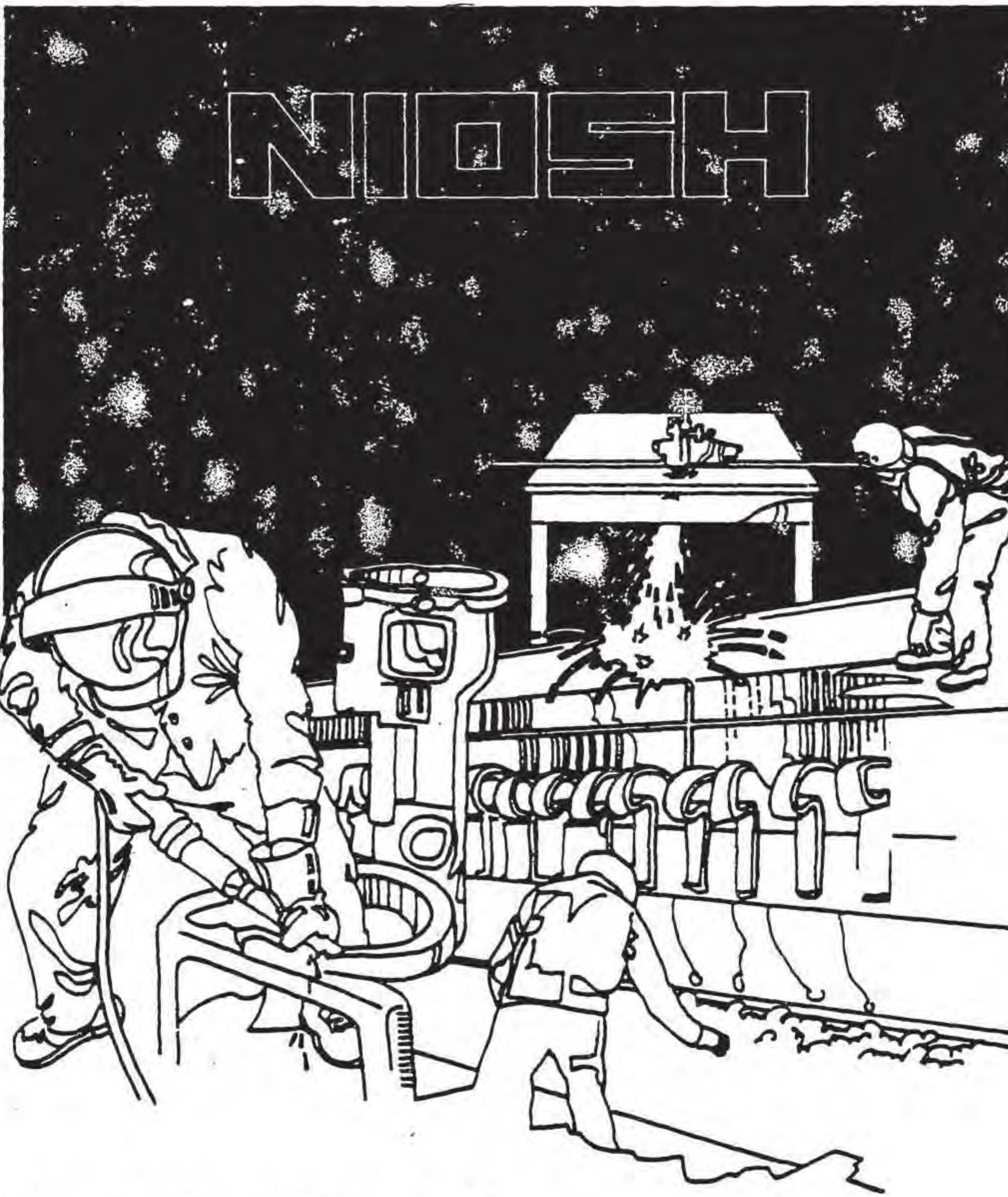
U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES ■ Public Health Service
Centers for Disease Control ■ National Institute for Occupational Safety and Health



Health Hazard Evaluation Report

HETA 81-335-1566
UNION CARBIDE CARIBE
PENUELAS, PUERTO RICO

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.

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I. SUMMARY

In June 1981, the National Institute for Occupational Safety and Health was requested to evaluate the potential health hazards from chemical exposures at the Union Carbide Caribe Petrochemical Plant, Penuelas, Puerto Rico. The requestor expressed especial concern regarding benzene exposures that might occur in many areas of the plant, including the Employee Relations (ER) Building where it was suspected that benzene-contaminated ground-water might be entering the building.

