U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
CENTER FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
CINCINNATI, OHIO 45226

HEALTH HAZARD EVALUATION DETERMINATION REPORT
HE 80-74-714

STANDARD PUBLISHING COMPANY
CINCINNATI, OHIO

July 1980

I. SUMMARY

On February 14, 1980, the National Institute for Occupational Safety and Health (NIOSH) received a request from the Standard Publishing Company in Cincinnati, Ohio, to evaluate complaints of eye and throat irritation from employees working in the platemaking process (SIC 2740). In addition, employees were also concerned with a peculiar odor and a white deposit on some of the equipment. These complaints initially developed after a new mercury vapor lamp was installed and while workers were running a negative lithographic plate process using Citation solvents.

To evaluate the causes of these complaints, NIOSH conducted a health hazard evaluation on March 4, 12 and April 3, 1980. Bulk samples of the Citation solvents were analyzed to identify chemical components. Environmental sampling was conducted and air circulation observations were made using smoke tubes.

Analysis of the bulk samples indicated that Citation Stencil Remover (CSR) contained mostly perchloroethylene (PCE) along with unidentifiable fatty acids. Compounds present in the Citation Developer (CD) were a mixture of aliphatic hydrocarbons, mostly in the C_9-C_{11} range.

Since PCE decomposition in ultraviolet and/or heated environments is not uncommon, a series of lamp/solvent tests were conducted focusing on CSR components. The results of these tests demonstrated the presence of thermal degradation products of CSR, phosgene and hydrogen chloride, detected at concentrations of 0.15 and 1 ppm, respectively. These vapors produced eye and upper respiratory irritation to exposed individuals present during the tests. The white film in the exposure rooms was attributed to the deposition of the fatty acid component in the CSR. Air circulation observations indicated a definite air current from the area where solvents are used, through the exposure (lamp) room, and into the stripper room where some of the symptomatic employees worked.

Based upon the results of the environmental air samples and personal observations by NIOSH investigators, NIOSH determined that employee complaints were attributed to PCE decomposition products, phosgene and hydrogen chloride, when perchloroethylene was used with the new high voltage, mercury vapor lamp. Recommendations for controlling this problem are presented on page 4 of this report.

II. INTRODUCTION

Under the Occupational Safety and Health Act of 1970*, NIOSH investigates the toxic effects of substances found in the workplace. The management at Standard Publishing Company requested such an evaluation from NIOSH to determine the cause of employee complaints of eye and throat irritation. The workplace was evaluated by means of environmental samples, air flow observations and information obtained from pertinent literature. Following the health hazard evaluation, on April 22, a letter was sent to the employer summarizing the environmental data.

III. BACKGROUND

Standard Publishing Company (SPC) employs about 450 people in the manufacturing and marketing of a variety of lithographic products. Activities range from processing artwork through platemaking, printing, assembling and packaging of printed material. The area of concern was the plateroom where lithographic plates are prepared for printing press use. Operations involve plate exposure (both negatives and positives) to ultraviolet light, followed by a series of chemical treatments using developers, etching agents, lacquers and stencil removers. The platemaking process employs two workers per shift. Mercury vapor lamps are used up to one hour per shift at 1-3 minutes per plate.

Standard Publishing Company utilizes a platemaking system developed and marketed by Printing Developments Incorporated (PDI). This system has been used by SPC for approximately 3 1/2 years and is mechanically similar for plates exposed from negatives or positives. There are, however, variations in the chemicals used in plate treatment. Negative plates are treated with Citation Developer and Citation Stencil Remover while positive plates are treated with Medallion Developer and Medallion Stencil Remover (MSR).

Since the installment of a new mercury vapor exposure lamp was the only process change within the last 3 1/2 years, both (new and old) lamps were comparatively evaluated. Technical information supplied by the lamp manufacturer indicated that the only major difference between the lamps was the power output: 5,000 watts - new lamp; 3,500 watts - old lamp. Emission spectra of both lamps were identical. Both ultraviolet mercury vapor lamps were equipped with a small centrifugal fan mounted on the external lamp housing. Each fan utilized ambient air to provide convection cooling for the lamps. Both lamps were located in the exposure room, an area downwind from a downdraft table where platemaking solvents were used (Figure 1).

