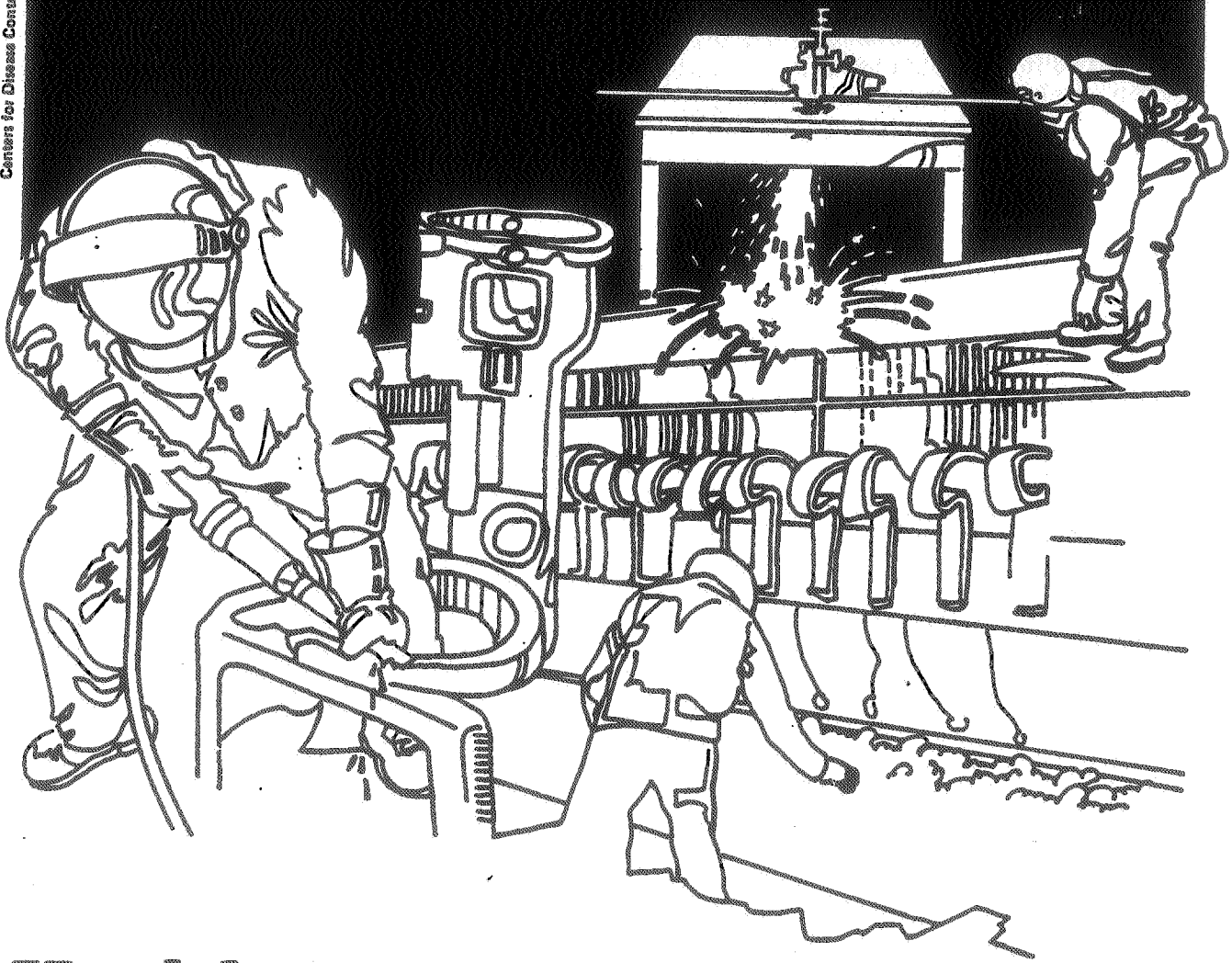


# NIOSH



## Health Hazard Evaluation Report

HETA 84-214-1633  
SHELD AHL, INC.  
NORTHFIELD, MINNESOTA

## 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 84-214-1633  
NOVEMBER 1985  
SHELDAHL, INC.  
NORTHFIELD, MINNESOTA

NIOSH INVESTIGATORS:  
Daniel Almaguer, I.H.  
Paul Seligman, M.D.

