U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES ■ Public Health Service
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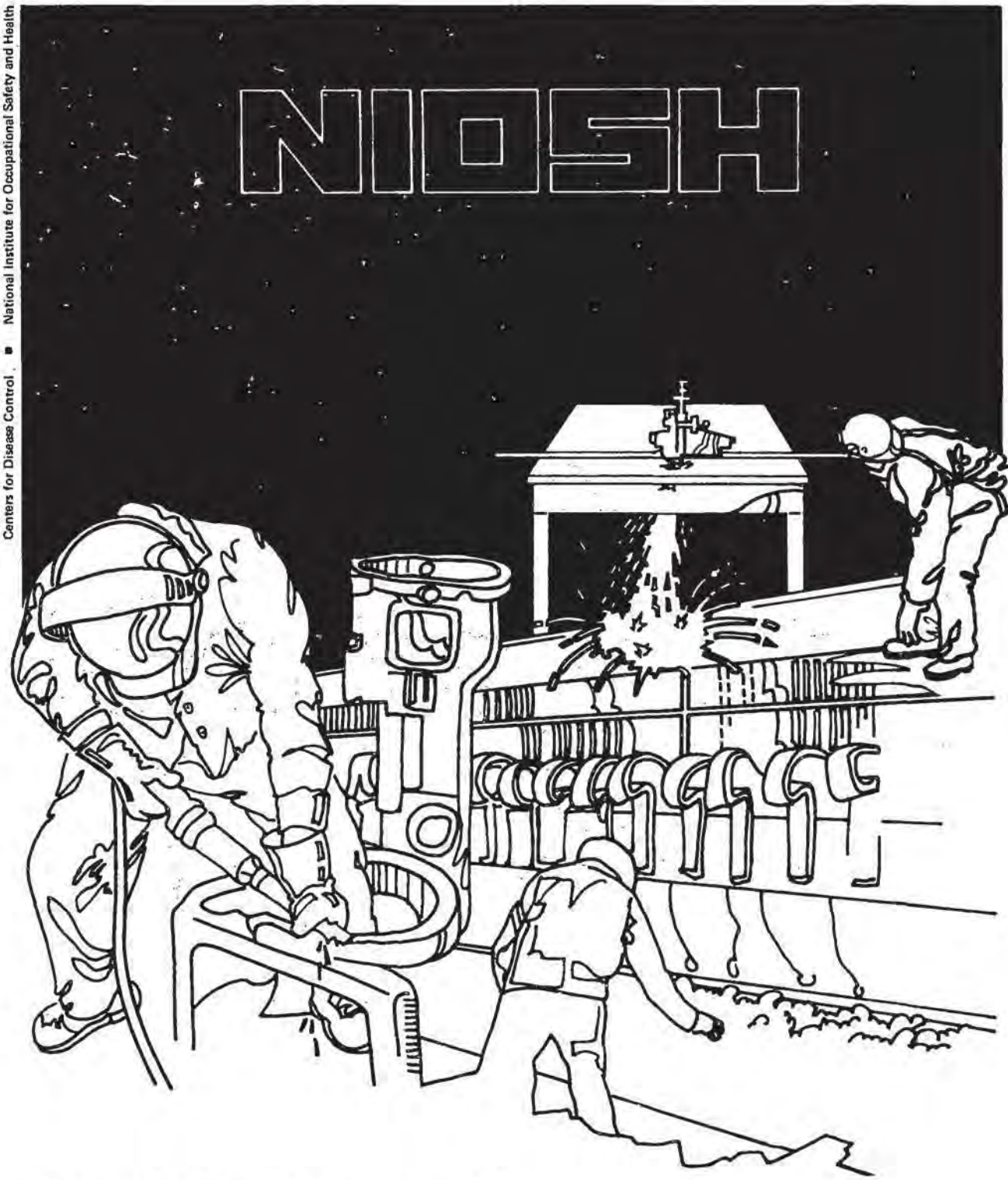

Health Hazard Evaluation Report

HETA 81-284-1292
UNION CARBIDE GRAFITO
YABUCOA, 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.

HETA 81-284-1292
FEBRUARY 1984 - REVISED
UNION CARBIDE GRAFITO
YABUCOA, PUERTO RICO

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I. SUMMARY

In July and October 1981, the National Institute for Occupational Safety and Health (NIOSH) conducted a Health Hazard Evaluation at the Union Carbide Grafito Plant, Yabucoa, Puerto Rico, to evaluate employee exposures to pitch, sulfur dioxide and nuisance dust. Personal breathing zone air samples were obtained for evaluation of exposures to sulfur dioxide, respirable dust, benzene solubles, and specific polynuclear aromatic hydrocarbons. Health questionnaires were completed on 97 exposed workers and on 36 less or non-exposed office and management workers. Physical examinations were performed on the sun-exposed areas of skin.

Fourteen(44%) of 32 personal air samples (range 0.1 to 1.5 ppm, mean 0.4 ppm.) for sulfur dioxide taken in the Graphitization Department exceeded NIOSH's recommended exposure criterion of 0.5 ppm. Eleven of the 14 elevated SO_2 levels were found on crane operators. However, none of the results exceeded the current OSHA standard of 5 ppm.