In July 1981, an initial visit was conducted during which 11 employees were interviewed and general area air samples were collected to determine air concentrations of organic vapors and carbon black. A followup survey was conducted in October 1983. Twenty-six Utility Unit employees and five office employees who worked in the ER Building were interviewed. Personal and area air samples were taken in the Utility Unit to evaluate exposure to hydrazine, morpholine, cyclohexylamine and benzene. Also, general area air samples were collected in the ER Building to evaluate possible organic vapor contamination.

In the first survey the highest organic vapor concentrations were found in an area sample taken above a sewer opening near the caustic addition unit: benzene (134 mg/m^3), toluene (43 mg/m^3), xylene (33 mg/m^3), and styrene (30 mg/m^3). Only the benzene level (NIOSH recommendation 3.2 mg/m^3 OSHA standard 32 mg/m^3) exceeded the relevant criteria. Levels for carbon black in the Acetylene Black bagging area were 0.3 mg/m^3 which was within the NIOSH recommendation of 3.5 mg/m^3. During the second visit, exposures of Utility Unit workers to hydrazine, morpholine, and cyclohexylamine were all below the limits of detection. Personal samples for benzene ranged from less than 0.03 mg/m^3 to 0.10 mg/m^3. In the occupied areas of the ER Building, area air concentrations of benzene ranged from 0.1 to 1.1 mg/m^3 with a mean of 0.4 mg/m^3. A "condemned" ER mens' restroom, which was no longer used because measurements taken by the Company had found benzene levels up to 126 mg/m^3 in this room, had a benzene level of 1.7 mg/m^3. (One hundred benzene samples collected by Union Carbide in the ER Building during August and September 1983 ranged from 0.3 to 126 mg/m^3, with a mean of 12 mg/m^3.)

During the first visit, symptoms reported to be experienced at work by the 11 employees interviewed included mucous membrane irritation (8), episodes of chest discomfort at work (6), anxiety or nervousness at work (5), low back pain (6), rash (3), and miscarriage (1). During the second visit, five employees who worked in the ER Building reported noticing a chemical odor occasionally in the building, especially during the rainy season. Eighteen of the 26 Utility Unit employees

reported experiencing symptoms of mucous membrane irritation while working in the Utility Unit, and four Utility Unit employees described experiencing objectionable chemical odors while attending employee training sessions in the ER building. Utility Unit employee interviews regarding respirator use suggest that there might have been some confusion among these employees regarding the care and use of their respirators.

On the days of testing, measured chemical exposures in areas usually occupied by employees did not exceed the criteria of this report, but potential for excessive employee exposure to benzene existed in the Employee Relations Building because of Benzene-contaminated ground water that could cause excessive benzene levels to be present episodically in some areas of the building. Frequent environmental monitoring will be necessary to assure that possibly harmful exposure to benzene does not occur to employees working in this building. Recommendations concerning the ER building and the respiratory protection program are contained in Section VIII. Since the time of the survey the company has mothballed this operation.

KEYWORDS: SIC 2869, 2911 Benzene, Toluene, Xylene, Carbon Black.

II. INTRODUCTION

In June 1981, the National Institute for Occupational Safety and Health received a request from the Union de Trabajadores Petroquimicos to evaluate potential health hazards from chemical exposures at the Union Carbide Caribe Petrochemical Plant in Penuelas, Puerto Rico. The requestor expressed especial concern regarding benzene exposures that might occur in many areas of the plant, including the Employee Relations (ER) Building where it was suspected that benzene-contaminated ground-water might be entering the building.

An initial visit was conducted in July 1981. An interim report containing preliminary results and recommendations from the first survey was issued in September 1981. After lengthy discussions between NIOSH and Union Carbide regarding access to company industrial hygiene data and the scope of the follow-up study, a follow-up survey was conducted in October 1983. A letter containing the preliminary results and recommendations from the second visit was distributed in November 1983. A letter containing the final industrial hygiene results was issued in March 1984.

III. BACKGROUND

The Union Carbide Caribe (UCCI) facility is a petrochemical complex which occupied 738 acres and employed up to 1,300 workers. The plant could produce (when the respective units were operating) ethylene oxide, glycol ethers, polyethylene, olefins, cumene, phenol, acetone, bis-phenol A, butanol, butadiene, and acetylene black.

Several years prior to the survey the company became aware that the ground water under the plant site was contaminated with solvents--primarily benzene, toluene, and xylene. The source of the chemical contamination was thought to be one or more of the several large petrochemical plants that formerly operated in the area. Occasionally, especially during periods of heavy rain, solvent odors would become quite noticeable in certain areas of the plant site. These odors were particularly noticeable in the ER building and the Company had expended considerable effort to discover the pathways through which the solvents entered this building and to prevent such entrance. The company periodically withdrew the solvent mixture from the water table and used this solvent mixture as fuel in the Utility Unit boilers.

