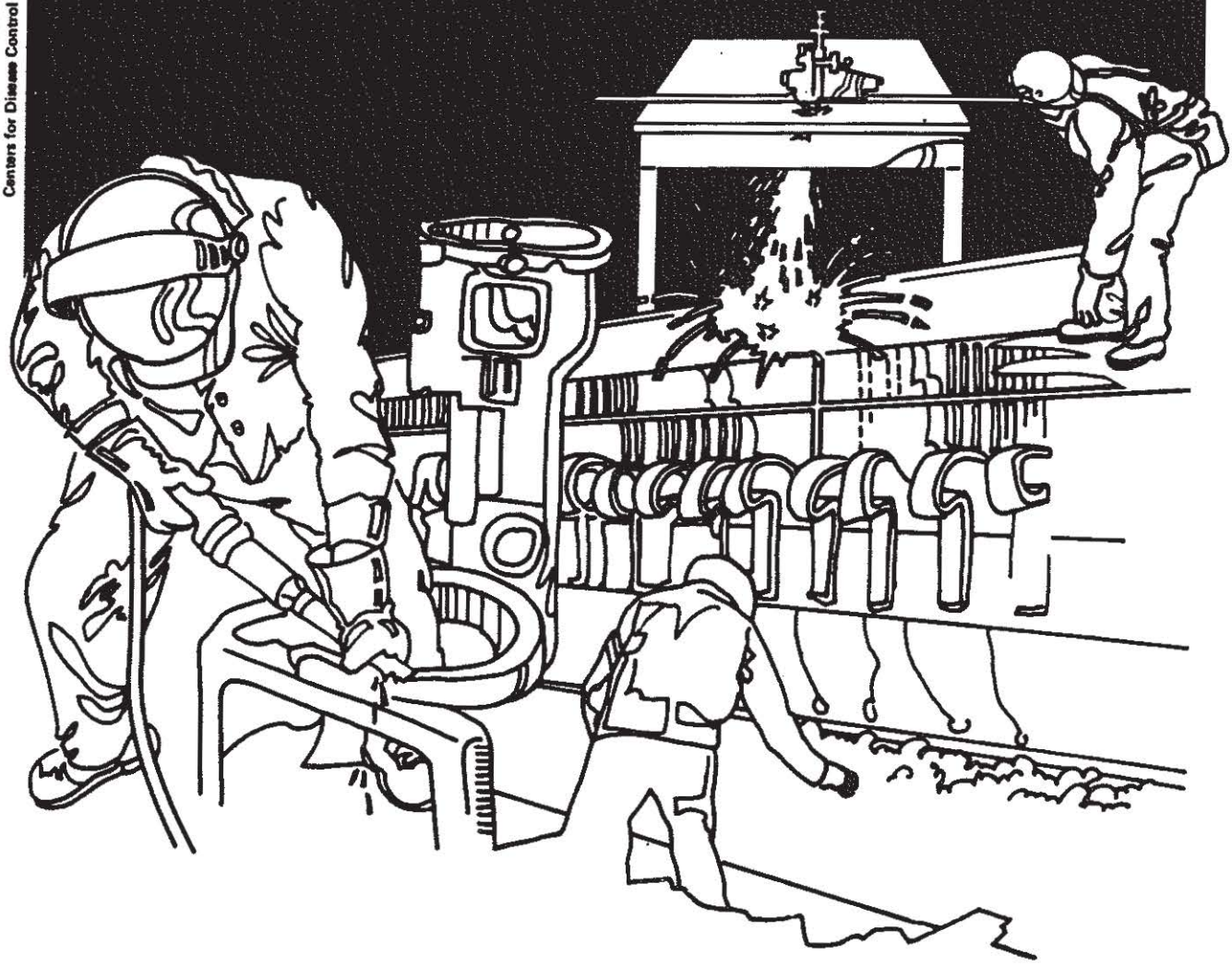
U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES ■ Public Health Service
Centers for Disease Control ■ National Institute for Occupational Safety and Health

NIOSH



Health Hazard Evaluation Report

HHE 80-203-960
PHILLIPS CHEMICAL COMPANY
TOLEDO, OHIO

PREFACE

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

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

HE 80-203-960
October 1981
Phillips Chemical Company
Toledo, Ohio

NIOSH INVESTIGATORS:
James M. Boiano, IH
Michael T. Donohue, PA

I. SUMMARY

On July 12, 1980, the National Institute for Occupational Safety and Health (NIOSH) received a confidential request for a health hazard evaluation from employees of Local 7-346, Oil, Chemical and Atomic Workers Union (OCAW). NIOSH was requested to evaluate possible adverse health effects of workers exposed to carbon black, carbon monoxide, and welding fumes at Phillips Chemical Company's carbon black plant in Toledo, Ohio.

An initial site visit was made on August 19, 1980. A follow-up environmental/medical evaluation of 28 production workers was conducted on December 17-18, 1980. Environmental samples were collected for carbon black and their cyclohexane extractables, polynuclear aromatic hydrocarbons (PNA's) found in the cyclohexane extract, carbon monoxide (CO), and iron oxide fume. The medical evaluation consisted of pre and post-shift CO levels in exhaled air, pulmonary function testing, and confidential medical questionnaires.

Environmental levels of carbon black averaged 1.01 milligrams per cubic meter of air (mg/M^3) (range: 0.20-2.84 mg/M^3) for 22 personal samples. None of the samples exceed the OSHA standard of 3.5 mg/M^3. Parallel samples for cyclohexane extractables averaged 0.04 mg/M^3 (range: nondetectable to 0.19 mg/M^3); two of these samples exceed the NIOSH criteria of 0.1 mg/M^3. Small quantities (ng/M^3) of fluoranthene, pyrene, and/or benzo(a)pyrene were found in 20 of the 22 personal samples.