The results of personal samples for respirable dust ranged from non-detectable to 0.2 mg/m^3 and were well below the OSHA standard of 5 mg/m^3 for nuisance dust.

Eight (44%) of 18 personal samples (range ND to 2.7 mg/m^3, Mean 0.4 mg/m^3) for pitch volatiles taken in the Mill and Mix, and Pitch Impregnation Departments were found to exceed the OSHA standard for coal tar pitch volatiles (benzene solubles) of 0.2 mg/m^3. All 18 workers sampled were found to be working in atmospheres containing measurable levels of polynuclear aromatic hydrocarbons (PNAs), compounds that are known carcinogens and for which no safe level of exposure is now known. All of the 18 workers wore respirators during at least part of their workshift so that their actual respiratory exposure may be less than that measured.

The health questionnaire revealed that those production workers who responded had a statistically significant excess (compared to office and management controls) of eye irritation (43% vs 6%), difficulty hearing (19% vs 0%), back pain (43% vs 17%), cough (23% vs 6%), phlegm (19% vs 0%) and dyspnea on exertion (15% vs 0%). When smoking was accounted for, however, the excess of cough and phlegm was no longer statistically significant. Production workers reported experiencing phototoxic skin reactions when they were in the sun following exposure to pitch fume or dust. Physical examination findings revealed evidence of erythema or skin peeling (suggestive of phototoxic dermatitis) in 14 exposed workers and in 1 office control.

On the basis of the data obtained in this evaluation, NIOSH has determined that a health hazard from exposure to sulfur dioxide existed in the Graphitization Department at the Union Carbide Grafito Plant, Yabucoa, Puerto Rico. Sulfur dioxide exposures (particularly for crane operators) were found to exceed NIOSH's recommended standard of 0.5 mg/m^3; however, all of the results were below the current OSHA standard of 5 ppm. In addition, polynuclear aromatic compounds (PNA's) were found in the air of the Mill and Mix and Pitch Impregnation Areas. Health and safety recommendations are included in the body of the report.

KEYWORDS: SIC 3624, sulfur dioxide, polynuclear aromatic hydrocarbons, pitch, phototoxic dermatitis.

II. INTRODUCTION

On April 21, 1981, the National Institute for Occupational Safety and Health (NIOSH) received a request for a health hazard evaluation from the president of the Union Independente de Trabajadores de UCC representing workers at the Union Carbide Grafito plant, Yabucoa, Puerto Rico. The request expressed concern about workers' exposure to graphite particulates, iron oxide, and sulfur dioxide, and listed complaints of skin, respiratory, eye and central nervous system symptoms, in addition to fatigue, nausea and allergies.

On July 21, 1981, NIOSH conducted an initial site visit and preliminary survey. An opening conference was held with union and company representatives in which the nature and scope of the request and plans for the survey were discussed. The initial evaluation included a walk-through of the plant, collection of bulk samples in various areas for laboratory analysis, and interviews with four workers. NIOSH distributed interim report #1 for this investigation in August, 1981. Interim recommendations centered on suggested repair of an exhaust ventilation duct in the formation unit, engineering controls in the pitch impregnation unit, and worker instruction regarding access to medical and industrial hygiene data.

A follow up survey was conducted on October 19-22, 1981, to collect personal air samples for sulfur dioxide, respirable dust, coal tar pitch volatiles (benzene solubles) and specific polynuclear aromatic hydrocarbons (PNAs). In addition medical questionnaires were administered to 133 workers at the plant, and skin examinations were performed on all participating workers.

III. BACKGROUND

Union Carbide Grafito employs under 800 workers, of whom the majority are engaged in production. The manufacture of graphite electrodes consists basically of five steps: forming, baking, pitch impregnation (PI), grafitizing and machining. The principal raw materials are petroleum coke and pitch. They are transported to the plant where they are either stored or lifted to the top of UCG's 8 story milling and mixing building. The coke is crushed, sized, milled, then combined with flour and pitch and sent to weighing hoppers.

The batch flows by gravity to a mixer. During mixing, the pitch melts and disperses uniformly through the batch. After mixing, the mix is fed into a cooler where air is drawn through the unit to cool the mix to prevent sagging after extrusion.

Following cooling, the mix flows into an extrusion press which contains a mud cylinder. An extrusion die is attached to the end of the mud cylinder and a hydraulic extension ram forces the mud through the extruder head. The electrode is cut to the desired length, then rolled into a temperature-controlled tank for cooling. In the baking process, which is the next phase, the "green" electrodes are packed in "saggers" with a sized packing medium to prevent distortion or slumping as the electrodes are heated through the temperature range where the pitch is liquid. The electrodes are baked for up to 3 weeks, depending on size, and undergo considerable expansion and then shrinkage as they are cooled.

In pitch impregnation, baked electrodes are preheated and placed in an autoclave which is evacuated to a low pressure . Hot pitch is then pumped into the autoclave and held under pressure until the electrode is completely impregnated.

In graphitization, the electrodes are further processed with coke, and then heated to high temperature in an electrically fired furnace.

The electrothermic graphite electrodes are machined and threaded on both ends so they can be joined lengthwise and fed continuously into electric furnaces. Tapered threaded nipples of the proper size are used as the joining agents in this assembly.

