



Health Hazard Evaluation Report

HETA 83-248-1515 ARCO PHILADELPHIA REFINERY PHILADELPHIA, PENNSYLVANIA

PREFACE

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

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

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

HETA 83-248-1515 October 1984 ARCO PHILADELPHIA REFINERY PHILADELPHIA, PENNSYLVANIA

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I. Summary

On April 22, 1983, the National Institute for Occupational Safety and Health (NIOSH) received a request to evaluate possible skin rashes and irritation due to skin contact with "fractionator bottoms", thought to contain polynuclear aromatic hydrocarbons (PAH) at the ARCO Philadelphia Refinery (APR), Philadelphia, Pennsylvania.

On May 4, 1983, a NIOSH industrial hygienist conducted a preliminary walk-through of the catalytic cracker area, eating areas (one in the computer control area and one in the block house), locker rooms, and sample preparation room. To assess the extent of skin problems related to such exposure, a NIOSH medical officer conducted a site visit at the plant also in May 1983, administered a questionnaire to 24 employees on the fluid catalytic cracking unit (FCCU), and performed limited dermatological examinations of selected workers. Eight of the 24 workers reported that potentially work-associated rashes had occurred at some time during their employment in the FCCU. Physical examination showed that at least four of the current employees had a rash. Although it was not possible to show conclusively a work-association in all of these workers reporting or exhibiting rashes, the temporal association and exposure history in three or four workers is suggestive of an association with exposures at work. However, due to the limited nature of the exposures to the bottoms (i.e., a single sampling done once a day lasting five minutes by a single person), it seems unlikely that this exposure alone is sufficient to explain the skin problems observed. Additional exposure, including catalyst dust and oils present on workers' boots or absorbed on workers' clothing from other exposure sources may also be important in the etiology of these skin problems. A bulk sample of fractionator bottoms was collected by the NIOSH medical officer and relayed to the NIOSH industrial hygienist for chemical characterization. Seventeen (17) PNA's were identified in this sample. Some of these PNA's are known to cause dermatitis and skin cancer in humans.

Based on these results, NIOSH concludes that there may have been a health hazard from exposure to chemicals at the fluid catalytic cracking unit at the ARCO Philadelphia Refinery. Recent improvements in training and access to information concerning the chemicals to which the workers are exposed have improved the workers' ability to reduce exposures. Additional steps to aid in reducing exposures are contained in the Recommendation Section of this report.

KEYWORDS: SIC (2911) Petroleum refining, polycyclic aromatic hydrocarbons, dermatitis, skin rashes, skin irritation, fluid catalytic cracking unit.

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II. Introduction

On April 22, 1983, NIOSH received a request for a health hazard evaluation at the ARCO Philadelphia Refinery (APR), Philadelphia, Pennsylvania. The request was submitted by the Atlantic Independent Union and asked that NIOSH investigate the possibility that skin rashes and skin irritation were due to skin contact with "fractionator bottoms" containing polynuclear aromatic hydrocarbons (PNA or PAH). On May 4, 1983, a NIOSH industrial hygienist initiated a preliminary investigation into this matter. A NIOSH medical officer visited the plant on May 19, 20, 24, and 25, 1983 to assess the extent of the skin problems.

III. Background

The APR was founded in the late 1800s to distill and refine petroleum. It reached a maximum employment in the late 1940s of 3000, and currently employs 600 people. Since the mid 1960s, major renovations have occurred at the plant. It refines crude petroleum into a number of products, and contains an advanced fluid catalytic cracking unit (FCCU) which was constructed during the late 1970s and early 1980s and went into operation in May, 1981. The unit employs 26 people which includes one supervisor and five foremen. The 20 workers are divided into four rotation shifts with one foreman and four workers per shift on the average. Each worker performs all jobs on the unit on a weekly rotating schedule. The four jobs include work in the catalytic processing area, in the heavy oil area, in the light oil area, and in the control room. All processes at the plant are contained in closed reaction vessels. However, when leaks occur, when maintenance is needed, or when sampling of reaction intermediates or products takes place, workers may be exposed to various crude or refined oil compounds. Prior to the start up of the FCCU unit in May 1981, the employees received five months of operations and safety training in the operation of the fluid catalytic cracking unit.

IV Evalution Design and Methods

A. Environmental

A bulk sample of the fractionator bottoms was collected for analysis of benzene-soluble polynuclear aromatics.