Petroleum distillate products were the feedstocks for the petrochemical complex. In the olefin unit these petroleum distillates underwent thermal cracking to generate olefins, which were then piped to the various production units as an intermediate feedstock. The petroleum distillates were heated in a bank of furnaces and piped to a separation system gas fractionator that separated the light ends from the heavy ends. The light ends (H_2, CH_4, C_3H_8, C_2H_4, C_2H_6, C_2H_2, and C_4H_6) were piped to compressors, then to separators to separate the various substances. The heavy end., which left the gas fractionator, were separated into benzene, toluene, xylene, C_5's and C_9's. Some of the heavy ends were used to fuel UCCI's Utilities Unit.

The oxide II unit produced primarily ethylene oxide and ethylene glycol, along with triethylene glycol, TEG glycol, ethyl cellosolve, carbitol and ET glycol (ETG). In this unit, ethylene was combined with oxygen to form ethylene oxide which was stored in the liquid phase. Ethylene oxide was reacted with water to form glycol. The glycol was then piped to different glycol processes. Glycol refining separated the light (monoglycols) from heavy glycols. The heavy glycols were reacted with ethylene oxide to form triglycol and other mixed heavy glycols. There was also a refining and further separation of glycols.

The polyethylene plant, which was built in the early 1970's, utilized a high-pressure process and could produce 300 million lbs. of polyethylene per year. Ethylene was mixed with initiators, then compressed to 30,000 to 38,000 pounds per square inch (psi) before entering a reactor where it was preheated to 160-170' C to inititate an exothermic reaction. The process stream was then passed through a special valve which allowed a reduction in the pressure. The entire reactor area was enclosed by roofless concrete walls, which were 14 inches thick. Unreacted agents were removed from the process stream, and the polyethylene passed through a primary and secondary separator. It was extruded, pelletized, dried and loaded in 50,000 lb. van loaders for cargo shipping. The polyethylene unit also included a hot process area where additives were mixed with the polyethylene. In the hot process, the polyethylene was remelted and various additives (antioxidants, antiblocking agents, slip agents and diatomaceous earth) were loaded in hoppers and mixed with the polyethylene. The polyethylene was then extruded, pelletized, dried and loaded for shipping.

UCCI had its own Utility Unit which was capable of producing some of the electricity, steam, water and air used in UCCI's processes. The steam section had three boilers that delivered steam at pressures ranging from 200 to 1,100 psi throughout the plant. The water section was responsible for demineralizing boiler feed water; pumping process water, sea water, and cycle cooling water; and generating potable water from wells in Yauco and Penuelas. The air unit provided process and instrument air for the plant.

The acetylene black unit utilized acetylene to produce acetylene black (a form of carbon black), which was widely used in the car battery, licorice, and cosmetics (mascara) industries. Acetylene was fed into a complex of retorts where it was pyrolized. Acetylene black was drawn off the top of the retorts, collected in a cyclone, passed through primary and secondary filters, densified (i.e. pressed together to remove air), then loaded in bagging silos and finally hoppered in 12-pound bags. The bags were placed under the silos manually. After they were filled, the bags passed through a conveyor system which pressed the air out of the bags, sealed them, and transported them to the loading dock. Carbon coke was also formed in the retorts. It dropped onto a conveyor system below the retorts and was transferred to hoppers outside the building where it was bagged (by contract workers) and shipped to a landfill.

The butanol unit produced C_4 aldehydes and alcohols. The process begins with an oxygen unit which produced O_2; nitrogen was a byproduct. The O_2 was mixed in the Texaco-Syn Gas system. This reaction partially oxidized the petroleum distillates; CO_2, which was also produced, was later removed. C_3H_6 (propylene) was added to the partially oxidized naphtha in the presence of a catalyst in the LPO Reaction System to form C_4 aldehydes, isobutonal and n-buty alcohol. The n-butyl alcohol was refined.

IV. EVALUATION DESIGN AND METHODS

A. Environmental

1. First Visit

NIOSH investigators conducted an initial survey on July 15-17, 1981. At that time, area samples for organic vapors were collected by two different methods. 3M OVM (organic vapor monitor) badges were used to collect samples to be used for qualitative analysis. Air samples were also collected on charcoal tubes using portable sampling pumps at a flow rate of 200 cc/min. Bulk samples of substances were also obtained to aid in laboratory analysis of the samples. Air samples for organic vapors were collected at the Olefin Hydrotreater Unit, Gas Fractionation Column α2, Caustic Addition Unit, Ethylene Oxide Unit, and the Wastewater Treatment Plant.

General area air samples for carbon black were taken at the acetylene black bagging booth α1 and beneath the flattener unit. Respirable dust samples were collected on preweighed polyvinyl chloride (PVC) filters by means of a portable pump equipped with a 10 mm nylon cyclone at a flow rate of 1.7 liters per minute. General area air samples for total dust were taken in the same locations using preweighed PVC filters and portable pumps calibrated at 2.0 liters per minute. General area air samples for respirable and total dust were also taken in the Polyethylene Polyfinishing Unit Batch Unit α1 using the same methods described above.