IV. METHOD AND MATERIALS

A. Environmental

Personal sampling was conducted in the graphitization area for sulfur dioxide, respirable dust and airborne particulates. Personal sampling in the milling and mixing building and the pitch impregnation unit was conducted for coal tar pitch volatiles (benzene solubles) and specific polynuclear aromatic hydrocarbons (PNAs). PNAs included were phenanthrene, anthracene, fluorathene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluorathene, benzo(e)pyrene, benzo(a)pyrene, peryline, indino(123 CD)pyrene, benzo (GHI)perylene and dibenzo(AH)anthracene.

Personal breathing zone air samples for sulfur dioxide were collected by passing air through a filter train, consisting of a cellulose ester membrane filter followed by an impregnated cellulose filter containing potassium hydroxide at a flow rate of 1 liter per minute (L/min). Particulate matter is collected on the first filter, while sulfur dioxide passes through the first filter and is collected on the second filter. The samples were collected with portable battery operated pumps and analyzed by ion chromatography according to NIOSH Method P&CAM 268.

Personal breathing zone air samples for respirable dust (less than 10 microns mass median aerodynamic diameter) were collected by passing air through a 10 mm nylon cyclone at a flow rate of 1.7 L/min. The samples were collected on M5 filters (polyvinyl chloride filters) and analyzed gravimetrically.

Airborne particulates in the graphitazation area were collected on Andersen Ambient Particle Sizing Samplers for particle size distribution analysis. Each Andersen sampler contained nine filters (impaction plates) and backup filters. The first two stages contained glass fiber filters with a 23 mm hole in the center and the last seven stages contained DM-800 filters. The samples were collected at a flow rate of 1 cubic foot of air per minute. The filters were analyzed gravimetrically.

Personal air samples for benzene solubles and specific PNA's were collected on Gelman glass fiber/silver membrane filters with porous polymer tube backups at a flow rate of 1.75 1/min. The filters and porous polymer tubes were desorbed with benzene. Only the filter extract was used for analysis of benzene solubles. PNA's were determined by HRGC-SIM-MS analysis of both filters and porous polymer tubes. A total of 14 specific PNA's were involved in the analyses. A labeled recovery standard of 200 ng of d_{12} - chrysene was spiked in each sample before extraction and an internal quantitation standard of 200 ng of d_{10} - anthracene was added to each sample at the end of the sample preparation (i.e., before GC-MS analysis). The mean recovery of d_{12} - chrysene was 85% but each sample was individually corrected for its own measured recovery. The lower limit of quantitation was 2 ng/sample. A variable recovery based on submitted quality control sample results was noted for some of the PNA compounds. The problem appeared to be a result of the extraction and concentration procedures used. The results being reported, therefore, are approximate in some cases and should be considered minimum values.

B. Medical

Workers involved in plant operations and maintenance in 5 areas were randomly selected from the employee list, interviewed by questionnaire, and were submitted to a physical examination of the skin. The five areas were: Mill and Mix, Pitch Impregnating (PI), Graphitizing, Bake, and Maintenance Shops. Plant management and office workers were selected randomly as less or non-exposed controls for an administered questionnaire and physical examination of the skin. The participants were interviewed privately, in either Spanish or English, depending on the preference of the employee. The interview consisted of questions regarding past medical history, current symptoms, respiratory problems, social history, and occupational history.

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.

Listed below are the evaluation criteria for the substances sampled in this evaluation.

ENVIRONMENTAL CRITERIA

Substance	8 hr. TWA Exposure level	Source	OSHA Standard
Sulfur dioxide	0.5 ppm	NIOSH	5 ppm
Respirable Nuisance dust	5 mg/m^3	OSHA	5 mg/m^3
Coal Tar Pitch Volatiles -as benzene solubles	0.2 mg/m^3	OSHA	0.2 mg/m^3

Toxicity

Pitch

Coal tar pitch is a residual from the fractional distillation of coal tar and is thought to contain thousands of components of which only about 300 have been identified. The benzene soluble fraction of coal tar pitch has been shown to contain substances called polynuclear aromatic hydrocarbons (PNAs). Several of these PNAs such as benzo(a)pyrene, benzanthracene, and pyrene have been shown to be carcinogenic in animals. Petroleum pitch is the residue from the fractional distillation of petroleum products. Petroleum pitch contains many of the same compounds such as the PNAs found in coal tar pitch but such compounds are usually found in lower concentrations in petroleum derived pitch.

Exposure to coal tar products has been reported to produce phototoxic effects, such as erythema, burning, and itching of the skin following sun exposure, photophobia and conjunctivitis. From the epidemiologic and experimental toxicologic evidence on coal tar products, NIOSH has concluded that they are carcinogenic and can increase the risk of lung and skin cancer in exposed workers.[1]

The NIOSH standard for coal tar products such as coal tar derived pitch is 0.1 mg/m^3 (cyclohexane soluble production). NIOSH has not recommended a standard for petroleum derived pitch. The Federal Standard (8 TWA) for "coal tar pitch volatiles" (benzene soluble fraction) has been set at 0.2 mg/m^3. For this purpose "coal tar pitch volatiles" (CTPV) were defined as including the fused polycyclic hydrocarbons which volatilize from the distillation residues of coal, petroleum, wood and other organic matter", and thus

the standard includes coal tar pitch as well as petroleum products such as petroleum pitch. In May 1982 OSHA proposed to delete all but the coal tar derived products from the CTPV Standard because the non-coal tar derived products might be less toxic. After receiving numerous comments OSHA decided to continue including petroleum pitch in the CTPV standard (48 2764, Jan. 21, 1983).