## I. SUMMARY

On February 27, 1984, the Amalgamated Clothing and Textiles Workers Union, requested that the National Institute for Occupational Safety and Health (NIOSH) conduct a Health Hazard Evaluation at Sheldahl Inc., Northfield, Minnesota. The requestor expressed concerns about potential employee exposures to several chemicals used in the manufacture of flexible printed circuitry.

On April 5, 1984, NIOSH investigators visited the facility and conducted an initial survey. In June 1984, environmental samples were collected to assess potential employee exposures in two areas of the facility. Samples collected in Lamination Department #14 indicated that employees were potentially exposed to methylene chloride in excess of the NIOSH recommended standard of 75 parts per million (ppm); sample results ranged from 72 ppm to 85 ppm as an 8-hour time weighted average (TWA) concentration. Samples collected for methyl ethyl ketone, ethyl acetate, toluene, 2-ethoxy ethyl acetate, and petroleum naphtha were below the applicable environmental criteria and samples collected for toluene diisocyanate (TDI) and methylene bisphenyl isocyanate (MDI) were below the analytical limit of detection. Samples collected in the Wet Processing Department showed concentrations of anhydrous ammonia and 2-butoxy ethanol below the applicable environmental criteria and samples collected for sulfuric acid were below the analytical limit of detection.

On November 14-16, 1984, NIOSH conducted further environmental sampling and medical monitoring of employees working in Lamination Departments #12 and #14. Environmental sampling results show that employees working in these departments were potentially exposed to methylene chloride in excess of the NIOSH recommended standard of 75 ppm. Methylene chloride sample results ranged from 26 ppm to 132 ppm as a TWA concentration while short-term sampling of employees performing clean-up operations ranged from 122 ppm to 1752 ppm. Carbon monoxide was detected at concentrations ranging from 2.6 ppm to 30 ppm and five of ten employees sampled had combined exposures to methylene chloride and carbon monoxide in excess of the NIOSH recommended standard. Employees were wearing NIOSH/MSHA approved air purifying respirators during clean-up operations when methylene chloride concentrations were highest which would have provided the employees some degree of protection. Medical monitoring results show that carboxyhemoglobin (COHb) levels for non-smokers rose from a mean pre-shift level of 1.9% to a mean post-shift level of 2.4% and that COHb levels for smokers actually declined from mean pre-shift levels of 7.1% to mean post-shift levels of 5.4%. The criteria used to indicate excessive absorption of methylene chloride is a post-shift COHb level greater than or equal to 5% in nonsmokers and 10% in smokers. These medical monitoring results indicate that employees were not absorbing excessive amounts of methylene chloride during the survey

period. However, the company's Occupational Safety and Health Administration (OSHA) 200 logs for the years 1981 to 1983 show reports of illness compatible with overexposure to methylene chloride.

---

Based on the environmental data collected during this evaluation, a potential health hazard from exposure to methylene chloride exists for employees working in Lamination Departments #12 & #14. Recommendations for reducing employee exposures are contained in Section VIII of this report.

---

KEYWORDS: SIC 3679, flexible electronic circuitry, methylene chloride, carbon monoxide

## II. INTRODUCTION

On February 27, 1984, the National Institute for Occupational Safety and Health (NIOSH) received a request from the Amalgamated Clothing and Textile Workers Union to conduct a health hazard evaluation at Sheldahl Inc., Northfield, Minnesota. The requestor was concerned with employee exposures to various chemical substances used in the manufacture of flexible printed circuitry.

On April 5, 1984, NIOSH investigators conducted an initial survey which included an opening conference with representatives of management and the employees (union). Current employees were interviewed, company medical records and OSHA 200 logs were reviewed, a walk through survey of the facility was conducted and discussions were held with management regarding previous industrial hygiene monitoring conducted by the engineering department and a private consultant. On June 1, 1984, a status letter was sent to the company and the union informing them of the results of the initial survey and of plans for future surveys.

On June 12 & 13, 1984, a follow-up environmental survey was conducted to characterize employee exposures to the various chemical substances used at the facility. General area and personal breathing zone air samples were collected in the Laminations Department (#14) and the Wet Processing Department. On September 24, 1984, a letter was sent to the union and the management informing all parties of the environmental sampling results.