Most carbon monoxide area measurements ranged between 5 and 20 ppm (NIOSH criteria: 35 ppm; 200 ppm ceiling). Levels up to 350 ppm were detected on the third level between the baghouses - an area where workers spent little time. A sample collected for iron oxide fume (as Fe) during carbon steel welding was 0.17 mg/M^3 (evaluation criteria - 5.0 mg/M^3).

The medical results of this evaluation revealed no significant decrement in FEV_1, FVC, and FEV_1/FVC for any worker. Direct CO measurements of exhaled air were not remarkable when shift differentials were compared. The health questionnaires given both groups underscored health complaints of nasal irritation and shortness of breath in the production workers.

On the basis of the data collected in this survey, NIOSH determined that a hazard of overexposure to carbon black containing PNA (via cyclohexane extractable fraction) did exist at Phillips Chemical Company at the time of this survey. NIOSH recognizes that PNA's, which were detected in the personal air samples, have carcinogenic or cocarcinogenic potential. Therefore, NIOSH recommends that exposure be controlled to the lowest reliable analytical detection level. Recommendations to protect the health and safety of the workers are presented in Section VIII of this report.

KEYWORDS: SIC 2895 (Carbon Black Manufacturing), Carbon black, cyclohexane extractable fraction, fluoranthene, pyrene, benzo(a)pyrene, PNA, carbon monoxide, iron oxide fume, carboxyhemoglobin, pulmonary function, nasal irritation, dyspnea.

II. INTRODUCTION

Under the Occupational Safety and Health Act of 1970, NIOSH investigates the toxic effects of substances found in the workplace. On July 12, 1980 NIOSH received a confidential request from authorized representatives of Local 7-346, Oil, Chemical and Atomic Workers Union (OCAW) to evaluate environmental conditions and possible adverse health effects in workers exposed to carbon black, carbon monoxide, and welding fumes at Phillips Chemical Company, Toledo, Ohio. The request specified three areas of concern: the shipping warehouse including the rerun deck, the welding shop, and the bag filter area.

The initial site visit was conducted on August 19, 1980. Refusal by the company to permit the administration of confidential medical interviews during the initial evaluation necessitated obtaining a warrant to complete the investigation. The environmental/medical evaluation was conducted on December 17 and 18, 1980.

III. BACKGROUND

A. Plant Description:

Phillips Chemical Company, a division of Phillips Petroleum, manufactures several grades of Philblack carbon black for use primarily in the tire industry. The plant has been in operation since 1969, and employs 33 hourly and 18 salaried employees. Hourly employees include: 9 control room operators; 11 maintenance technicians (welders, electricians, and mechanics); 9 utility persons (hopper car loaders and cleanup men); 3 laboratory technicians; and 1 warehouse person. All but four hourly workers are on the first shift. The second and third shifts are each "manned" by two control room operators. The workshifts are 8 a.m.-4 p.m., 4 p.m. to midnight, and midnight to 8 a.m. During most of 1980 the plant was operating at about 50% of production capacity because of a slump in auto sales. As a result, five utility men were laid off after the initial visit and remained in that status through the follow-up evaluation in December.

A few days prior to the follow-up evaluation, nearly 35,000 pounds of carbon black spilled onto the warehouse roof during loading of one of the carbon black storage tanks. Company maintenance and utility men were involved in the initial cleanup of the spill. The carbon black was reportedly shoveled into bags and dropped off the warehouse roof into a dumpster.

During the NIOSH survey, the company contracted a firm specializing in industrial waste cleanup to remove the remainder of the spill. Workers, wearing protective gear, removed the spill by vacuum. The contract cleanup work was completed on December 17th. During this day

company employees were engaged in routine work activities. The following day most company maintenance men were involved in plant-wide cleanup, at which time nearly all of the plant grounds were hosed down with water to remove wind-blown carbon black that resulted from the spill and initial cleanup activities.

B. Process Description:

Carbon black is manufactured at the Toledo facility by the oil furnace process. In this "closed" system process carbon black is continuously produced by burning a mixture of oil and natural gas in a reactor with a deficiency of air. Seven reactors are used; 4 on line #1 and 3 on line #2, with each line capable of producing one grade of carbon black at any given time. Gaseous by-products and water vapor are also formed during the reaction. As the products leave the reactor, they are water-quenched to reduce the temperature and terminate the reaction. Cyclones, and to a greater extent, bag filters are used to separate carbon black from the water vapor and combustion off-gases. The off-gases are recovered and conveyed to a boiler for utilization of the combustibles present. The filtered carbon black is then removed by reverse air flow and pneumatically transferred to a surge tank where lignosulfonate is added to produce wet pellets. The pelletized carbon black is then dried in a rotary kiln and conveyed via bucket elevator into one of seven 250,000-pound capacity storage tanks from where it is gravity fed into hopper cars and trucks or packaged into 50-pound bags. Process equipment including reactors, cyclones, baghouses and storage tanks are located outdoors.

The grades of carbon black produced at this facility include N-231, N-375, N-299, N-339, N-326, N-330, N-341, and N-347. (Grades are determined by the physical properties of the carbon black) Grades N-231 and N-375 were the only grades manufactured during this survey. Grade N-231 was continuously produced during both days. Production of N-375 started at 4:00 p.m. on December 17th and ran continuously through the next day.

C. Description of the Areas of Concern:

1. Rerun Deck:

The rerun deck is a 20' x 20' platform located about 25 feet above the warehouse floor. Maintenance workers enter this area to make periodic adjustments on the carbon black recycling equipment (i.e., blowers, rotary feeders) supported by this deck.