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

*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 and Human Services, following a written request by an 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.

IV. METHODS AND MATERIALS

On March 12, bulk samples of Citation Developer and Citation Stencil Remover were collected and later analyzed by gas chromatographic/mass spectrographic (GC/MS) procedures to verify and/or identify chemical components. Also, at this time, Citation Stencil Remover was tested with the new lamp (method described below). The highly irritating vapors and the fine white particulate generated during this test (no sampling conducted) necessitated a follow-up study (April 3) in order to further characterize the problem.

Prior to the follow-up study, results were obtained on the GC/MS analyses of the bulk citation solvents. Perchloroethylene was verified as a major chemical constituent in CSR along with unidentifiable fatty acids. Compounds present in CD were a mixture of aliphatic hydrocarbons, mostly in the C_9-C_{11} range.

Because the platemaking process was used on an infrequent basis and certain control measures recommended by PDI had already been implemented by SPC to reduce solvent evaporation (i.e., downdraft table for all plate treatments and a covered metal can for solvent saturated towels) negligible concentrations of PCE were anticipated under normal working conditions. Therefore, in order to effectively test the hypothesis of PCE decomposition with the new lamp, a protocol was developed to test some of the platemaking solvents (CSR and MSR) at concentrations well above those normally present during their use. Pure PCE was incorporated in the test protocol to (1) verify its decomposition in CSR with the new lamp, (2) verify the contrary with the old lamp, and (3) determine the origin of the white deposition in the exposure room. Medallion and Citation developers were not tested because their chemical compositions were not conducive to ultraviolet breakdown.

Each test consisted of applying CSR, MSR or PCE to a paper towel and allowing the vapors to be drawn into the cooling fan intake of each exposure lamp for two minutes. Immediately following, detector tubes were used to sample for PCE decomposition products including phosgene, hydrogen chloride and chlorine. Detector tube sampling for ozone was also conducted since it is usually present in UV environments.

The order in which the chemicals were tested was important from a practical standpoint. Perchloroethylene was tested last with the new lamp because it, like the CSR, was expected to decompose. Leaving the PCE/new lamp test to last enabled completion of the other tests prior to contaminating the exposure (lamp) room.

V. EVALUATION CRITERIA

Perchloroethylene decomposition by heat and/or ultraviolet radiation is well documented in the literature (1-4). Major PCE degradation products include phosgene, hydrogen chloride and chlorine. Of particular interest, however, is the fact that even though PCE may be used at concentrations well below its permissible exposure limit (PEL), in the presence of heat/ultraviolet light it can quickly dissociate to form highly irritating compounds whose PEL's can be several orders of magnitude below the parent compound.

The environmental evaluation criteria and the primary health effects of the substances evaluated are summarized in Table I.

VI. RESULTS AND DISCUSSION

The results of the environmental sampling are provided in Table II. Positive findings were obtained when testing CSR or PCE with the new exposure lamp. In the CSR/new lamp test, highly irritating vapors and a fine white particulate were generated. The odor and effects were similar to those obtained in the PCE/new lamp test. This was expected since PCE is major chemical component in CSR. The vapors from both positive tests produced eye and upper respiratory tract irritation to individuals present during these tests. The only difference between the PCE and CSR new lamp tests was the generation of a fine white particulate, which appears to be due to the fatty acid component in the CSR. The PCE/new lamp test detector tube sampling revealed phosgene and hydrogen chloride at concentrations of $\sim$0.15 and $\sim$1.0 ppm, respectively. Phosgene ($\sim$0.09 ppm) was also detected in the stripper room and may explain some of the worker complaints from this area. Although chlorine was not detected, its presence was evident by smell. Ozone was not detected in any of the tests.

Air circulation observations indicate that the plateroom was under negative pressure. Prevailing air currents were evident from the vicinity of the downdraft table, through the exposure room and into the stripper room. It, therefore, appears that when CSR was being used on the downdraft table uncaptured CSR vapors were carried into the exposure room where contact with the exposure lamp produces CSR (PCE) decomposition.

VII. CONCLUSIONS

Based on the test results, it appears that the increased power output (heat) of the new exposure lamp was responsible for PCE decomposition/fatty acid particulate generation when CSR vapors came into contact with the new exposure lamp.

