

## XI. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this report are currently available, upon request, from NIOSH, Division of Technical Services, Publications Dissemination, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), Springfield, Virginia 22161. PPG shall post a copy of the determination for a period of 30 days upon receipt of the report, in accordance with 42 CFR Part 85.11(c).

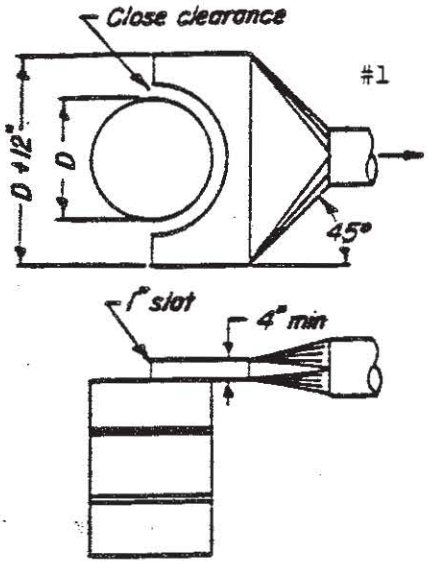
Copies of this report have been sent to:

1. PPG Industries/Natrium Plant
2. International Chemical Workers Union, Local 45
3. U.S. Department of Labor, Region III
4. NIOSH, Region III

FIGURE 1

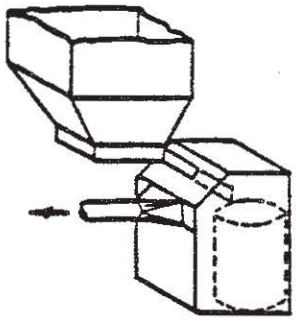
SPECIFIC OPERATIONS

#1



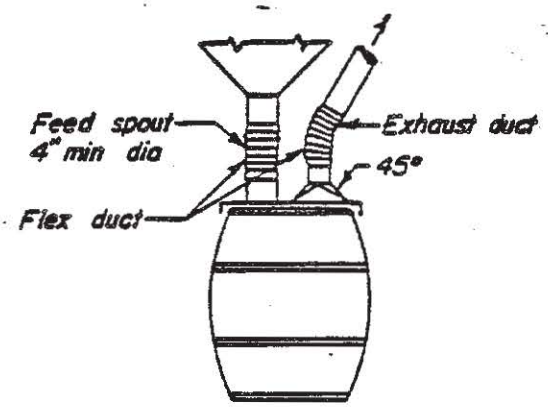

Q = 100 cfm/sq ft barrel top min
Duct velocity = 3500 minimum
Entry loss = 0.25 VP + 1.78 slot VP
Manual loading.

#2



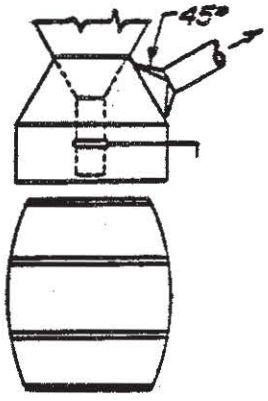
Q=150 cfm/sq ft open face area
Duct velocity = 3500 fpm minimum
Entry loss = 0.25 VP for 45° taper

#3




Q = 50 cfm x drum dia (ft) for weighted lid
150 cfm x drum dia (ft) for loose lid
Duct velocity = 3500 fpm minimum
Entry loss = 0.25 VP

#4




Q = 300-400 cfm
Duct velocity = 3500 fpm min
Entry loss = 0.25 VP

| AMERICAN CONFERENCE OF GOVERNMENTAL INDUSTRIAL HYGIENISTS | |
|---|---|
| BARREL FILLING | |
| DATE 1-64 | VS-303 |

DEPARTMENT OF HEALTH AND HUMAN SERVICES
PUBLIC HEALTH SERVICE
CENTERS FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
ROBERT A. TAFT LABORATORIES
4676 COLUMBIA PARKWAY, CINCINNATI, OHIO 45226

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE, $300

Third Class Mail

U.S.MAIL

POSTAGE AND FEES PAID
U.S. DEPARTMENT OF HHS
HHS 396