2. Train Shed:

This "shed" is part of the warehouse and is situated directly below the carbon black storage tanks. Carbon black is manually loaded into the hopper cars through flexible supply lines. Vacuum lines are attached to the same compartment to reduce carbon black dust emissions and facilitate the loading process. Although this shed can accomodate several rail cars, only two cars were loaded at any one time.

3. Warehouse:

The warehouse, including the train shed, occupies 36,000 square feet and is used to store 50-pound bags of carbon black. Historically, bagging was quite common, but now is only done on request.

4. Bag Filter Area:

Two baghouses - a ten compartment bag house for line #1 reactors, and an eight compartment baghouse for line #2 reactors - are located between the reactor lines. Two elevated walkways are located between the baghouses and are traversed by the control room operators once per shift for inspection of reverse-air-flow valves (normally takes several minutes). All workers are required to log time spent in this area.

5. Welding Shop:

The Welding Shop is approximately 60 x 40 x 25 feet and has two 10 x 20 foot doors. Welding is done in the shop on an infrequent basis. It is usually done on plant equipment in situ.

D. Personal Protective Equipment:

Hard hats, safety glasses and shoes are required in all plant locations. Disposable respirators are required in the shipping warehouse building including the rerun deck and train shed, and in the Quality Control lab whenever carbon black is assayed. Prior to the initial site visit in August, the use of respirators in these areas was optional. Workers are provided with full-body clothing, shower facilities, and separate change rooms.

E. Personal Monitoring:

The company conducts environmental monitoring for carbon black dust and carbon monoxide on a quarterly basis. In cases of overexposure, the employee is notified by letter of his exposure level, the environmental criteria, and company recommendations to control exposure.

VI. METHODS AND MATERIALS

A. Environmental:

Carbon Black:

Bulk samples of the eight grades of carbon black were obtained. Pelletized and nonpelletized types were available only for grades N-231 and N-375, both manufactured during the evaluation. The other grades were only available in pelletized form. All bulk samples were analyzed for cyclohexane extractables by NIOSH Method P & CAM 217. An aliquot of the extract was further analyzed for five polynuclear aromatic hydrocarbons (PNA)* including fluoranthene, pyrene, benzo(a)pyrene (B(a)P), chrysene, and benzo(a)anthracene (B(a)A) by reverse-phase high pressure liquid chromatography utilizing Waters Associates HPLC system equipped with a Vydac 201 TP column running an acetonitrile/methanol/water solvent gradient. Retention times of the specific peaks were compared with those of known standard compounds for analyte identification. Quantitative data were obtained by comparison of the peak areas in the chromatograms of the samples with the standard curves.

Personal and general area air samples were collected to evaluate worker exposure to carbon black. Since it was impossible to differentiate between PNA contaminated (cyclohexane extractable fraction greater than 0.1%) and noncontaminated carbon blacks in these samples, all samples were assumed to contain PNA contaminated carbon black and were analyzed accordingly. Samples were collected in pairs, one for carbon black, the other for cyclohexane extractables and the PNA compounds identified in the bulk sample analyses. Carbon black samples were collected on tared 0.8u 37mm acrylonitrile polyvinyl chloride copolymer M5 filters and analyzed gravimetrically for total weight gain. Samples for cyclohexane extractables and PNA's were collected on glass fiber/silver membrane (GF/Ag) filter combinations and analyzed for cyclohexane extractables by NIOSH Method P & CAM 217.

All samples were collected with personal sampling pumps operating at 2.0 liters per minute (lpm). Since pyrene and fluoranthene were detected in the bulk sample of N-231, the filters were further analyzed for these two PNA's. The PNA compounds collected on these filters were separated by the HPLC system described earlier, and analyzed by fluorescence spectrometry utilizing a Perkin Elmer 204A fluorescence spectrophotometer equipped with a P-E micro-flo-cell accessory kit. The detection limits were 5 nanograms per sample for both compounds.

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* PNA may also be referred to in the literature as Polycyclic Aromatic Hydrocarbons (PAH) or particulate polycyclic organic material (PPOM).

Carbon Monoxide:

Short-term general area carbon monoxide measurements were taken on both days with a calibrated direct-reading Ecolyzer Model 6000 at the following plant locations: between the baghouses on all three levels, in the vicinity of the reactors, and at the rerun deck, welding shop, and control room. Concentrations (in ppm) were recorded only after a steady meter reading was obtained on the instrument (usually 15-60 seconds) No personal monitoring was conducted because of the lack of appreciable CO levels and/or work activity in these areas.

Iron Oxide Fumes:

One personal breathing-zone sample for iron oxide fumes was collected on a 0.8u 37mm mixed cellulose ester membrane filter (closed-face) using a personal sampling pump calibrated at 1.5 lpm. The sample was analyzed for iron (Fe) by NIOSH Method P & CAM 127 using atomic absorption spectrophotometry.

Ventilation/Boiler Water Additives:

The laboratory hoods in the Quality Control lab were evaluated by means of air velocity measurements and visual inspection of the system components located on the roof. Measurements were taken at the face of each hood with the sash fully open using a calibrated thermal anemometer.

Product information supplied by the company was used to evaluate the boiler water additives.

B. Medical:

A total of 19 production workers completed pulmonary function tests, pre and post shift carboxyhemoglobin analysis in exhaled air, and standardized health questionnaires. Eighteen (18) supervisors/office workers with minimal carbon black exposure completed the same test battery as the production workers and comprise the control group. These data were compared between groups to ascertain any differences between control and exposed workers.

Pulmonary function tests include measurement of forced vital capacity (FVC) and one-second forced expiratory volume (FEV_1) and calculation of the ratio FEV_1/FVC. FVC measures the total amount of air that can be forced out of the lungs after breathing in as deeply as possible; FEV_1 measures the amount of air that can be exhaled in the first

second. FEV_1 can be impaired by cigarette-related lung damage or some other conditions. Any condition that impairs FVC also impairs FEV_1, but the reverse is not true. FEV_1/FVC, along with FEV_1 and FVC, is used to evaluate breathing function.