On November 14-16, 1984, NIOSH investigators conducted further environmental sampling and medical monitoring of employees working in Laminations Departments #12 and #14 where methylene chloride was used as a major component of the adhesives and as a cleaning agent for the laminating machines and parts. Personal breathing zone air samples were collected for methylene chloride and carbon monoxide to characterize employee exposures throughout the work shift and short-term sampling was conducted to assess employee exposures during clean-up operations. Medical monitoring for carboxyhemoglobin (COHb) was conducted and questionnaires were administered to employees. On February 28, 1985, a letter was sent to the union and the management informing them of the results of environmental sampling and medical monitoring. Additionally, letters were sent to those individuals who participated in the medical portion of the survey informing them of the results.

## III. BACKGROUND

### A. Plant Production and Workforce

Sheldahl Inc., began manufacturing electronic materials in the 1950's and began manufacturing flexible printed circuitry in 1964. At the time of this evaluation the company employed approximately 650 workers, including 300 administrative personnel, 340 production workers and 12 maintenance workers.

## B. Process Description and Employee Duties

Mixing of adhesives involves combining the various components that make an adhesive, and blending them together on a power mixer. Components include solid resins such as polyester, epoxy or nylon; solvents such as methylene chloride, methyl ethyl ketone (MEK), acetone, and smaller quantities of 1,1,2-trichloroethane, methanol, and others; and additives such as powders, dyes, and isocyanate curing agents.

The prepared adhesive is coated onto a flexible substrate, often times copper foil, and sent thru a drying tunnel on the laminator to dry the adhesive. It is then combined with another flexible substrate such as a polyester or polyamide film using heat and pressure, to make a completed laminate. A variety of laminates are sold in roll form to outside customers. Copper/film laminates are used internally to make flexible printed circuitry.

Prior to wet processing the products go through indexing and image placement. Depending on the circuit configuration, the laminate with the screened image may then be sent thru any of these wet processes; 1) electro-copper plate to deposit a layer of copper in punched holes in the laminate, 2) electro-solder plate to deposit a thin layer of 60/40 tin-lead solder over exposed copper surfaces, 3) gold electroplate to deposit a layer of gold over a copper/nickel surface, 4) alkaline etch to remove exposed copper from a laminate using an ammonia based etchant, followed by a dilute sodium hydroxide strip to remove the screening ink and a HCl spray to clean the surface, 5) sodium persulfate etch to remove exposed copper from piece parts, this etch is not used for laminates in roll form, 6) roll-tin to apply a layer of 60/40 tin lead solder to selected copper surfaces from molten solder pot.

## C. Engineering, Administrative, and Personal Protective Controls

All employees working in the facility are required to wear safety glasses and contact lenses are prohibited through out the production areas of the facility. Other personal protective equipment such as air purifying respirators is used according to the job being performed. Engineering controls include local exhaust ventilation at several processes in the wet processing and laminations departments.

The company maintains no on-site medical facility. The Northfield Clinic provides medical back-up for the plant. No pre-employment, annual, or termination physicals are required. Workers in the punch press area and boiler operators receive annual audiometric examinations. Information provided during the initial survey indicated that cadmium sulfide compounds are required occasionally and that employees working at these operations are medically monitored for cadmium exposure.

#### IV. EVALUATION DESIGN AND METHOD

##### A. Environmental

In April 1984, an initial survey was conducted and information was collected about those processes which were of major concern to the requestor. Three departments were identified by the union as areas where workers had complained of work-related health effects.

In June 1984, a follow-up environmental survey was conducted. Based on information collected during the initial survey, environmental samples were collected for various chemicals used in the Wet Processing Department and the Laminations Department (#14). Sampling in the third department of concern to the union representatives was cancelled due to the fact that this process was not being utilized and had not been used since the time of the initial survey. Air sampling and analytical methodologies for sampled substances, along with other pertinent data, are presented in Table 1.

In November 1984, a second environmental survey and a medical survey were conducted. Environmental sampling of the Laminations Departments #12 and #14 was necessary to further characterize employee exposures to methylene chloride and carbon monoxide. Table 1 lists all pertinent sampling and analytical methodologies for methylene chloride and carbon monoxide.