2. Second Visit

A followup survey was conducted on October 19-20, 1983, to evaluate Utility Unit worker's exposures to hydrazine, morpholine, cyclohexylamine and benzene. Also, air samples were collected in the Employee Relations Building to evaluate possible organic vapor contamination of the offices and classrooms being used at that time.

Utility Unit

For each of the three boiler additives (hydrazine, morpholine and cyclohexylamine), two personal breathing-zone air samples were collected from utility workers and one area air sample was collected in the Chemical Shack from near the chemical addition process. The samples were collected on silica gel tubes at a flow rate of 0.2 liters per minute and analyzed by gas chromatography using NIOSH Method PaCAM 248 for hydrazine and NIOSH Method S-150 for morpholine and cyclohexylamine.[8]

Six personal breathing-zone air samples for benzene were collected from utility workers, and one area air sample was collected from near the quench oil pumps. The samples were collected on charcoal tubes at a flow rate of 0.2 liters per minute and analyzed by gas chromatography using NIOSH Method S-311.[8] During the days of testing, the solvent fuel (primarily benzene, toluene, and xylene) periodically obtained from the contaminated water table was not used to fuel the Utility Unit boilers.

Employee Relations Building

Thirteen area air samples were collected in classrooms, offices, and restrooms in the Employee Relations Building and in the Laboratory Building. The samples were drawn at 0.2 liters per minute through charcoal tubes for five to seven hours. A sample from a restroom that had been closed due to the episodic presence of excessive benzene concentrations was screened by gas chromatography/mass spectrophotometry. The major contaminants were n-pentane, n-hexane, benzene, ethyl benzene, and xylene; thus, the remaining 12 samples were analyzed for these compounds by gas chromatography using NIOSH Method 127.[9]

B. Medical

All available employees on the day and afternoon shifts in the Utility Department were interviewed, as were five randomly selected employees who worked in the ER Building. In addition to the above activities, the UCCI Medical Director was interviewed regarding the company program for monitoring employee health.

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 only 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. Toxicity

The adverse health effects from excess exposure (exposures to airborne concentrations above the evaluation criteria) are summarized below:

Benzene

Benzene is a colorless liquid. Acute exposure causes central nervous system depression; typical symptoms may be light-headedness, headache, nausea, and abdominal discomfort. Chronic exposure results in depression of blood cell formation and is associated with an increased incidence of leukemia. Long term exposure to low concentrations has been followed by aplasia and fatty degeneration of the bone marrow.

In 1977 OSHA issued an emergency temporary standard of 1 ppm, but this standard was stayed by the federal courts, and the current Federal OSHA permissible exposure limit[1] is 10 ppm (32 mg/m^3.) During NIOSH testimony at the OSHA benzene hearings in July 1977, NIOSH recommended that benzene be considered carcinogenic in man and that exposures to benzene be kept as low as possible. A 1 ppm (3.2 mg/M^3) ceiling exposure limit was recommended largely on the basis of the sampling and analytical technology existing at that time.

Carbon Black

NIOSH recommends that occupational exposure to carbon black be controlled so that employees are not exposed to carbon black at a concentration greater than 3.5 mg/m^3, or to polycyclic aromatic hydrocarbons (PAHs) at a concentration greater than 0.1 milligrams, measured as the cyclohexane-extractable fraction, per cubic meter of air (0.1 mg/m^3), determined as a time weighted averaged (TWA) concentration for up to a 10-hour workshift in a 40-hour work week.[3] The present OSHA PEL is also 3.5 mg/m^3 TWA, measured as total dust over an 8-hour work shift.[2]

The NIOSH recommended occupational exposure limits are based on data indicating that carbon black may cause both temporary and permanent lung damage and skin irritation. Particulate polycylic organic material (PPOM), polynuclear aromatic hydrocarbons (PNAs) and PAHs are terms frequently encountered in the literature and often used interchangeably. Some of these PAHs such as 3, 4-benzpyrene, pyrene, and 1, 2-benzpyrene are formed during carbon black manufacture. Their adsorption on the carbon black could pose a risk of cancer after exposure to the carbon black.[3]

Ethylbenzene

Ethylbenzene is a colorless liquid that is an irritant of the skin and mucous membranes. At high concentrations it can produce confusion and extreme drowsiness. Humans exposed at 1000 ppm experienced eye irritation. At 2000 ppm they experienced lacrimation, nasal irritation and vertigo.[1] The ACGIH TLV[4] and the OSHA PEL is 100 ppm (435 mg/m^3).[2]