These measured breathing parameters (FEV_1 and FVC) are evaluated by comparing them to "predicted" values, which take into account age, height, sex, and race. Pulmonary function is considered "normal" if the FEV_1 and FVC are each 80% or more of their respective predicted value and FEV_1/FVC is 70% or more.

Pre-shift and post-shift breath samples for carbon monoxide (CO) were taken by having the workers blow the last half of a 20-second held inhalation into an Ecolyzer Carboximeter. The CO concentration of the samples was determined on the carboximeter. The amount of CO in the sample was converted to percent COHb in the workers' blood by Ringold equation.[1] The equation is $\%COHb = 0.5 + \frac{(CO \text{ in ppm})}{5}$.

NIOSH recommends that "normal" COHb levels in occupationally exposed individuals not exceed 5%.[3] This "normal" value does not take into consideration the smoking habits of the worker since the level of COHb in chronic cigarette smokers has generally been found to be in the 3-10 percent range prior to CO exposure.

Standardized health questionnaires were completed on all study participants.

V. EVALUATION CRITERIA

A. Environmental Standards:

To assess the concentrations of air contaminants found during this investigation, three primary sources of criteria were used: (1) NIOSH Criteria for recommended standards for occupational exposure to substances (Criteria Documents); (2) recommended Threshold Limit Values (TLV's) and their supporting documentation as set forth by the American Conference of Governmental Industrial Hygienists (ACGIH); and (3) occupational health standards promulgated by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.1000). These criteria are generally established at levels intended to protect workers occupationally exposed during an 8 or 10-hour workday, over a normal working lifetime. The environmental criteria of the substances evaluated in this study are presented below. Those which are the most stringent, and thus afford the best health protection for the worker, will be applied.

Substance	NIOSH[2,3] Recommended Criteria	ACGIH[4] TLV	OSHA[5] Standard
Carbon Black	3.5 mg/M^3 (PNA content, ie., cyclohexane extractable fraction, _ 1%) or 0.1 mg/M^3 cyclohexane extractable fraction	3.5 mg/M^3	3.5 mg/M^3
Carbon Monoxide	35 ppm 200 ppm (c)*	50 ppm 400 ppm (c)	50 ppm
Iron Oxide Fume (as Fe)	--	5 mg/M^3	10 mg/M^3

All values are time-weighted averages. * (c) - Ceiling level. NIOSH Criteria are based on a 10-hour workday. ACGIH and OSHA levels are based on an 8-hour workday.

In applying the NIOSH criteria it is necessary to determine whether the carbon black is PNA contaminated, ie, if it contains cyclohexane extractable substances at a concentration greater than 0.1% (1 mg/g) as determined via bulk sample analysis. The airborne exposure to the contaminated carbon black is determined by measuring the cyclohexane extractable fraction of personal breathing zone samples. As indicated above this should not exceed a 10 hour day TWA exposure of 0.1 mg/M^3 cyclohexane extractables. If the carbon black contains a cyclohexane extractable fraction of 0.1% or less, then the environmental limit of 3.5 mg/M^3 would apply.

The differentiation between PNA contaminated carbon black as that containing 0.1% cyclohexane extractable fraction is based on professional judgement, rather than on data delineating safe from unsafe concentrations of PNA's. This limit results in a maximum airborne PNA concentration of 0.035 mg/M^3 (as cyclohexane extractables) when carbon black is at its proposed limit of 3.5 mg/M^3. This is significantly lower than 0.1 mg/M^3 which was justified on the basis of feasibility of measurement, not on its safety.

The rationale in choosing the 0.1 mg/M^3 TWA limit for cyclohexane extractable fraction is chiefly based on the fact that with current monitoring methods it is the least concentration reliably detectable. The selection of cyclohexane extractable fraction rather than analysis of one or more specific PNA compounds is based on the argument presented in the NIOSH Criteria Documents for Coal Tar Products, Asphalt Fumes, and Coke Oven Emissions.[6,7,8] As reviewed in these documents PNA's contain many substances often thought or known to be carcinogenic. In addition there are factors affecting tumor yields and carcinogenic responses, including either enhancement or inhibition of carcinogenesis by compounds within the same class of chemicals. The concentration of specific compounds in any sample of PNA's are variable.

B. Physiological Effects:

Carbon Black:

Carbon black dust has not been shown to cause cancer, but there is evidence to suggest that it may cause adverse lung and heart changes.[2] Skin effects have also been noted in persons having had contact with carbon black. Epidemiologic studies of carbon black workers have produced no evidence of increased risk of disease or malignancy.[9,10]

Although carbon black by itself has not been shown to cause cancer, various studies have shown that PNA's, many of which are carcinogenic, are adsorbed on carbon black. There is, however, controversy concerning the fate of adsorbed PNA's following exposure to carbon black dust. Some studies have shown that the PNA's are bound so tightly to the carbon black particles that it renders them ineffective as carcinogens.[11,12,13] In contrast, other studies have shown that PNA's may be desorbed from carbon black by human plasma and under certain conditions such as acute respiratory infections.[14,15] These latter studies indicate that PNA contaminated carbon black may pose an increased cancer risk to exposed individuals. Therefore, NIOSH recommends that exposures be kept as low as feasible.