##### B. Medical

The medical portion of the study consisted of: 1) employees completing a self-administered questionnaire which asked about work-related symptoms, past medical history, smoking habits, occupational history, and use of respirators; 2) drawing of venous blood samples, pre- and post-shift, to assess carboxyhemoglobin (COHb) levels; and 3) providing a sample of exhaled air following 20 seconds of breath holding, pre- and post-shift, to measure carbon monoxide.

#### V. EVALUATION 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/Occupational Safety and Health Administration (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 required by the Occupational Safety and Health Act of 1970 (29 USC 651, et seq.) to meet 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.

#### A. Methylene chloride<sup>1,2</sup>

The current OSHA standard for methylene chloride is 500 parts of methylene chloride per million parts of air (ppm) averaged over an eight-hour work shift, with an acceptable ceiling level of 1000 ppm and a maximum peak concentration of 2000 ppm for 5 minutes in any two-hour period. NIOSH recommends that the OSHA permissible exposure limit be reduced to 75 ppm averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of 500 ppm averaged over a 15 minute period. The ACGIH recommends a TLV of 100 ppm as an 8-hour TWA and 500 ppm as a Short Term Exposure Limit (STEL).

NIOSH further recommends, that in the presence of exposure to carbon monoxide (CO) in the work environment at more than 9 ppm determined as a



TWA concentration for up to a 10-hour workday, exposure limits of CO, or methylene chloride or both shall be reduced to satisfy the relationship:

$$\frac{C(\text{CO})}{L(\text{CO})} + \frac{C(\text{CH}_2\text{Cl}_2)}{L(\text{CH}_2\text{Cl}_2)} < 1$$

where:

- C(CO) = TWA exposure concentration of CO in ppm
- L(CO) = the recommended TWA exposure limit of CO = 35 ppm
- C(CH<sub>2</sub>Cl<sub>2</sub>) = TWA exposure concentration of methylene chloride, ppm
- L(CH<sub>2</sub>Cl<sub>2</sub>) = the recommended TWA exposure limit of methylene chloride = 75 ppm

Methylene chloride is a volatile organic solvent that is easily absorbed by the lung (retention: 55-70%) and by direct skin contact with the liquid. Following absorption, it is partly metabolized to carbon monoxide (CO) and carbon dioxide. Carbon monoxide in the blood displaces oxygen in hemoglobin, reducing the red blood cells capacity to carry oxygen necessary for the function of all vital organs. The magnitude of exposure to methylene chloride may be measured by determining the levels of carboxyhemoglobin (COHb) in the blood or the amount of carbon monoxide in expired air.

Methylene chloride is considered to be a mild central nervous system toxicant. Symptoms of overexposure include headache, giddiness, irritability, numbness, and tingling in the limbs. Methylene chloride vapors may be irritating to the eyes and upper respiratory tract. Skin and eye burns may occur from direct contact with methylene chloride if not promptly removed.

An 8-hour exposure to about 150 ppm of methylene chloride vapor is equivalent to an 8-hour exposure to 35 ppm of CO. Exposure to these concentrations of methylene chloride or CO under sedentary conditions will increase blood COHb levels to about 5% of saturation at the end of exposure.<sup>3</sup> Physical exercise performed during exposure to methylene chloride vapor will produce higher COHb saturations than those found in sedentary workers. Under moderate workload an exposure of 100 ppm of methylene chloride for 7.5 hours may cause a COHb saturation of about 5% at the end of the exposure period.<sup>4</sup>

The combined effect of smoking and exposure to methylene chloride produces an additive increase in blood COHb values.

Individuals exposed to methylene chloride may experience an elevation in COHb levels as methylene chloride is partly metabolized to CO. The rise in COHb levels may be sufficient to stress individuals with underlying cardiac or pulmonary disease. Three myocardial infarctions, including a death following paint stripping in a basement have been reported.<sup>5</sup>

Exposures to CO and methylene chloride sufficient to produce COHb levels of 5% or greater have been shown to impair performance of certain

neurobehavioral tests which may result in the impairment of a worker's performance under difficult or demanding conditions.<sup>6</sup>

A recent draft report by the National Toxicology Program on the toxicology and carcinogenesis of methylene chloride describes its cancer-producing potential in both F344/N rats and B6C3F<sub>1</sub> mice.<sup>7</sup> For female F344/N rats, there was clear evidence of carcinogenicity as shown by increased incidences of neoplasms of the mammary glands. For both male and female B6C3F<sub>1</sub> mice, increased incidence of alveolar/bronchiolar neoplasms and hepatocellular neoplasms were demonstrated.