Hexane

Normal hexane is a mild upper respiratory irritant and causes central nervous system depression. In industry, mild symptoms such as dizziness have been observed when concentrations exceeded 1000 ppm but not when below 500 ppm.[5] Until recently, chronic effects from hexane and similar hydrocarbons had rarely been reported. However, in 1967, 17 cases of polyneuropothy were reported among workers exposed to n-hexane at concentrations between 500 and 1000 ppm. Subsequent animal studies demonstrated functional disturbances of the peripheral nerves of mice at 250 ppm but not at 100 ppm. Other studies reported n-hexane neuropathy among furniture workers and among workers exposed to n-hexane used as a solvent in plastic cements. It is postulated that 2, 5-hexanedione, a metalolite of n-hexane, is the neurotoxic agent.[1] The OSHA PEL for n-hexane is 500 ppm (1800 mg/m^3) and the ACGIH TLV[4] is 50 ppm (180 mg/m^3.) The NIOSH recommended exposure limit is 100 ppm (360 mg/m^3).

Napthalene

Overexposure to napthalene causes eye irritation, headache, confusion, malaise, sweating, abdominal pain, nausea and vomiting. Severe intoxication can result in destruction of the red blood cells. Skin contact may lead to hypersensitivity (allergic) dermatitis. High exposures on a long-term basis may produce cataracts.[1] The ACGIH TLV[4] of 10 ppm (50 mg/m^3) was set to avoid eye irritation. The OSHA PEL is also 10 ppm.

Pentane

Pentane is a colorless liquid that can irritate the mucous membranes. At extremely high concentrations it may produce extreme drowsiness. Repeated skin contact may cause defatting of the skin thus leading to drying and cracking of the skin.[1] The OSHA PEL for pentane is 1000 ppm (2,950 mg/m^3) and the ACGIH TLV is 600 ppm (1800 mg/m^3). The NIOSH recommended exposure limit is 120 ppm (354 mg/m^3).

Toluene

Toluene is a colorless liquid that can cause central nervous system depression. Humans exposed at 200 ppm for four hours experienced mild fatigue, weakness, confusion, and lacrimation. Humans exposed to 600-800 ppm experienced euphoria, headache, dizziness, and nausea in addition to the above symptoms. Prolonged skin contact may cause defatting of the skin, thus producing drying and cracking of the skin.[1] The ACGIH TLV and the NIOSH recommended exposure limit is 100 ppm (375 mg/m^3). The OSHA PEL is 200 ppm (750 mg/m^3).

Xylene

Xylene vapor may cause irritation of the eyes, nose, and throat. Repeated or prolonged skin contact with xylene may cause drying and defatting of the skin which may lead to dermatitis. Liquid xylene is irritating to the eyes and mucous membranes, and aspiration of a few milliliters may cause chemical pneumonitis, pulmonary edema, and hemorrhage. Repeated exposure of the eyes to high concentrations of xylene vapor may cause reversible eye damage. Acute exposure to xylene vapor may cause central nervous system depression and minor reversible effects upon liver and kidneys. At high concentrations xylene vapor may cause dizziness, staggering, drowsiness, and unconsciousness.[6] Workers exposed to concentrations above 200 ppm complain of loss of appetite, nausea, vomiting, and abdominal pain. Brief exposure of humans to 200 ppm has caused irritation of the eyes, nose, and throat.[6]

The current OSHA standard for xylene is 100 ppm (435 mg/m^3) averaged over an 8-hour work shift.[2] NIOSH has recommended that the permissible exposure limit be changed to 100 ppm, averaged over a work shift of up to 10 hours per day, 40 hours per week, with an acceptable ceiling level of 200 ppm averaged over a 10-minute exposure.[7] The ACGIH TLV[4] is 100 ppm (435 mg/m^3) with a short term exposure limit (STEL) of 150 ppm (655 mg/m^3) for a 15-minute exposure.[4]

VI. RESULTS

A. Environmental

1. July 1981

An area sample above a sewer opening near the Caustic Addition Unit yielded the following organic vapor concentrations: benzene (134 mg/m^3), toluene (43 mg/m^3), xylene (33 mg/m^3), and styrene (30 mg/m^3). At the Olefin Unit hydrogenator 0.53 mg/m^3 of styrene was found. Organic vapor detected in the pyrolysis oil area were: benzene (1.0 mg/m^3), toluene (0.3 mg/m^3), styrene (0.8 mg/m^3) and naphthalene (0.5 mg/m^3). There were no organic vapors detected downwind of the distilling section of the wastewater treatment plant.

Airborne dust concentrations in the area of the acetylene black bagging booth and beneath the flattener unit were 0.3 mg/m^3 and 0.1 mg/m^3, respectively. Side-by-side samples collected using cyclone preselectors showed that all of the dust was in the respirable size range. The evaluation criterion is 3.5 mg/m^3.

The polyethylene polyfinishing area had 3.9 mg/m^3 of total dust and 0.3 mg/m^3 of respirable dust.