Carbon Monoxide:

Carbon monoxide (CO) is a by-product of incomplete combustion generated most commonly by the internal combustion engine. CO causes tissue damage by preventing the blood from carrying sufficient oxygen. Since CO causes damage by oxygen deprivation, symptoms are referable to those tissues with the greatest oxygen consumption - the brain and heart. Exposures to concentrations of 500 to 1000 ppm causes development of headache, rapid heartbeat, nausea, weakness, mental confusion, and in some instances hallucinations. Smokers suffer from the additive effect of the CO concentration in their cigarettes, compounding their occupational CO exposure.

Iron Oxide:

Inhalation of iron oxide fumes or dust may cause a benign lung condition termed siderosis. Little or no physical disability appears to be caused by the presence of iron oxide in the lungs unless there is mixed exposure to other chemicals. For example, workers with concomittant exposure to silica may develop a lung condition termed "mixed dust pneumoconiosis".[16] More recently, epidemiologic evidence has shown an increased risk of cancer in welders exposed to iron oxide and asbestos in combination.[17]

VI. RESULTS AND DISCUSSION

A. Environmental:

Carbon Black - Analysis of Bulk Samples:

The results of the bulk carbon black analyses for cyclohexane extractables and PNA's are presented in Table I. Two of the 8 grades of carbon black, namely N-231 and N-299, contain cyclohexane extractable fraction in excess of the 0.1% criterion for its classification as PNA contaminated carbon black. Grade 231 ranged from 0.28-0.80% cyclohexane extractables. Grade M-299 contained 0.12% cyclohexane extractables. Both grades did not contain detectable quantities of fluoranthene, pyrene, benzo(a)pyrene, chrysene, or benzo(a)anthracene. There are, however, a large number of other PNA's, some of which are carcinogenic, that may be present in these grades.

Carbon black grades N-375 (manufactured during this survey) and N-341 did not contain greater than 0.1% cyclohexane extractables. Low, but detectable, quantities of fluoranthene and pyrene, ranging to 7 and 25 ppm, respectively, were found in the extract of these bulk samples. Cyclohexane extractables and PNA's were not detected in the other grades.

The results from samples N-231 and N-375 suggest that, for the substances analyzed, there appear to be no chemical differences between pelletized and nonpelletized types.

Carbon Black - Analysis of Environmental Samples

The results of the personal samples for carbon black and its cyclohexane extractable fraction are presented in Tables II and III. The mean carbon black concentration was 1.01 mg/M^3 (S.D. + 0.81; range: 0.20-2.84 mg/M^3) for 22 samples. None of the samples exceeded the OSHA standard of 3.5 mg/M^3 for carbon black. Samples obtained from hopper car loaders and from maintenance workers making adjustments on the rerun blowers had the highest levels. Average carbon black

levels for each day were the same indicating that the company cleanup activities conducted on December 18 did not bias the values obtained on that day.

Concentrations of cyclohexane extractable fraction averaged 0.04 mg/M^3 (S.D. $\pm$ 0.04; range: nondetectable to 0.19 mg/M^3) for the 22 samples. Two of the samples were in excess of the NIOSH recommended criteria 0.1 mg/M^3 for cyclohexane extractables. Both samples were taken on employees spending part of their workday adjusting the rerun blowers.

Small quantities of fluoranthene, pyrene, and/or benzo(a)pyrene B(a)P were detected in 20 of the 22 personal samples. Fluoranthene levels ranged up to 30 nanograms per cubic meter (ng/M^3). Pyrene levels ranged up to 137 ng/M^3. Only semiquantitative data was reported for B(a)P since this compound was not anticipated in these samples based on the results for the bulk sample analysis. The lab reported only those samples with peak heights greater than 10mm on the chromatogram. Instrument settings are given in Table II.

The results of the general area air sampling are presented in Table IV. Samples were collected on both days at the following locations: baghouses, rerun deck, train shed, and product warehouse. The carbon black concentrations were highest in the rerun deck with time-weighted average (TWA) concentrations averaging 7.18 mg/M^3. Carbon black concentrations in the train shed ranged up to 1.55 mg/M^3. Levels in the warehouse and between the baghouses ranged up to 0.52 mg/M^3.

The concentration of cyclohexane extractables from samples collected in these areas were below 0.04 mg/M^3 except for the sample collected in the rerun deck area on December 18. The TWA concentration of cyclohexane extractables in this sample was 0.12 mg/M^3, which exceeds the NIOSH criteria of 0.10 mg/M^3.

Carbon monoxide (CO) concentrations at selected plant locations are presented in Table V. Average concentrations for these short-term measurements ranged up to 20 ppm at all locations sampled except on the third level gantry between the baghouses. CO levels on this level ranged between 10 and 350 ppm. The higher levels resulted from periodic off-gassing of the reverse-air-flow valves. The NIOSH criteria, by comparison, is 35 ppm as a time-weighted average in any 10 hour workshift with a ceiling limit of 200 ppm not to be exceeded at anytime during the workshift. Concentrations in excess of the NIOSH criteria were not indicative of employee exposure since no workers were present on the gantry. These levels do, however, represent potential exposures to control room operators and maintenance men.

The iron oxide fume TWA concentration for the sample taken on the maintenance technician welding on a line #2 carbon steel reactor was 0.17 mg/M^3. This concentration is below the TLV of 5.0 mg/M^3 for iron oxide fume (as Fe).

Ventilation Measurements/Boiler Water Additives

Ventilation measurements of the laboratory hoods in the Quality Control lab were taken with a calibrated thermal anemometer. The average velocity across the face of each hood was 90 feet per minute (fpm), which is below the minimum face velocity of 100 fpm recommended by ACGIH for moderately toxic chemicals (such as toluene) so that to insure that vapors are contained within the hood.[18] Inspection of the fans and ducting (located on the roof) revealed no evidence of deterioration or malfunction.

Information provided by the company on each of the boiler water additives were evaluated. Judging from their infrequent use and the relative small quantities needed per treatment, current use should not present adverse health effects when existing precautions are taken.