This sample was analyzed following NIOSH Technical Bulletin, TB-001, issued December 1, 1982. Approximately 250 mg of the bulk sample was desorbed in 5 ml of benzene with sonication for 30 minutes. The solution was filtered through a 0.45 micron nylon filter and an aliquot of the filtered solution was analyzed via gas chromatography using a flame ionization detector.

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B. Medical

The May investigation included a questionnaire and interview of 24 of the 26 people who work on the FCCU (Unit 868). One worker was on a sick leave, and another worker was not present during any of the shifts during the time period that interview took place. The questionnaire was administered by the NIOSH investigator to each person and was intended to evaluate the presence of irritative symptoms and other general health problems. In addition, limited dermatological examinations were conducted on selected workers based on questionnaire results.

V. Evaluation Criteria

Polycyclic aromatic hydrocarbons (PAH) form a class of complex hydrocarbon chemicals which are generally formed as a result of the incomplete combustion of certain hydrocarbon fuels including plant materials, petroleum, and coal. Many chemicals are classified as PAHs. Some have been studied individually (3), but much of the research on PAHs has been done on mixtures of chemicals.

In a recently completed industrial hygiene survey of nine petroleum refineries including FCCUs, NIOSH found that workers were exposed to numerous PAHs, usually at low microgram per cubic meter concentrations. The lighter weight, 2- and 3-ring PAHs were found in the highest concentrations. The lighter molecular weight PHAs are not considered as carcinogenic as the heavier PAHs (4). A number of recommendations were published in the report of this survey (pp. 66-67) and it should be consulted for further details.

PAHs are known to cause a variety of adverse health effects in both experimental animals and humans. Much of the research on PAHs has dealt with their effects on skin since skin testing is relatively simple. Skin exposure is common in the workplace. These effects include skin irritation and irritant dermatitis, allergic dermatitis, and photosensitivity dermatitis. Photosensitivity means that when a chemical is placed on the skin and then the skin is exposed to ultraviolet light (as in sunshine) there is an increase in the severity of the skin inflammation. In addition, PAHs may cause inflammation of hair follicles, acne, and changes in the pigmentation of the skin (either an increase or decrease).

In addition to these inflammatory effects, PAHs have been known for years to cause various types of tumors of the skin, ranging from benign keratosis (darkened wart-like non-cancerous growths) to cancer of the skin. A detailed discussion of these skin effects is contained in references 1 & 2.

A number of epidemiological studies of petrochemical workers have been done in the last 10-20 years to deterine whether these workers are at higher risk of developing cancers due to their exposure to petrochemicals.

Most of these studies have shown that petrochemical workers have a lower risk of dying at a given age than the general population. This is known as the "healthy worker effect" and is expected since workers are able to work and, therefore, are healthier as a group than the general population which includes many ill and debilitated individuals. Some of these studies have shown no increase in cancer in these workers (5, 7, 11). However, other studies have shown increases in the cancer rate in general (6, 9, 10, 12, 13) or in cancers of a particular site (brain, 6, 14; bone, 7; lung, 8;). In 1982, an entire volume of the Annals of the NY Acad Science (15) was devoted to the issue of whether petrochemical workers have an increased risk of developing brain cancer. In addition to showing an increase in death due to certain cancers. some studies have shown that the risk of developing cancer increases with increased duration of employment in the petrochemical industry (6, 13, 14). None of these studies, though, discusses whether there is an increased rate of skin cancer in refinery workers since this type of cancer frequently does not cause death.

In summary, the issue of increased rates of cancer in petrochemical workers is not yet resolved. A more detailed discussion of these studies is contained in reference 4, pp. A-1 to A-6.

VI Results

A. Environmental

Analysis of the bulk fractionator bottom sample revealed the following 17 PNA (polynuclear aromatic) compounds to be present:

Acenaphthylene 220 Acenaphthene 63 Fluorene 180 Phenanthrene 780	rams per	gram)
Anthracene 52 Fluoranthene 51 Pyrene 1000 Benzo (c) Phenanthrene 100 Benz (a) anthracene 600 Chrysene 1800 Benzo (e) pyrene 65 Benzo (b) fluoranthene 510 Benzo (k) fluoranthene 69 Benzo (a) pyrene 560 Dibenz (a,h) anthracene 400 Benz (g,h,i) perylene 400 Indeno (1,2,3,-cd) pyrene 400		

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B. Medical

Twenty-four workers on the FCCU were interviewed in May 1983. All were male; 19 were white and five were black. The mean age of the group was 32 years (range 22-49). The mean job duration on FCCU was 22.4 months (range 6-24).

Ten workers reported eye irritation. Five of these attributed the eye irritation to catalyst dust, two to working with VDT's, and the other three to allergies or non-work causes.