VIII. RECOMMENDATIONS

1. Substitute CSR with a stencil remover that contains no chlorinated hydrocarbons and is of low toxicity.

2. Prevent PCE solvent vapors from entering the exposure room by providing this area with positive pressure ventilation.

IX. REFERENCES

1. Andersson, H. F., Dahlberg, J. A. and Wettstrom, R., Phosgene Formation During Welding in Air Contaminated with Perchloroethylene. Ann. Occupational Hygiene 18:129-132, 1975.

2. Noweir, M. H., Pfitzer, E., and Hatch, T. F., Decomposition of Chlorinated Hydrocarbons: A Review. American Industrial Hygiene Association J., 33:454-460, 1972.

3. Andersson, H. F., Dahlberg, J. A., and Wettstrom, R., On the Formation of Phosgene and Trichloroacetyl Chloride in the Non-Sensitized Photo-oxidation of Perchloroethylene in Air. Acta Chem Scand, Ser A29(4), 473-4, 1975.

4. Rinzema, L. C., and Silverstein, L. G., Hazards From Chlorinated Hydrocarbon Decomposition Hazards From Chlorinated Hydrocarbon Decomposition During Welding. American Industrial Hygiene Association J., 33:35-40, 1972.

5. NIOSH Criteria for a Recommended Standard . . . Occupational Exposure to Chlorine, DHEW (NIOSH) Publication Number 76-170.

6. Threshold Limit Values for Chemical Substances in Workroom Air Adopted by ACGIH, 1979, P.O. Box 1937, Cincinnati, Ohio 45201.

7. NIOSH Criteria for a Recommended Standard . . . Occupational Exposure to Phosgene, DHEW (NIOSH) Publication Number 76-137.

8. NIOSH Criteria for a Recommended Standard . . . Occupational Exposure to Tetrachloroethylene (Perchloroethylene), DHEW (NIOSH) Publication Number 76-185.

X. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this complete Determination 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 of this report have been sent to:

a. Standard Publishing Company, Cincinnati, Ohio
b. Graphic Arts International Union, local 508, Cincinnati, Ohio
c. Graphic Arts International Union, headquarters, Washington, D.C.
d. Printing Developments, Inc., Racine, Wisconsin
e. U.S. Department of Labor, Occupational Safety and Health Administration, Region V, Chicago, Illinois
f. NIOSH, Region V

For the purpose of informing the approximately 6 "affected" employees, the employer shall promptly post this determination report for a period of 30 calendar days in a prominent place(s) near where exposed employees work.

XI. AUTHORSHIP AND ACKNOWLEDGEMENTS

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Table I

Evaluation Criteria

Standard Publishing Company
Cincinnati, Ohio

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Substance	Recommended Environmental Limit	Source	Primary Health Effects
Chlorine	0.5 ppm/15 min ceiling	NIOSH (5)	Irritation of skin, eyes and respiratory tract
Hydrogen chloride	5 ppm/8 hr ceiling	ACGIH (6)	Eyes, skin, upper respiratory tract irritation
Ozone	0.1 ppm 8 hr TWA	ACGIH (6)	Irritation of eyes, mucous membranes and respiratory tract
Phosgene	0.1 ppm 10 hr TWA 0.2 ppm/15 min ceiling	NIOSH (7)	Irritation of skin, eyes and respiratory tract
Perchloroethylene	50 ppm/10 hour TWA 100 ppm/15 min ceiling	NIOSH (8)	Eyes and upper respiratory tract irritation, CNS depressant

Table II

Detector Tube Sampling Results

Standard Publishing Company
Cincinnati, Ohio

HHE 80-74

Platemaking Chemical or Component	Old Lamp (3500 Watts)	New Lamp (5000 Watts)
MSR	N.D.	N.D.
PCE	N.D.	HCI, phosgene detected No particulate generated
CSR	Not tested	Similar odor and effects as with PCE Fine particulate generated

