U.S. Department of Health, Education, and Welfare
Center for Disease Control
National Institute for Occupational Safety and Health
Cincinnati, Ohio 45226

Health Hazard Evaluation Determination
Report No. 76-74-393

Great Lakes Research Corporation
Elizabethton, Tennessee

May 1977

I. TOXICITY DETERMINATION

Some of the workers employed in the carbon fiber production pilot plant have exhibited a reddening or lightening of their hair color, presumably due to some type of exposure to chemical or physical agents in the working environment. This study was not successful in determining the cause of the hair discoloration. Therefore, it is not possible to state what the potential consequences might be to the health of the workers from exposure to such agents. For the sake of prudence, it is recommended that all process emissions be captured at their source and removed from the process areas through the use of local exhaust ventilation.

II. DISTRIBUTION AND AVAILABILITY OF DETERMINATION 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. Information regarding its availability through NTIS can be obtained from NIOSH, Publications Office at the Cincinnati address.

Copies have been sent to:

A. Great Lakes Research Corporation - Elizabethton, Tennessee
B. Oil, Chemical, and Atomic Workers Union - Washington, D.C.
   Local 3903 - Elizabethton, Tennessee
C. Tennessee Department of Public Health - Nashville, Tennessee
D. U.S. Department of Labor, OSHA - Region IV
E. NIOSH Regional Consultant - Region IV

For the purposes of informing the approximately 20 "affected employees", the employer will promptly "post" this report for a period of 30 calendar days in a prominent place near where affected employees work.

III. INTRODUCTION

Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6), authorizes the Secretary of Health, Education, and Welfare, following a written request by 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 National Institute for Occupational Safety and Health (NIOSH) received such a request from an employer representative regarding exposure of employees to Orlon carbonization by-products at the Great Lakes Research Corporation (GLRC) in Elizabethton, Tennessee. The primary reason for the request was a discoloration of some workers' hair in the pilot plant where carbon fibers are produced from the carbonization of Orlon. Workers with dark hair noticed a reddening of the exposed tips; one worker with light brown hair noticed a further lightening in the color of the exposed hair. The discoloration resembled hair bleaching which might normally be observed from the application of a mild hydrogen peroxide solution or very prolonged exposure to direct sunlight.

IV. HEALTH HAZARD EVALUATION

A. Plant Process - Conditions of Use

The Pilot Plant of Great Lakes Research Corporation in Elizabethton, Tennessee, operates a process which converts Orlon Acrylic Tow (a DuPont product) into carbon and graphite fibers. The Orlon is first stretched in steam to get the proper fiber orientation and then passed through a high temperature air oven (oxidizer) where the polymers change color (white to black). The darkening is accompanied by partial oxidation. It is reported by company management that low levels of hydrogen cyanide (HCN) are produced at this point. After partial oxidation, the fibers do not melt when heated, as Orlon would.

After the oxidizer, the material is carbonized to produce carbon fibers. About 50% of the weight of the material is lost in this operation. Some tars collect at the entrance of the carbonization stage and a white ash collects at the entrance of the highest temperature zone. Local exhaust ducts are positioned at the entrance and exits of most ovens.

In a subsequent step, further heating in an electric graphite tube furnace is used to produce a higher Young's modulus in the carbon filaments. An essentially ash-free carbon or graphite fiber results. A size may subsequently be applied to the fibers.

In the adjacent Packaging and Testing area, a solution of calcium hypochlorite is used occasionally to wash graphite components. However, the usage is quite small, only about 2 pounds of calcium hypochlorite per month.

B. Evaluation Design and Methods

Orlon is composed of polyacrylonitrile. The primary toxic material which is expected from thermal destruction of Orlon is cyanide.[1] Mr. T. C. Whitson, industrial hygienist from the Division of Occupational and Radiological Health, Tennessee Department of Public Health, and personnel of Great Lakes Research Corporation have made measurements of airborne cyanide concentrations and determined that these levels are not excessive during normal operating conditions. Therefore, NIOSH made no effort to measure airborne cyanide levels.