It was advisable to continue including petroleum pitch in the CTPV standard since petroleum pitch contains many of the same PNA compounds as does coal tar pitch. In addition research results of the application of petroleum and coal tar derived pitch on the skin of mice reported by Bingham, Trosset, Warshaw [3] in 1980, indicated that "raw petroleum pitch is as carcinogenic as a comparable concentration of benzo(a) pyrene (BAP), while raw coal tar pitch is somewhat more carcinogenic than a comparable concentration of BAP". Since petroleum pitch apears to have an animal carcinogenic potency of a magnitude similar to that of coal tar pitch, the standard of .2 mg/m^3(benzene soluble) has been used in this report for both petroleum and coal tar derived pitch. While compliance with this standard should reduce the incidence of cancer, no absolute safe concentration can be established for a carcinogen at this time. Therefore, the recommended limit should be regarded as an upper limit of exposure and every effort should be made to keep exposure as low as is technically feasible.

Sulfur Dioxide[4]

Sulfur Dioxide (SO_2) is a colorless gas at ambient temperatures with a characteristic strong odor. The present OSHA Federal Standard is 5 ppm (13 mg/m^3) as a TWA. The NIOSH recommendation is 0.5 ppm (1.3 mg/m^3) TWA.

The gas is irritating to the mucous membranes of the upper respiratory tract. Chronic exposure may result in nasopharyngitis, altered sense of smell, and chronic bronchitis symptoms such as cough, increased mucous secretion, and dyspnea on exertion.

VI. RESULTS

A. Environmental

The results of the air sampling for respirable dust in the Graphitization Department are contained in Table I. Personal breathing zone concentrations ranged from non-detectable to 0.2 mg/m^3 (TWA). The OSHA standard for the respirable fraction of inert or nuisance dust is 5 mg/m^3 (TWA). In addition six sets of air samples were collected on Andersen samplers in the graphitization area to determine the size of the dust particles. The mass mean diameters of these six sample sets ranged from 3.9 to 8.8 microns and

the geometric standard deviations of the six sample sets ranged from 2.0 to 10.1 microns. Thus over half the total dust measured was in the respirable range of less than 10 microns in diameter.

Personal air samples for sulfur dioxide in the graphitization area ranged from 0.1 to 1.5 ppm TWA (Table II). The OSHA Standard is 5 ppm (parts per million) TWA; none of the samples exceeded the OSHA standard. The NIOSH recommended criterion is 0.5 ppm TWA. Fourteen of 32 personal samples exceeded the NIOSH recommended criterion. Eleven of the 14 samples which were above the NIOSH criterion were collected in the breathing zone of crane operators.

The results of the samples for benzene solubles and PNAs are presented in Table III. On the 18 personal samples collected, benzene soluble concentrations ranged from non-detected to 2.7 mg/m^3, with a mean of 0.43 mg/m^3. Eight of the samples exceeded the OSHA standard of 0.2 mg/m^3 for coal tar pitch volatiles measured as benzene solubles.

Levels for seven to eleven PNAs were measured on each of the 18 personal samples. Concentrations of PNAs ranged from 0.01 ug/m^3 to 193 ug/m^3. All workers sampled were therefore documented as being exposed to levels of known carcinogens--PNAs, for which no safe level of exposure is known.

It should be noted that the two workers in the Mill and Mix building were wearing disposable organic vapor respirators during their work shift and thus their respiratory exposure would be less than that measured. The 16 sampled workers in the pitch impregnation (PI) area wore organic vapor respirators during the periods when the autoclaves were opened and clouds of vapors and gas escaped. Thus their respiratory exposure also is likely to be less than that measured by personal sampling. The protection afforded by the respirators will depend to a large extent upon the fit of the respirators on each employee. The plant has a qualitative fit testing program. It should also be noted that the plant was in the progress of redesigning and shortly was to begin replacing all the mixers in the Mill and Mix Building.

During the walk-through of the plant, conducted on July 21, 1981, work practices and processes were observed. The milling area has local exhaust ventilation which is connected to a baghouse. Collected dust is reused. Air which passes through the cooler is sent through an electrostatic precipitator for cleaning. A local exhaust ventilation duct near the shaker was severely abraded and not connected to the shaker. Open ports, which presented the potential for fugitive dust escapes, were observed in the weighing area. Vapor escapes were observed at the mixing area. At the time of the follow-up survey, October 19-21, 1981, the electrostatic precipitator

which exhausts the coolers in the milling and mixing building was inoperative due to a fire which had disabled the electrostatic precipitator the week before the survey. Thus, measurements in this area did not constitute normal workplace exposure and employees in this area wore respirators during peak exposure periods.

B. Medical

A total of 133 workers participated in the followup study. An analysis of the study's exposed participants by department is shown below:

Department

	Mill & Mix	(PI) Pitch Impregnation	Grafi-tization	Bake	Maintenance Shop
Maintenance	2	5	11	1	2
Production	23	19	27	7	0
Totals	25	24	38	8	2

Total Exposed Participants = 97

The management employees in the control group consisted of the following: 10 supervisors, 1 foreman, 6 accountants, 5 industrial engineers, 4 health and safety personnel, 3 production planners, 3 clerks and 1 employee relations specialist. All study participants were men. Age characteristics and past medical histories of the participants are given in Table IV. Age and medical histories were not significantly different between production and control groups.