Twelve of the 24 reported having rashes at some point during their employment of the FCCU, but only eight thought that their rashes were possibly related to work exposures. The other four included conditions predating employment on the FCCU or conditions with an etiology not compatible with chemical exposures. Of the eight reporting rashes with a possible work association, only three reported having a current rash. Most rashes were described as small, localized areas of redness and scaling usually located either on the calves or ankles or on the lower arms.

The duration of the rashes in the individuals ranged from one week to approximately 1.5 years. Most of the people reported that the rashes were of short duration (less than one month); and with the following exceptions they were unable to associate them with particular exposures at work. Two or three individuals associated rashes with the period during which the FCCU was shut down for steam cleaning of the lines. One individual attributed his rash to association with the light oil products; one individual associated rash with exposure to catalyst; and two individuals associated rash with exposure to chemicals absorbed by their socks from oil-wetted boots.

Physical examinations of ten workers showed two workers with tinea versicolor (a superficial fungus infection); one worker with icthyosis (scaly skin); one worker with isolated areas of hypopigmentation (loss of skin color) but no active rash or skin irritation; one worker with a few scattered pimples on the upper midback; one worker with a cracking, scaling lesion on the right ring finger; two workers with rashes on their ankles, one of which was very slight; one worker with a small pigmented nevus (mole) under his right eye and a 4mm red macule (flat spot) on his left shoulder; and one worker with a one-to-two cm² patch of scaly skin on his left forearm. None of these lesions was resembled consistent with photosensitivity reaction, chloracne, or folliculitis. Four resembled contact dermatitis and one showed hypopigmentation. As mentioned earlier, only three or four of these lesions could be associated by the workers with exposures at work, and the exposures were diverse. No one attributed any skin problems to direct exposures to sampling of the fractionator bottoms. Some did suggest that symptoms may have been related to the period of time when the FCCU lines were being cleaned and there was exposure to the fractionator bottoms residues.

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VII. Discussion and Conclusions

Based on the results of the fractionator bottom analysis and medical evaluations conducted in May 1983, NIOSH has determined that a health hazard may exist from exposure to miscellaneous chemicals at the FCCU at APR. No specific chemical agent could be implicated. However, the interviews suggested that dust from the catalyst and oil residues in and about the FCCU which could contaminate workers' shoes and work clothes may have contributed to some of the cases of dermatitis. Although it is difficult to evaluate each individual case with respect to relationship to work at least two or three of the cases do seem to have a clear temporal and physical association with exposures at the FCCU. The most significant exposures appear to be from blowing catalyst dust and from oil products contaminating the boots, socks, and lower legs of the workclothes of workers on the unit. Use of the coveralls provided by the company, as well as the practice of showering at the end of the workday appear to help reduce the exposures. Due to the short duration of work in this unit and the youth of the workers, no skin tumors could be expected, as these take several years to develop. The new individual air hoods which the ARCO industrial hygienist has supplied for the workers on the FCCU appear to have solved the problem of catalyst dust exposure to the eyes and respiratory tract. In addition, the use of safety goggles and glasses appears to be effective in reducing irritation from this type of exposure.

VIII Recommendations

- l. Operators should be properly trained regarding the possible health hazards of certain operations and the most effective way to perform these operations to minimize exposures. An example of this is the collection of process stream samples. Operators should be instructed to stand upwind of the sampling port and to use the proper clothing and/or equipment (e.g., gloves) to prevent dermal contact. Sampling loops should be used on all open-spigot sampling ports. The American Petroleum Institute is currently investigating the proper sampling methods and equipment for refineries. When they are released, these recommendations should be followed.
- 2. ARCO should launder workers' coveralls by a dry cleaning method on a weekly basis (or more often, if necesary) since laundering with ordinary detergents may be insufficient to remove some of the oil products present. Laundering of work clothes at home may contaminate non-work clothes or the clothes of family members.
- 3. ARCO should provide workers with oil-resistant or oil-proof work boots, and replace contaminated boots with new boots. In addition, workers should be advised not to wear socks which have become soaked, discolored, or otherwise contaminated by oil.
- 4. The ventilator and lights in the sample preparation room adjacent to the block house should be repaired to reduce exposure to the sampled compounds and to provide adequate lighting when preparing the samples.

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IX. References

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XI. <u>Distribution</u> and Availability of Report

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- 1. ARCO Philadelphia Refinery
- 2. Atlantic Independent Union
- 3. NIOSH Region III
- 4. OSHA Region III

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.