A site visit to the GLRC pilot plant was made on June 24, 1976, by Mr. Paul Roper and Gordon Nifong, Ph.D., of the NIOSH Region IV office. A walk-through survey of the carbon fiber areas was conducted. Several exposed employees were interviewed. Samples were collected of settled dust, process residues, unused Orlon, and human hair which had turned red. These samples were analyzed by the laboratories of the NIOSH Division of Physical Sciences and Engineering in Cincinnati, Ohio. The analyses were aimed at identifying any material in the environment which might be responsible for the hair discoloration.

The laboratory attempted to identify what types of substances were produced from the heating of Orlon by trying to simulate process conditions at the oxidizer. Samples of the Orlon were placed in an oven at process temperatures, heated for 15 to 30 minutes, with a continuous flow of air over the surface of the sample. The effluents were subjected to gas chromatography/mass spectroscopy analysis. N,N - dimethylformamide (DMF), 1-octanol, and 1-decanol were found. DMF was to be expected, since it is a solvent used in the production of Orlon, and some residue of DMF probably remains on the fibers. Detector tubes for nitrogen compounds such as hydrogen cyanide, oxides of nitrogen, ammonia, and amines gave positive results. This, too, was expected since Orlon is polyacrylonitrile.

Settled dusts, process residues, and human hair samples were analyzed in an attempt to detect any unusual components. Analytical techniques which were employed included gas chromatography, emission spectroscopy, and x-ray diffraction. These analyses failed to detect the presence of any unexpected contaminants or of substances suspected to cause alteration of hair color.

It was noted that the hair discoloration occurred only on exposed portions of the body such as the head and forearms. This suggested that the discoloration might be caused by a material present in the form of dust or absorbed in dust particles which settled on the hair and reacted in the presence of moisture to discolor the hair. Therefore, a sample of settled carbon dust from machine surfaces around the oxidizer and carbonizers was submitted for analysis.

Initially, the presence of any oxidizing material was determined by the iodometric method. A portion of the sample was dissolved in water and acidified with a sulfuric acid solution. Then, potassium iodide crystals and starch solution were added to observe the color change of the mixture. A blue coloration was observed, which indicated the presence of an oxidizing material.

Then, gas chromatography/mass spectroscopy analysis of the sample was performed. No chlorinated organic compounds were detected in the sample. The only major compound detected was carbon dioxide, which resulted from heating the carbon. The small trace components present were not in sufficient quantities to permit identification.

Next, an infrared spectrophotometric method was applied. A portion of the sample was leached overnight with carbon tetrachloride. The infrared spectrum of the resultant solution was compared to a spectrum of the pure solvent. No detectable difference between the two spectra was observed. This indicated that there was no oil present on the sample. Another portion of the sample was ground with potassium bromide and pressed into a pellet. The infrared spectrum of the pellet was compared with the spectrum of Orlon from the Sadtler reference files. The absorbance bands present in the sample matched those of Orlon in shape and frequency, although not all of the absorption bands of Orlon were present in the sample. Thus, the sample was considered to be carbonized Orlon since decomposition of the Orlon would occur with carbonization and, therefore, absorbance bands of the decomposed functional groups would either be reduced in size or absent.

In addition, several spot tests and chemical methods were employed to identify the oxidizing material present in the sample. An acidified sample solution gave no indication of the presence of cyanide by the Drager detector tube. A neutral solution of the sample was tested for the presence of chromate and permanganate. No permanganate or chromate was detected. No hexavalent chromium was detected by the diphenylcarbazide spectrophotometric method. Also, no nitrite was detected in the sample by the N-1-naphthylethylenediamine dihydrochloride method.

In order to analyze for inorganic chlorine compounds, the ion specific electrode method was initially employed for the determination of chloride. The analysis indicated that the sample contained 3.5 mg of chloride per gram of carbon dust. After the chloride measurement, attempts were made to analyze for chlorite and hypochlorite in the sample, but the indigo discoloration method failed to give any clear indication of the presence of the chlorite or hypochlorite.