Frequencies of reported symptoms are shown in Table V. Compared with office and management controls, the production employees showed statistically significant excesses (at the P=.05 level) for eye irritation, difficulty hearing, back pain, cough, phlegm, and dyspnea on exertion. However the production employees had a significantly (at P=.01 level) higher proportion of men who smoked (61%) than did the management employees (42%). When smoking is controlled for in the analysis, the difference in phlegm or cough is not statistically significant (Table VI).

Many production employees reported experiencing episodes of skin peeling suggestive of phototoxic dermatitis. These reports were most common among workers presently employed in the Mill and Mix (13/25) and pitch impregnation (8/24) areas. No bake employees and only 2 of 30 workers in the graphitization area and 3 of 36 administrative controls reported such skin

peeling. Physical examination revealed lesions consistent with phototoxic dermatitis (erythematous and/or peeling skin of sun-exposed areas) in 14 of 97 production workers and 1 of 36 control workers.

Workers in the Mill and Mix, and Pitch Impregnation Departments stated that they were most subject to suffering phototoxic reactions following work-shifts spent in the "pitch passage" in the Mill and Mix building, or in the pitch storage area of the Pitch Impregnation Department. In the "pitch passage" one worker per shift would transport the pitch with a front end loader and occasionally would have to handle the pitch using manual tools. In the mill and mix area a front end loader was also used but during most shifts the worker would spend some time loading pitch onto a conveyer belt using a shovel. In both work areas employees were provided barrier creams and protective clothing. Employees' skin would unavoidably become covered with pitch dust.

The workers reported that they could not go into the sun for several days following a work shift spent in the pitch storage and handling areas because such exposure would cause a severe phototoxic reaction resembling severe sunburn, in which the skin would redden, blister, and then peel. The other employees who work in the Pitch Impregnation or Mill and Mix Department but not in the storage areas did not usually have direct contact with the pitch, and they reported experiencing fewer problems with phototoxic reactions.

VII. DISCUSSION

The Pitch Impregnation Department (PI) had no exhaust ventilation. A large cloud of vapors and gases was observed whenever an autoclave was opened. To date, engineering controls in this area have been inadaquate but management is currently installing a new Pitch Impregnation Department which will have the effect of reducing emissions of pitch volatiles.

Because of the potential for harmful exposure to PNAs or other substances the company requires all employees working in the Mill and Mix building (except those on the ground floor) to wear a company supplied disposable respirator. The company also requires employees in the Pitch Impregnation (PI) area to wear a respirator when the autoclaves are opened and the aforementioned clouds of vapors and gases escape. Since exposures to measurable levels of carcinogens were documented in the PI area during the NIOSH survey, it would be advisable for the company to reassess the need for PI workers to wear suitable respirators at all times until environmental measurements demonstrate that no potential harmful exposures are present except when the autoclaves are being opened.

The high temperatures needed to produce graphitization of carbon atoms appear to drive off sulfur compounds in the process. Nearly half of the personal air samples for sulfur dioxide obtained in the graphitization area were above the NIOSH recommended criterion of 0.5 ppm and most of these were obtained on the overhead crane operators. (No samples exceeded the 5 pm OSHA SO_2 Standard but this limit may not prevent adverse health effects in exposed employees).

Although the graphitization unit is open on three sides, the ventilation is inadequate to prevent overexposure to sulfur dioxide in this area. Union Carbide's environmental staff should investigate this situation and institute engineering controls to reduce SO_2 exposures in this area. In addition, several of the crane cabs had leaks near window seals and some had improperly functioning air conditioning units. These crane cabs should continue to be inspected and repaired.

The workers exposed to pitch reported that they had had recurring episodes of phototoxic reactions. Similar phototoxic reactions have been reported in workers handling pitch in other locations and the reaction is likely to be due to phototoxic properties of the pitch. Efforts should be made to decrease the amount of personal handling required for the pitch so that contamination of worker's skin with pitch dust can be lessened. Workers who come in contact with pitch or coke should be provided with protective, disposable clothing on an as needed basis. Employees are provided with complete cleanup facilities for showering after their work shift. It is possible that sun screen agents that contain benzophenones such as Uval® (Dome Laboratories) or Solbar® (Person & Convey, Inc.) may lessen the phototoxic response due to skin contamination with pitch. Workers who must go out in the sun following work in areas with high airborne pitch concentrations may find such agents of benefit in decreasing the intensity of phototoxic reactions.

VIII. RECOMMENDATIONS

1. Continue to maintain the graphitization area crane cab window seals and air conditioning units.

2. Continue industrial hygiene/engineering study to control sulfur dioxide exposures at the Graphitization Department.

3. Continue to proceed with the pitch impregnation process installation.

4. Disposable protective clothing on an as needed basis should be provided to workers in the pitch vaults and pitch melting areas. Work practices in Mill and Mix and Pitch Impregnation should be modified to decrease the amount of personal handling of pitch. In addition, adequate cleanup facilities for post-shift cleanup should continue to be available to workers in these areas.