2. October 1983 Survey

Utility Unit

Utility worker exposures to hydrazine, morpholine, and cyclohexylamine were all below the limits of detection. These workers showed personal breathing zone (PBZ) benzene levels ranging from less than 0.03 mg/m^3 to 0.10 mg/m^3 with a mean of 0.07 mg/m^3 (Table 1). (The Utility Unit workers wore organic vapor respirators when in areas posted for respirator use, so their actual exposures to benzene may be less than the levels measured.)

Employee Relations (ER) Building

Air concentrations of pentane, hexane, benzene, ethyl benzene, and xylene are presented in Table II. Benzene concentrations ranged from 0.1 to 1.1 mg/m^3, with a mean of 0.4 mg/m^3 in occupied areas of the building. One of the suspected pathways for the entrance of benzene into the ER Building from the benzene contaminated groundwater, a "condemned" ER men's restroom, had a benzene level of 1.7 mg/M^3. Classrooms no. 1 and 2 were the most contaminated rooms that were being used at the time of the survey.

Union Carbide Sampling Results

The Union Carbide Company provided a statistical summary of the 1982-1983 air monitoring data collected by Union Carbide. Eighty-eight personal breathing-zone (PBZ) air samples for measuring benzene concentrations in production areas of the plant ranged from less than 0.1 parts per million (ppm) to 3.2 ppm, with a mean of 0.3 ppm. Thirteen PBZ air concentrations for hydrazine taken in 1983 were all below detectable levels (<0.01 ppm).

In August and September 1983, air samples for benzene, toluene, and xylene were collected in the Employee Relations Building. One hundred benzene concentrations ranged from 0.1 to 42 ppm with a mean of 4.0 ppm. (After these results were obtained, the "condemned" rest room [highest benzene concentration 43 ppm, mean 8 ppm] was closed.) Ninety-seven toluene concentrations ranged from less than 0.1 ppm to 11.5 ppm with a mean of 1.0 ppm. One hundred and one xylene samples ranged from 0.3 to 314 ppm, with a mean of 42 ppm.

Respirator Program

As part of the evaluation all employees in the energy unit were interviewed regarding their use of respirators. The Utility Unit employees reported that the respiratory protection program had received much greater emphasis in the last two to three years and that supervisors were quite effective in enforcing use of respirators in posted areas around the storage tanks, in the boiler area, and in the chemical shack. (Comfo II half-face respirators with organic vapor cartridges were used.) The employees said that prior to 2-3 years ago however, masks were seldom used in the energy unit; several mentioned that the use of respirators was made mandatory in the chemical shack about May 1983.

When the energy unit employees were asked about what procedures they used to care for their respirators, most could not recall the proper procedures for respirator care. The shift supervisor stated that workers were supposed to record the number of hours that the respirators were used in order to judge the end of service life for the cartridges. The workers, however, stated that they would request new cartridges only when they noted a chemical odor while using the mask. Most would clean their mask only by occasionally wiping it out with a handkerchief. A few stated that they thought they should periodically clean the mask with alcohol. Others thought that there should be an area with detergent and wash basins for cleaning the masks, but they stated that the only facility available for them to clean the respirators was the handwashing basin in the employee locker room. No employees were aware of any procedure to have a person knowledgeable in the care of respirators periodically examine the respirators for deterioration and evaluate the function of their respirators. The plant°s written standard Procedure for Respiratory Protection (revised 6-7-82) did not include procedures for cleaning and inspecting respirators that are assigned to workers for long-term use.

B. Medical

1. First Visit (July 1981)

During the first visit, interviews were conducted with seven randomly selected workers as well as three workers who requested interviews and one employee who was reported to have possible occupationally related health symptoms. These employees were from the following areas of the plant: Acetylene Black, Polyethylene Addition, Hydrotreatment Maintenance, Olefins, and Gas Treatment. One interviewed worker had recently had a miscarriage while working her first week in the Polyethylene Addition unit, where she had to lift 50-100 pound bags routinely. Prior to her transfer she had worked in the Cumene Unit, where she reported that frequent benzene spills had occurred. Symptoms reported by the other interviewed employees included mucous membrane irritation while at work (8), episodes of chest discomfort at work (6), anxiety or nervousness at work (5), low back pain (6), and rash (3). Several workers said that they had difficulty obtaining access to their own medical records or the environmental monitoring data of the areas where they worked. All interviewed workers reported wearing respiratory protection devices at least part of the time while at work. However, no workers reported having undergone fit testing for these respiratory protection devices.