In the last attempt to determine the possible oxidizing agent present in the sample, one of the chemists used his own hair for the bleaching experiment. The color of hair was black, and the following color changes were observed by immersing the hair in the solutions listed below:

Black Hair + H_2O_2	reddish color
Black Hair + Trace hypochlorite	no change
Black Hair + H_2O_2 + hypochlorite	dark rust color
Black Hair + HCl	no change
Black Hair + NaOH	slight brownish color Hair dissolves with kinky appearance (hair was originally straight)
Black Hair + HNO_3	brownish color
Black Hair + HCN	no change

Since hydrogen peroxide turned the black hair to reddish color, attempts were made to detect hydrogen peroxide by a spot test. But due to the inadequacy of the method used, no positive indication was observed.

Thus, in summary, a positive indication for the presence of an oxidizing agent in the bulk carbon dust sample was observed, but a positive identification of the particular oxidizing material was not made.

C. Conclusions and Recommendations

A major objective of this health hazard evaluation was to identify any potential health hazards associated with the manufacture of carbon fibers by Orlon carbonization at the pilot plant stage. It was already known that cyanide was the foremost toxic byproduct, and cyanide levels were controlled under normal operating conditions.

In order to identify any potential health hazards associated with carbon fiber exposure, Professor W.R. Lee of the Department of Occupational Health at the University of Manchester, England, was contacted. Professor Lee has conducted medical surveillance of workers at the Shirley Institute who were doing research on uses of carbon fibers, but who were not actually manufacturing the fibers themselves. Professor Lee observed the human effects of carbon fiber exposure in the group of workers which he studied to be short-term irritancy of the skin, conjunctiva of the eyes, and of the upper respiratory tract. The irritant effects were found to be of no greater toxicity than that found among workers exposed to fibrous glass.[2]

The NIOSH study was not successful in identifying the cause of the hair discoloration observed at the GLRC carbon fiber production pilot plant. Therefore, it is not possible to state what the potential consequences to health of exposure to this agent might be. For the sake of prudence, it is recommended that all process emissions be captured at their source and removed from the process areas through the use of local exhaust ventilation. Because of the cyanide content of ash produced during the carbonization stage, it is recommended that dust masks be provided the personnel performing servicing or maintenance of process equipment in this area.

Some workers may find the hair discoloration objectionable in a cosmetic sense. Since there seems to be a strong possibility that the discoloration is produced by a direct contact of a settled air contaminant with the the hair, the discoloration might be prevented through the use of protective head coverings and showering thoroughly at the completion of the work shift. These options should be made available to the workers.

V. REFERENCES

1. Chemical Abstracts, Vol. 62, 12355e (1965)

2. Professor W. R. Lee, Department of Occupational Health, University of Manchester, England, Personal Letter, August 25, 1976.

VI. AUTHORSHIP AND ACKNOWLEDGMENTS

Report Prepared By: C. Paul Roper, Jr.
Regional Industrial Hygienist
Public Health Service, Region IV
Division of Prevention
Atlanta, Georgia

Originating Office: Jerome P. Flesch
Hazard Evaluation and Technical Assistance Branch
NIOSH
Cincinnati, Ohio

Laboratory Analyses By: Staff
Division of Physical Sciences and Engineering
NIOSH
Cincinnati, Ohio

Richard E. Kupel
Laboratory Coordinator

Ardith A. Grote
Chemist

Charles V. Cooper
Physical Science Technician

Soo Wang Kim
Chemist

Michele L. Bolyard
Chemist

Donald D. Dollberg, Ph.D.
Chemist

Lloyd E. Stettler, Ph.D.
Biophysical and Particulate Measurements
Support Section
Division of Biomedical and Behavioral Science
NIOSH
Cincinnati, Ohio