B. Medical:

Mean values for pulmonary function tests results (FEV_1/FVC%) in the "exposed" group were 79% for the entire group, 76% for smokers and 81% for nonsmokers. Mean (FEV_1/FVC%) values in the "control" group were 79% for the entire group, 78% for smokers and 81% for nonsmokers. Results, in all case comparisons, evidenced no statistically significant difference (see Table VI).

The analysis of pre and post shift carboxyhemoglobin levels and the resultant shift differentials evidenced no major differences between groups except between smokers and nonsmokers in both study groups (see Table VII). The health questionnaires underscored a disproportional rate of health complaints among the production workers. Seven (37%) workers complained of nasal irritation, and four (21%) of the same workers complained of shortness of breath. In each of these instances, carbon black was implicated as the major causative factor. A single health complaint of shortness of breath was noted within the control group, and carbon black was not considered a causative factor.

VII. CONCLUSION

Based on the data collected during this survey, NIOSH determined that a hazard of overexposure to carbon black containing PNA's (analyzed via the cyclohexane soluble fraction) did exist at the time of this survey.

The presence of PNA's in the personal samples is cause for concern since the carcinogenic potential of these compounds is well-documented. The results of the medical questionnaires revealed complaints of nasal irritation and dyspnea in the production workers. The pulmonary function tests results and the calculated % COHb levels in exhaled air were similar when shift differentials and/or smoking habits were compared.

VIII. RECOMMENDATIONS

1. Carbon black dust/cyclohexane extractable concentrations in the rerun deck should be reduced. As early as December 1979 the company informed employees that it had intended to relocate the rerun deck outdoors. The company should implement this recommendation. In the interim, appropriate respiratory protection should be used.

2. The apparent variable cyclohexane extractable fraction in grade N-231 would indicate a need for continuing quality control to assure that the extractable contaminants are less than 0.1% in this grade as well as the other grades of carbon black.

3. The company should continue environmental monitoring of the workers for carbon black dust. In addition, worker exposure to cyclohexane extractables and PNA's should be evaluated.

4. The face velocity of the laboratory hoods in the Quality Control lab should be increased to at least 100 fpm. Visible gauges, audible alarm or pressure activated devices should be installed to indicate/insure that the required air velocity is maintained.

5. Medical surveillance of all carbon black workers should be instituted. Each worker should receive a yearly physical examination with emphasis given to the lungs, heart, and skin. This annual exam should also include pulmonary function tests.

6. Skin contact with carbon black should be avoided.

7. Workers entering the area between the baghouse, especially on the third level gantry, should be provided with CO sensors with audible alarm so that the workers are instantly informed of high CO exposures.

8. A joint labor-management training program on the effects of exposure or contact with carbon black, proper work practices, etc., should be instituted.

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X. AUTHORSHIP AND ACKNOWLEDGEMENTS

Evaluation Conducted and Report Prepared By:	James M. Boiano Industrial Hygienist Industrial Hygiene Section Michael T. Donohue Physician's Assistant-Certified Medical Section
Environmental Evaluation Assistance:	Larry DeArmond Industrial Hygiene Technician Industrial Hygiene Section
Medical Evaluation Assistance:	James E. Boyd Pulmonary Technician Support Services Branch
Originating Office:	Hazard Evaluations and Technical Assistance Branch Division of Surveillance, Hazard Evaluations, and Field Studies

Report Typed By: Patty Johnson
Secretary
Industrial Hygiene Section

XI. DISTRIBUTION AND AVAILABILITY OF REPORT

Copies of this report are currently available, upon request, from NIOSH, Division of Technical Services, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), 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. Phillips Chemical Company, Toledo, Ohio
2. Local Representatives of the Oil, Chemical, and Atomic Workers Union
3. OCAW, International
4. Phillips Petroleum Company, Barttesville, Oklahoma
5. U.S. Dept. of Labor (OSHA), Region V
6. NIOSH, Region V

For the purposes of informing the 28 "affected employees," the employer shall promptly "post" the determination report, for a period of 30 calendar days, in a prominent place near where exposed employees work.

TABLE I

Cyclohexane Extracts from the Various Sample Grades of Carbon Black

Phillips Chemical Company
Toledo, Ohio
HE 80-203

December 17-18, 1980

Carbon Black Grade	Pelletized	Production Date	Total Cyclohexane Extractable Fraction (mg/g)	Percent Cyclohexane Extractables (%)	Polynuclear Aromatic Hydrocarbons (PNA) ug/g				
					Fluoranthene	Pyrene	B(a)A	Chrysene	B(a)P
N-231	No	12/18/80	4.4	0.44	<1.00	<2.49	<0.50	<1.50	<0.5
N-231	Yes	12/18/80	2.8	0.28	<1.00	<2.49	<0.50	<1.50	<0.5
N-375	No	12/18/80	<0.4	<0.04	3.39	12.40	<0.50	<1.50	<0.5
N-375	Yes	12/18/80	<0.4	<0.04	1.30	7.70	<0.50	<1.50	<0.5
N-231	Yes	12/17/80	8.0	0.80	<1.00	<2.49	<0.50	<1.50	<0.5
N-299	Yes	12/16/80	1.2	0.12	<1.00	<2.49	<0.50	<1.50	<0.5
N-339	Yes	5/80	<0.4	<0.04	<1.00	<2.49	<0.50	<1.50	<0.5
N-326	Yes	2/80	<0.4	<0.04	<1.00	<2.49	<0.50	<1.50	<0.5
N-330	Yes	2/80	<0.4	<0.04	<1.00	2.85	<0.50	<1.50	<0.5
N-341	Yes	2/80	<0.4	<0.04	7.00	25.0	<0.50	<1.50	<0.5
N-347	Yes	----	<0.4	<0.04	<1.00	<2.49	<0.50	<1.50	<0.5
Limit of Detection:			0.4		1.00	2.49	0.50	1.50	0.5

mg/g = milligrams per gram
ug/g = micrograms per gram
B(a)A = Benzo(a)anthracene
B(a)P = Benzo(a)pyrene