IX. REFERENCES

1. Criteria for a recommended standard: Occupational exposure to Coal Tar Products, DHEW (NIOSH) Publication No. 78-107.

2. General Industry Standards: Occupational safety and health administration. Safety and health standards (29 CFR 1910).

3. Carcinogenic Potential of Petroleum Hydrocarbons: A critical review of the literature. Eula Bingham, Roth Trosset, David Warshaw. Journal of Environmental Pathology and Taxicology 3:453-563.3 (1980).

4. Occupational Diseases: A guide to their recognition. USDHEW, PHS, CDC, NIOSH. Publication NO. 77-181.

X. AUTHORSHIP AND ACKNOWLEDGEMENTS

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XI. DISTRIBUTION AND AVAILABILITY OF REPORT

Copies of this report are currently available upon request from NIOSH, Division of Standards Development and Technology Transfer, 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 Carbide Grafito, Yabucoa, Puerto Rico

2. Union Independente de Trabajadores de UCC

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

TABLE I

*AIR SAMPLING FOR RESPIRABLE DUST: GRAPHITIZATION AREA

UNION CARBIDE GRAFITO
YABUCOA, PUERTO RICO
HE 81-284

October 20-21, 1981

Job/Location	Date Of Sample	Time Of Sample	Sample Volume (liters)	Concentration (mg/M^3)
Cleaning	10/20/81	0641-1312	665	0.1
Furnace Loader Unit #4	10/20/81	0615-1304	695	0.0
System Operator	10/20/81	0627-1307	680	0.2
Furnace Loader	10/20/81	0624-1308	686	0.2
Cleaning	10/20/81	0645-1314	661	0.1
Utility Man	10/21/81	2235-0523	694	ND
Heater, Unit #2	10/21/81	2232-0511	678	0.1
Heater, Unit #6	10/21/81	2229-0505	673	0.2
System Operator	10/21/81	2230-0523	702	0.1
Utility Man	10/21/81	2234-0506	667	ND
System Operator	10/21/81	2227-0514	692	0.0
Michigan Loader	10/21/81	2222-0505	685	ND
System Operator	10/21/81	2226-0502	673	0.1
Heater, Unit 1	10/21/81	2236-0525	695	0.1
Heater, Unit 5	10/21/81	2226-0500	670	0.2

OSHA PEL for respirable fraction of inert or nuisance dust is 5 mg/M^3

ND = Not Detected
* All air samples are personal breathing zone samples

TABLE II

AIR SAMPLING FOR SULFUR DIOXIDE: GRAPHITIZATION AREA

UNION CARBIDE GRAFITO
YABUCOA, PUERTO RICO
HE 81-284

October 20-21, 1981

Job/Location	Date Of Sample	Type Of Sample	Time Of Sample	Sample Volume (liters)	Sulfur Dioxide Concentration (PPM)
Crane Operator #1	10/19/81	Personal	1408-2113	425	0.8
Furnace Loader, Unit #4	10/19/81	Personal	1450-2124	394	0.2
Furnace Loader, Unit #2	10/19/81	Personal	1434-2111	397	0.5
Laborer, Unit #2	10/19/81	Personal	1436-2110	394	0.4
Furnace Loader, Unit #1	10/19/81	Personal	1446-2106	380	0.2
Laborer	10/19/81	Personal	1418-2118	420	0.2
Crane Operator #2	10/19/81	Personal	1406-2110	424	0.8
Crane Operator #8	10/19/81	Personal	1420-2121	421	0.9
Furnace Loader	10/19/81	Personal	1424-2115	411	0.1
Furnace Loader, Unit #1	10/19/81	Personal	1445-2112	387	0.1
Furnace Operator, Unit #6	10/20/81	Personal	0651-1309	378	0.8
Furnace Operator, Unit #2	10/20/81	Personal	0635-1317	402	0.6
Furnace Loader, Unit #1	10/20/81	Personal	0712-1301	349	0.2
5' above ground, between Units 101 and 103	10/20/81	Area	0718-1325	367	0.0
Crane Operator #5	10/20/81	Personal	0654-1311	378	1.5
Crane Operator #1	10/20/81	Personal	0705-1329	384	0.4
Crane Operator #8	10/20/81	Personal	0639-1308	389	1.1
Furnace Loader, Unit #5	10/20/81	Personal	0630-1306	396	0.3
Crane Operator #2	10/20/81	Personal	0644-1337	413	1.1
Furnace Loader, Unit #5	10/20/81	Personal	0631-1300	389	0.4
Furnace Operator, Unit #4	10/20/81	Personal	0613-1300	407	0.4
Crane Operator #7	10/20/81	Personal	Pump stopped, sample invalidated		
Furnace Loader, Unit #5	10/21/81	Personal	2216-0500	404	0.2
Furnace Loader, Unit #6	10/21/81	Personal	2214-0506	412	0.1
Furnace Loader, Unit #3	10/21/81	Personal	2217-0503	406	0.3
Furnace Loader, Unit #1	10/21/81	Personal	2213-0523	430	0.6
Crane Operator #7	10/21/81	Personal	2210-0511	421	1.2
Crane Operator #3	10/21/81	Personal	2209-0514	425	0.6
Crane Operator #6	10/21/81	Personal	2204-0521	437	1.5
Crane Operator #5	10/21/81	Personal	2207-0508	421	0.1
Crane Operator #8	10/21/81	Personal	2205-0516	431	0.6
Crane Operator #2	10/21/81	Personal	2206-0523	437	0.8
Furnace Loader, Unit #2	10/21/81	Personal	2221-0520	419	0.2
Furnace Loader, Unit #4	10/21/81	Personal	2220-0522	422	0.4
OSHA PEL -					5 ppm
NIOSH Recommended Criteria -					0.5 ppm