2. Second Visit (October 1983)

At the interviews conducted during the second visit, the employees who worked in the ER Building (ER) reported occasionally noticing a chemical odor in the building. These odors were thought to be due to seepage into the building of ground water contaminated with various chemicals (benzene, xylene, toluene, etc.) that were postulated to have leaked from a petrochemical plant (not owned by Union Carbide) that formerly operated in the area. The employees reported that these odors were first noticed in the ER building approximately 3 years earlier and were generally worse in the rainy season). The odors were usually strongest in the northeastern corner of the building near the main entrance. The five employees described the odor as noticeable but not strong enough to be objectionable. None of these employees reported any health problems that might be related to occupational factors.

Eighteen Utility Unit employees reported experiencing symptoms of mucous membrane irritation while working in the Utility Unit. These symptoms were especially frequent when the affected employees were exposed to fuel (reclaimed from refining operations) while working in the boiler or storage tank areas. Four employees in the Energy Unit reported experiencing objectionable chemical odors while attending employee training sessions in the ER Building. The Medical Director reported that he periodically performed blood counts on all plant employees with potential for benzene exposure (including those employees in the Utility Unit and ER Building) and that he had not detected any abnormalities related to benzene exposure.

VII. DISCUSSION AND CONCLUSIONS

The industrial hygiene measurements taken on the first visit found area airborne chemical levels that were within existing exposure criteria with the exception of one general area air sample for benzene. The observed operating procedures and equipment maintenance operations appeared adequate with the exception of local dust exhaust ventilation in the polyethylene addition unit that was ineffective because the dust capture baghouse was full and incapable of collecting any more dust.

At the first visit NIOSH investigators recommended that a respirator fit testing program should be instituted and that the company's policies regarding work assignments for pregnant employees be reviewed. In addition, they believed that the company and union should consider instituting a program to inform workers about the procedures employees could follow to have access to their medical and environmental exposure records. The recomendations made following the first survey are reproduced in Appendix A.

During the second NIOSH visit, worker exposures to benzene, hydrazine, morpholine, and cyclohexylamine in the Utility Unit were found to be well within the evaluation criteria. The Energy Unit workers reported occasionally experiencing mucous membrane irritation, but did not report any other effects which might be due to chemical exposure.

The employees in the Employee Relations building reported occasionally noticing chemical odors while working in the ER uilding. Several workers from the Utility Unit also mentioned noticing chemical odors while attending classes in the ER building. Ironically, this office building was found to present the greatest potential for excessive exposure to organic vapors (particularly benzene, xylene, and hexane) among the work sites at this plant. The ER Building had benzene air levels up to 42 ppm in August and September 1983. The source of contamination was thought to be the water table, which seemed to have been previously polluted by one or more of the several large petrochemical plants that formerly operated in the area. The workers and the company reported that the above-ground organic vapor levels tended to be higher during the rainy season when the water table rises.

The pathways for the entrance of contamination from the water table into the Employee Relations Building had not been fully elucidated. However, two of the restrooms appeared to be significant routes for contaminants to enter the rest of the ER building. Consequently, after the company discovered that high levels of benzene were occasionally present in these rooms (August-September 1983 survey), these restrooms were closed to employees. Followup air sampling by NIOSH in October 1983 (when these restrooms were exhausted to the outside so that they were under a negative pressure relative to the rest of the building) did show much lower levels of contamination in the building. However, it is not known whether the cleaner air resulted from ventilation improvements in the building or from other environmental changes, such as, a lowering of the water table.

Therefore, it is recommended that Union Carbide continue to evaluate the ER building benzene contamination problem with thorough and frequent air monitoring of the building, and make whatever changes are necessary to lower the year-round benzene concentrations to the lowest feasible level.

The results of the Utility Unit employee interviews regarding respirator use suggest that there may be some confusion among the Utility Department employees regarding the care and use of their respirators. It would, therefore, be advisable to schedule additional instruction periods concerning respirator care and use for the operators and maintanence personnel in the utilities unit. It would also be advisable to enforce an effective method that ensures that the respirator cartridges are changed with sufficent frequency. The cartridges should be changed at the end of the shift when the respirators are used for most of the shift, and at least once weekly for respirators used only for short periods on a daily basis. In addition, a facility should be provided where the respirators can be adequately cleaned and disinfected and the respirators should be periodically checked for component deterioration by a person who thoroughly understands respirators to assure that the masks are properly functioning. For respirators used daily only for brief periods, the face piece should be wiped with a damp cloth at the end of each work shift and the respirator should be thoroughly washed and sanitized at least weekly. Respirators used more extensively will require more frequent cleansing.

VIII. RECOMMENDATIONS

1. Union Carbide should continue to evaluate the ER building benzene contamination problem with thorough and frequent air monitoring of the building, and make whatever changes are necessary to lower the year-round benzene concentrations to the lowest feasible level. Until the benzene problem in the "contaminated" restrooms is alleviated, these rooms should remain closed and should be continously exhausted to the outside so that they are maintained under a negative pressure relative to the rest of the building.