TABLE II

Environmental Concentrations of Carbon Black, Cyclohexane Extractable Fraction, Fluoranthene, and Pyrene in Personal Samples

Phillips Chemical Company
Toledo, Ohio
HE 80-203

December 17, 1980

Work Location(s)	Job Classification	Sample Time (min.)	Sample Volume (M^3)	Carbon Black (mg/M^3)	Cyclohexane Extractable Compounds: Total Extract (mg/M^3)	Fluoranthene (ng/M^3)	Pyrene (ng/M^3)	B(a)P
Plantwide & Rerun Deck	Maint. Tech.	504	1.01	1.19	N.D.	N.D.	26	
Plantwide & Rerun Deck	Maint. Tech.	501	1.00	1.28	0.07	7	22	*
Train Shed	Utility Person	493	0.99	1.56	0.07	20	66	*
Plantwide	Utility Person	492	0.98	1.30	0.03	11	40	*
Plantwide	Utility Person	492	0.98	1.07	0.05	6	23	*
Train Shed	Utility Person	491	0.98	2.36	0.03	N.D.	15	
Plantwide	Maint. Tech.	484	0.97	0.53	0.03	12	30	*
Plantwide	Maint. Tech.	481	0.96	0.51	0.03	--	10	*
[illegible]ide	Maint. Tech.	482	0.96	0.62	N.D.	N.D.	10	*
[illegible]ib	Warehouse Person	480	0.96	0.20	N.D.	N.D.	N.D.	*
Plantwide	Maint. Tech.	480	0.96	0.51	0.03	N.D.	8	*
Mean ± Standard Deviation:				1.01±0.62	0.03±0.02	6±7	23±18	--
Evaluation Criteria:				3.50	0.10	**	**	**
Laboratory Limit of Detection: mass (mg or ng)/sample:					0.02	5	5	

N.D. = Nondetectable
mg/M^3 = Milligrams of substance per cubic meter of air
ng/M^3 = Nanograms of substance per cubic meter of air
*Benzo(a)pyrene was detected in these samples at a peak height greater than 10mm on the chromatogram. Instrument parameters are presented below:

cx = 363nm slit = 10
cm = 440nm slit = 20
photomultiplier gain = 4
sensitivity range = 10
response = slow
chart span = 10mv
chart speed = 0.5cm/min.

**PNA's are potential human carcinogens. Exposure should be kept as low as possible.

TABLE III

Environmental C[illegible]ations of Carbon Black, Cyclohexane Extractable Fraction[illegible]oranthene, and Pyrene in Personal Samples

Phillips Chemical Company
Toledo, Ohio
HE 80-203

December 18, 1980

Work Location(s)	Job Classification	Sample Time (min.)	Sample Volume (M^3)	Carbon Black (mg/M^3)	Cyclohexane Extractable Compounds: Total Extract (mg/M^3)	Fluoranthene (ng/M^3)	Pyrene (ng/M^3)	B(a)P
Plantwide & rerun deck	Maint. Tech.	514	1.03	2.64	0.19	7	52	
Trainshed	Utility Person	510	1.02	2.84	0.08	30	137	*
Plantwide	Maint. Tech.	478	0.95	0.85	0.04	20	73	*
Plantwide	Maint. Tech.	467	0.93	0.46	0.02	N.D.	N.D.	
Tool Crib	Warehouse Person	510	1.02	0.22	0.02	N.D.	N.D.	*
Plantwide	Maint. Tech.	459	0.92	0.86	0.06	14	26	*
Plantwide	Maint. Tech.	248	0.50	0.38	0.04	N.D.	12	*
Plantwide	Maint. Tech.	499	1.00	0.20	0.02	N.D.	N.D.	*
Plantwide	Maint. Tech.	498	1.00	0.49	0.02	N.D.	9	*
Plantwide & rerun deck	Maint. Tech.	496	1.00	1.93	0.12	12	47	*
Plantwide	Utility Person	494	0.99	0.21	0.02	N.D.	N.D.	
Mean ± Standard Deviation:				1.01±0.99	0.05±0.05	8±10	32±43	--
Evaluation Criteria:				3.50	0.10	**	**	**
Laboratory Limit of Detection:					0.02	5	5	

N.D. = Nondetectable
mg/M^3 = milligrams of substance per cubic meter of air
ng/M^3 = nanograms of substance per cubic meter of air
*Benzo(a)pyrene was detected in these samples at peak heights greater than 10mm on the chromatogram. Refer to Table II for instrument settings.
**PNA's are potential human carcinogens. Exposure should be kept as low as feasible.