Table III

Benzene Solubles and Polynuclear Aromatic Hydrocarbons

Union Carbide Grafito
Yabucoa, Puerto Rico
October 19-20, 1981

Job Location	Time of Sample		Benzene Soluble Concentration (mg/M³)	Phenanthrene (ug/M³)	Anthracene (ug/M³)	Fluoranthene (ug/M³)	Pyrene (ug/M³)	Benzo(A) anthracene (ug/M³)	Chrysene (ug/M³)	Benzo(E) Pyrene (ug/M³)	Benzo(A) Pyrene (ug/M³)	Perylene (ug/M³)	Benzo(GHI) Perylene (ug/M³)	Dibenz (AH) Anthracene
Valve	15:01-21:32	Filter	0.32	-	-	0.29	1.9	2.9	5.9	1.3	1.4	0.41	-	-
Operator		PP Tube	-	14	1.5	2.2	9.5	-	-	-	-	-	-	-
PI		Total	0.32	14	1.5	2.5	11	2.9	5.9	1.3	1.4	0.41	-	-
Helper	15:27-21:31	Filter	2.7	-	-	1.5	9.1	4.1	8.2	4.0	4.1	1.0	-	-
PI		PP Tube	-	4.9	0.47	0.74	1.2	-	-	-	-	-	-	-
		Total	2.7	4.9	0.47	2.2	10	4.1	8.2	4.0	4.1	1.0	-	-
Crane	15:31-21:32	Filter	0.17	-	-	0.08	0.4	0.49	0.97	0.33	0.4	0.12	-	-
Operator		PP Tube	-	7.9	1.0	1.2	2.4	-	-	-	-	-	-	-
PI		Total	0.17	7.9	1.0	1.3	2.8	0.49	0.97	0.33	0.4	0.12	-	-
Crane	15:34-21:33	Filter	0.16	-	-	0.09	0.29	0.74	1.5	0.43	0.62	0.16	-	-
Operator		PP Tube	-	3.2	0.41	0.62	1.4	-	-	-	-	-	-	-
PI		Total	0.16	3.2	0.41	0.71	1.7	0.74	1.5	0.43	0.62	0.16	-	-
Crane	15:41-21:30	Filter	N.D.	-	-	0.15	0.29	0.46	0.92	0.23	0.31	0.09	-	-
Operator		PP Tube	-	4.1	0.52	0.82	1.4	-	-	-	-	-	-	-
Baking		Total	N.D.	4.1	0.52	0.97	1.7	0.46	0.92	0.23	0.31	0.09	-	-
Pitch	16:22-21:41	Filter	0.27	-	-	6.8	6.1	2.5	3.1	1.8	3.6	1.0	-	-
Operator		PP Tube	-	193	52	39	27	-	-	-	-	-	-	-
Milling		Total	0.27	193	52	46	33	2.5	3.1	1.8	3.6	1.0	-	-
Laborer	16:35-21:39	Filter	0.17	-	-	3.2	4.5	1.6	2.4	0.51	0.73	0.28	-	-
Milling		PP Tube	-	6.8	1.3	1.2	0.85	-	-	-	-	-	-	-
		Total	0.17	6.8	1.3	4.4	5.4	1.6	2.4	0.51	0.73	0.28	-	-
Console	16:42-21:42	Filter	N.D.	-	-	1.3	1.7	0.53	1.1	0.18	0.34	0.11	-	-
Operator		PP Tube	-	98	34	21	13	-	-	-	-	-	-	-
Milling		Total	N.D	98	34	22	15	0.53	1.1	0.18	0.34	0.11	-	-

Table III (Continued)