2. It would be advisable to schedule additional instruction periods concerning respirator care and use for the operators and maintenance personnel in the utilities unit. It would also be advisable to enforce an effective method that ensures that the respirator cartridges are changed with sufficent frequency. In addition a facility should be provided where the respirators can be adequately cleaned and disinfected and the respirators should be periodically checked for component deterioration by a person who thoroughly understands respirators, to assure that the masks are properly functioning.

3. The recommendations made following the first survey are contained in appendix A.

IX. REFERENCES

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X. 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. Union de Trabajadores Petroquimicos, Penuelas, Puerto Rico
2. Union Carbide Caribe, Penuelas, Puerto Rico
3. NIOSH, Region II
4. OSHA, Region II

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 Benzene, Hydrazine, Morpholine, and Cyclohexylamine in the Utilities Unit

Union Carbide Corporation
Ponce, Puerto Rico
HETA 81-335

October 19, 1983

Job/Location	Sample Time	Concentration (mg/m^3) Benzene	Hydrazine	Morpholine	Cyclohexylamine
Outside Operator	7:20-13:15	0.08	-	-	-
Outside Operator	7:00-13:14	0.10	-	-	-
Outside Operator	13:57-20:07	0.06	-	-	-
Outside Helper	14:08-20:07	N.D.*	-	N.D.	N.D.
Pipefitter	7:38-14:36	0.04	-	-	-
Electrician	7:44-14:34	0.10	-	-	-
Boiler Operator	7:10-13:15	-	N.D.	-	-
Boiler Operator	13:55-20:07	-	N.D.	N.D.	N.D.
Area Sample Quench Oil Pump	8:30-15:16	0.11	-	-	-
Area Sample Chemical Shack	8:30-15:18	-	N.D.	N.D.	3.3
Evaluation Criteria		L.F.L.**	0.04, 2-hr ceiling	70	40
*N.D. = below limit of detection (mg/m^3)		(<0.003)	(<0.15)	(<0.15)	(<0.15)

**L.F.L. = lowest feasible level

Table II

Office Building Area Air Samples for Organic Vapors

Union Carbide Corporation
Ponce, Puerto Rico
HETA 81-335

October 19-20 1983

Location	Sample Time	Concentration (mg/m^3)				
		n-pentane	n-hexane	benzene	ethyl benzene	xylene
Classroom #2	9:00-15:56 (10/19)	0.4	16	1.1	1.0	2.6
Classroom #2	9:03-13:45 (10/20)	2.8	12	0.7	0.7	1.7
Classroom #5	9:03-15:50 (10/19)	N.D.	2.1	0.1	0.4	1.5
Classroom #5	9:08-13:50 (10/20)	N.D.	1.5	0.1	0.4	1.4
Mens' Room	9:08-15:55 (10/19)	N.D.	2.7	0.1	0.4	1.4
Mens' Room	9:08-13:50 (10/20)	0.4	1.8	0.1	0.4	1.4
Classroom #1	9:13-13:45 (10/20)	1.9	8.6	0.6	0.6	1.7
Secretarys' Office #1	9:18-13:50 (10/20)	N.D.	0.9	0.1	0.4	1.5
Labor Section Office	9:25-13:50 (10/20)	2.0	8.0	0.4	0.6	1.4
Lab - Hallway	9:39-14:04 (10/20)	N.D.	0.9	0.1	N.D.	0.5
Lab - Olefins/Oils	9:41-14:04 (10/20)	N.D.	0.4	0.002	N.D.	0.4
Condemned ER Mens' Room	8:57-13:45 (10/20)	1.9	34	1.7	2.1	5.9
Evaluation Criteria		350	360	L.F.L.	435	435

APPENDIX A

RECOMMENDATIONS MADE FOLLOWING FIRST VISIT TO UNION CARBIDE CARIBE INC. PENUELAS, PUERTO RICO

1. Policy and practices regarding potential exposures of pregnant women to chemical agents suspected or known to cause adverse reproductive outcomes should be reviewed. In particular, exposures to benzene, heavy lifting, or chemicals without labels of their actual contents should be avoided as much as possible.

2. A respiratory fit testing program is needed to insure that those working in areas where engineering controls are being installed or found to be technically infeasible are adequately protected.

3. Union and management should prepare educational materials and procedures insuring that workers are able to exercise their rights to personal medical and environmental data provided under the OSHA regulations concerning "Right to Know".

4. In areas where hazards have been identified and posted, (eg. benzene areas) Union Carbide Caribe should institute a program to control the sources of those emissions.

5. The local exhaust ventilation system in the polyethylene addition unit should be checked to ensure that it is operating before each shift begins work. The baghouse should be checked on a regular basis and cleaned out.

6. Industrial hygiene records concerning CO measurements and entry into confined spaces should be recorded and kept on file.