TABLE 1

Environmental Concentrations of Carbon Black, Cyclohexane Extractable Fraction, Fluoranthene, and Pyrene in General Area Samples

Phillips Chemical Company
Toledo, Ohio
HE 80-203

December 17-18, 1980

Date	Work Location(s)	Sample Time (min.)	Sample Volume (M^3)	Carbon Black (mg/M^3)	Cyclohexane Extractable Compounds: Total Extract (mg/M^3)	Cyclohexane Extractable Compounds: Fluoranthene (ng/M^3)	Cyclohexane Extractable Compounds: Pyrene (ng/M^3)
12/17	Betw. Baghouses Ground Level	455	0.91	0.27	N.D.	N.D.	7
12/17	Rerun Deck	443	0.89	6.23	0.03	N.D.	41
12/17	Trainshed Loading Level 20 ft. from Exit	450	0.90	1.55	N.D.	N.D.	N.D.
12/17	Trainshed Loading Level 50 ft. from Exit	450	0.90	0.25	N.D.	N.D.	10
12/17	Product Warehouse	435	0.87	0.07	--	N.D.	--
12/18	Betw. Baghouses Ground Level	461	0.92	0.21	0.02	N.D.	11
12/18	Rerun Deck	480	0.96	8.13	0.12	50	350
12/18	Trainshed Ground Level North Wall	477	0.95	1.18	N.D.	7	30
12/18	Trainshed Ground Level South Wall	477	0.95	0.89	0.04	--	14
12/18	Product Warehouse	480	0.96	0.52	0.02	N.D.	11
Evaluation Criteria:				3.50	0.10	--	--
Laboratory Limit of Detection: mass (mg or ng)/sample:					0.02	5	5

N.D. = Nondetectable
mg/M^3 = milligrams of substance per cubic meter of air
ng/M^3 = nanograms of substance per cubic meter of air (1 mg = 1 million ng).

TABLE V

Carbon Monoxide Concentrations

Phillips Chemical Company
Toledo, Ohio
HE 80-203

December 17-18, 1980

Plant Location	Carbon Monoxide Concentration (ppm)* December 17	December 18
Between Baghouses Ground Level	8-10	8-20
Second Level (Gantry)	10-18	8
Third Level (Gantry)	10-350[1]	10-350[1]
Warehouse	--	8
Rerun Deck	20	10
Welding Shop	8-10	8-10
Control Room	6-8	5
Outdoors	8-10	8

Evaluation Criteria: 35 ppm, 10 hour TWA
200 ppm, ceiling limit

Measurements taken with a calibrated Ecolyzer Model 6000.

*ppm = parts per million parts of air

1. These relatively higher levels resulted from periodic off-gassing of the reverse-air-flow valves.

Pulmona tion Results

Phillips nical Company
To do, Ohio
HL 80-203

December 17-18, 1980

	"Exposed" Group			"Control" Group		
	FEV_1 %	FVC %	FEV_1/FVC %	FEV_1 %	FVC %	FEV_1/FVC %
Smokers				**Smokers**		
1	100	104	76	1	75	88	71
2	99	104	77	2	101	102	80
3	100	105	77	3	91	100	73
4	105	121	75	4	97	91	86
5	80	90	70	5	99	99	82
6	82	92	76	6	98	115	67
7	110	112	80	7	89	101	72
				8	111	102	90
				9	100	102	79
Nonsmokers				**Nonsmokers**		
8	93	99	76	10	86	78	89
9	99	99	80	11	113	122	75
10	103	104	80	12	121	118	84
11	107	110	78	13	90	94	77
12	82	81	82	14	93	92	81
13	95	96	81	15	107	105	83
14	104	106	79	16	105	99	86
15	116	103	91	17	82	99	67
16	107	113	77	18	110	106	85
17	108	109	81				
18	90	94	77				
19	103	99	84				

Total (n=19)	x=99.11	x=102.27	x=79	Total (n=18)	x=98.22	x=100.72	x=79
	S.D.=10.47	S.D.=9.96	S.D.=3		S.D.=11.45	S.D.-10.32	S.D.=7
Smokers (n=7)	x=96.57	x=104.04	x=76	Smokers (n=9)	x=95.67	x=100.00	x=78
	S.D.=10.47	S.D.=9.96	S.D.=3		S.D.=9.39	S.D.=7.18	S.D.=8
Nonsmokers (n=12)	x=100.58	x=101.08	x=81	Nonsmokers (n=9)	x=100.78	x=101.44	x=81
	S.D.=8.88	S.D.=8.23	S.D.=4		S.D.=12.68	S.D.=12.63	S.D.=6

n = number x = mean S.D. = standa eviation

Calculated Pre & Post Carboxyhemoglobin Levels in Exhaled Air of "Exposed" and "Control" Workers

Phillips Chemical Company
Toledo, Ohio
HE 80-203

December 17-18, 1980

	"Exposed" Group			"Control" Group			
	Pre-Shift % COHb	Post-Shift % COHb	Difference % COHb		Pre-Shift % COHb	Post-Shift % COHb	Difference % COHb
Smokers				Smokers			
1	7.0	7.2	0.2	1	13.0	8.2	-4.8
2	12.0	12.0	0.0	2	8.2	13.0	4.8
3	7.2	13.0	5.8	3	7.8	12.0	4.2
4	7.0	12.0	5.0	4	7.8	7.6	-0.2
5	7.0	7.8	0.8	5	13.0	12.0	-1.0
6	8.2	12.0	3.8	6	4.0	3.4	-0.6
				7	12.0	12.0	0.0
				8	8.4	No Test	--
				9	13.0	No Test	--
NonSmokers				Nonsmokers			
7	0.6	1.2	0.6	10	2.0	0.6	-1.4
8	2.0	0.8	-1.2	11	0.0	0.0	0.0
9	0.8	0.6	-0.2	12	0.0	1.2	1.2
10	No Test	0.6	--	13	0.6	0.8	0.2
11	0.6	2.4	1.8	14	1.4	1.4	0.0
12	1.8	2.2	0.4	15	0.4	1.0	0.6
13	1.2	3.0	1.8	16	0.8	No Test	--
14	2.8	1.0	-1.8	17	0.2	No Test	--
15	1.4	1.0	-0.4				
16	1.4	2.6	1.2				
17	0.6	1.2	0.6				
18	0.6	No Test	--				

Total (n=18)

Smokers (n=6)

Nonsmokers (n=12)

Total (n=17)

Smokers (n=9)

Nonsmokers (n=8)

COHb = Carboxyhemoglobin