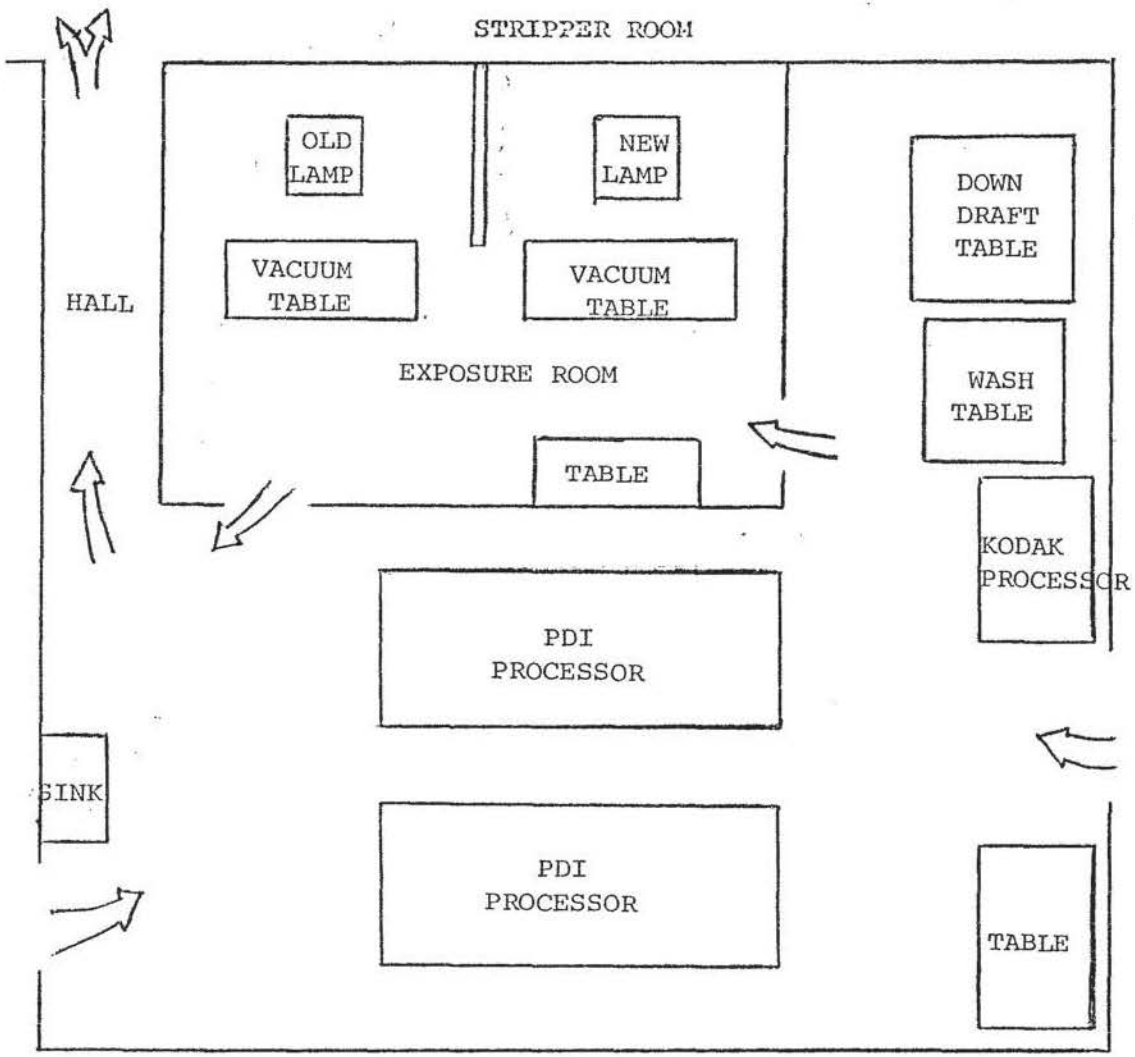
NOTE: All measurements were taken in the exposure room with Drager detector tubes

ND = Not Detected
MSR = Medallion Stencil Remover
PCE = Perchloroethylene
CSR = Citation Stencil Remover

FIGURE 1

PLATEROOM SCHEMATIC
STANDARD PUBLISHING COMPANY
CINCINNATI, OHIO

IE 80-74



NOTE: ARROWS INDICATE AIR MOVEMENT