Job Location	Time of Sample		Benzene Soluble Concentration (mg/M³)	Phenanthrene (ug/M³)	Anthracene (ug/M³)	Fluoranthene (ug/M³)	Pyrene (ug/M³)	Benzo(A) anthracene (ug/M³)	Chrysene (ug/M³)	Benzo(E) Pyrene (ug/M³)	Benzo(A) Pyrene (ug/M³)	Perylene (ug/M³)	Benzo(GHI) Perylene (ug/M³)	Dibeng (AH) Anthracene
Pitch Melting PI	15:24-21:32	Filter	1.5	1.6	-	-	1.5	1.1	3.0	9.3	4.4	-	6.2	12
		PP Tube	-	16	1.6	0.78	1.4	-	-	-	-	-	-	-
		Total	1.5	18	1.6	0.78	2.9	1.1	3.0	9.3	4.4	-	6.2	12
Valve Operator PI	15:26-21:32	Filter	0.33	-	-	-	0.79	0.79	1.7	6.7	1.6	-	-	-
		PP Tube	-	16	3.2	1.4	5.1	-	-	3.3	-	-	-	-
		Total	0.33	16	3.2	1.4	5.9	0.79	1.7	10	1.6	-	-	-
Crane Operator PI	7:44-13:38	Filter	0.13	-	-	0.21	0.81	0.93	1.9	0.33	0.51	0.16	-	-
		PP Tube	-	5.4	0.65	0.66	1.9	-	-	-	-	-	-	-
		Total	0.13	5.4	0.65	0.87	2.7	0.93	1.9	0.33	0.51	0.16	-	-
Valve Operator PI	7:31-13:39	Filter	0.25	-	-	0.26	1.3	2.2	4.5	0.76	0.13	0.31	-	-
		PP Tube	-	7.8	1.1	1.1	5.6	-	-	-	-	-	-	-
		Total	0.25	7.8	1.1	1.4	6.9	2.2	4.5	0.76	0.13	0.31	-	-
Rebake Handler Rebake	7:44-13:36	Filter	0.08	-	-	0.19	0.39	0.13	0.31	0.09	0.13	0.04	-	-
		PP Tube	-	3.3	0.28	0.41	0.36	-	-	-	-	-	-	-
		Total	0.08	3.3	0.28	0.60	0.75	0.13	0.31	0.09	0.13	0.04	-	-
Misc. Crane Operator PI	7:34-13:37	Filter	N.D.	-	-	0.13	0.38	0.20	0.44	0.15	0.13	0.04	-	-
		PP Tube	-	4.3	0.39	0.58	0.69	-	-	-	-	-	-	-
		Total	N.D.	4.3	0.39	0.71	1.1	0.20	0.44	0.15	0.13	0.04	-	-
Laborer PI	7:32-13:39	Filter	0.16	-	-	0.13	0.55	0.62	1.1	0.36	0.31	0.09	-	-
		PP Tube	-	4.2	0.45	0.56	1.4	-	-	-	-	-	-	-
		Total	0.16	4.2	0.45	0.69	2.0	0.62	1.1	0.36	0.31	0.09	-	-
Pitch Melting PI	7:33-13:37	Filter	1.1	1.3	0.2	0.39	3.6	2.7	4.2	2.5	3.3	1.0	0.07	0.52
		PP Tube	-	5.0	0.64	0.60	1.2	-	0.02	-	-	-	-	-
		Total	1.1	6.3	0.84	0.99	4.8	2.7	4.2	2.5	3.3	1.0	0.07	-
Rebake Crane Operator Rebake	7:44-13:38	Filter	0.09	-	-	0.14	0.47	0.06	0.10	0.03	0.03	0.01	0.07	0.52
		PP Tube	-	2.8	0.35	0.38	0.41	-	-	-	-	-	-	-
		Total	0.09	2.8	0.35	0.52	0.88	0.06	0.10	0.03	0.03	0.01	-	-
Valve Operator PI	7:29-13:38	Filter	0.25	-	-	-	-	-	1.1	5.3	1.1	-	-	-
		PP Tube	-	15	1.6	1.6	5.1	-	-	-	-	-	-	-
		Total	0.25	15	1.6	1.6	5.1	-	1.1	5.3	1.1	-	-	-

Table IV

DEMOGRAPHIC CHARACTERISTICS

I . Age of participants:

	mean age	range
a. Exposed workers N=97	34.3	19-56
b. Less exp. controls N=36	33.4	23-51

Total # of participants = 133

III. Past Medical Histories

	Exposed	Controls
a. Hypertension	8	5
b. Heart disease	2	0
c. Cancer	0	1
d. GI ulcer	0	1

Table V

Frequency of Reported Symptoms
Followup Survey
Union Carbide Grafito

HETA 81-284

Symptoms	(N = 97) Exposed Workers #	%	(N = 36) Controls 1 #	%	Rate Ratio		Test Significance
Eye irritation	42	43	6	16	2.6		*
Nasal Allergy	12	12	8	22	0.55		NS
Anxiety	14	14	3	8	-		NS
Skin Cancer	0	0	0	0	-		NS
Difficulty hearing	18	19	0	0	-		*
Nose bleeds	4	4	3	8	-		NS
Dermatitis	25	26	4	11	2.3		NS
Back Pain	42	43	6	17	2.6		*
Sore Throat	29	30	7	19	1.5		NS
Cough	22	23	2	6	4.1		*
Phlegm	18	19	0	0	-	-	*
Chronic Bronchitis (1)	6	6	0	0	-	-	NS
Dspnea on Exertion	15	15	0	0	-	-	*
Asthma	9	9	5	13	-	-	NS

(1) Cough $\bar{c}$ phlegm > 4 d/wk, > 2 mo/yr X2 more years
* Significant at p = .05 level
NS Not significant at P=.05 level

Table VI

Cough or phlegm
Among Exposed vs Control
Controlled for Smoking History

	Cough or Phlegm	Exposed	Controls
Current Smoker	+	11	1
	-	15	6
Previous Smoker	+	10	2
	-	23	7
Never Smoker	+	9	1
	-	28	15

X^2 Mantel Henzel = 1.95
Heterogeneity Chi square = 0.60
Estimate of Odds ratio = 3.0
lower confidence limit (95%) = .98
upper confidence limit (95%) = 9.03
p = .05

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