The excess risk of cancer to workers exposed to specific airborne concentrations of methylene chloride has not yet been determined. Recommendations for reducing employee exposures and protecting workers exposed to methylene chloride are contained in section VIII of this report.

#### B. Other Chemical Substances

While other chemical substances were sampled for during the course of this evaluation the concentrations detected were well below the applicable environmental criteria. Therefore, no discussion of their toxicological effects are presented. Environmental criteria for each substance are contained at the bottom of the appropriate table of results for comparison to the environmental sampling data.

## VI. RESULTS AND DISCUSSION

In June 1984, environmental sampling was conducted in two areas of the facility, Laminations Department #14 and the Wet Processing Department. Substances sampled for in the Laminations Department included methylene chloride, ethyl acetate, toluene, 2-ethoxy ethyl acetate, petroleum naphtha, methyl ethyl ketone, 2,4-toluene diisocyanate (TDI) and methylene bisphenyl diisocyanate (MDI). Sampling results indicated detectable levels of methylene chloride, ethyl acetate, toluene, 2-ethoxy ethyl acetate, petroleum naphtha, and methyl ethyl ketone. These sampling results indicated a potential for employee exposures in excess of the NIOSH recommended standards for methylene chloride in the Laminations Department at the #1 and #4 laminators. Employees were noted wearing disposable organic vapor respirators during clean-up operations, however, NIOSH does not recommend the use of air purifying respirators due the lack of adequate warning properties of methylene chloride. All other sample results were below the acceptable environmental criteria. Table 2 details the methylene chloride sample results and Tables 3 thru 6 detail sample results for substances sampled which were detectable but below the applicable environmental criteria. TDI, MDI and sulfuric acid were not detected in any of the samples collected.

The survey of November 1984, included personal breathing zone air sampling of 14 employees working in Laminations Departments #12 and #14, ten of these employees were monitored for long term exposures to both methylene chloride and carbon monoxide. Personal breathing zone air sample results indicate concentrations of methylene chloride in excess of the applicable environmental criteria. Time-weighted average concentrations for the duration of sampling ranged from 25 ppm to 132 ppm. Short-term sample results ranged from 112 ppm to 1752 ppm. Additionally, levels of carbon monoxide were detected in excess of 9 ppm on six of ten employees throughout the three day sample period, with levels ranging from 2.6 ppm to 30 ppm. Combined exposures to methylene chloride and carbon monoxide (see formula, page 2) indicate overexposures to 5 out of the 10 employees sampled, see Tables 7 and 8 for complete sample results.

Additionally, employees with potential methylene chloride exposure were asked to participate in the medical portion of this survey. Seventeen (61%) of 28 employees in Department #14 and 4 (57%) of 7 employees in Department #12 participated.

Demographic data of the population studied are presented in Table 9. All employees answered questions related to three primary symptom complexes; respiratory/mucous membrane irritation; skin rash; and central nervous system effects. A response to a question was considered significant when the employee felt that the symptom occurred more than half the time while at work. Table 10 summarizes the responses to the symptom questionnaire. Three of 21 employees were believed to have mucous membrane irritation (eye and nose symptoms) that could not be explained by a known allergic condition. One employee gave a history of respiratory irritation (cough, wheezing, shortness of breath) that could not be related to previous allergic or asthmatic conditions. No employee gave a history of significant CNS complaints (defined as three or more of the symptoms listed).

The results of the pre- and post-shift blood carboxyhemoglobin levels and exhaled carbon monoxide are presented in Table 11. The findings for non-smokers and smokers are presented separately, due to the contribution of carbon monoxide in cigarette smoke to the measured COHb levels. Of the forty blood samples that were obtained, 13 were unable to be analyzed by the laboratory due to the presence of tiny clots in the specimens.

For non-smokers, the mean pre-shift COHb level of 1.9% rose to a mean post-shift level of 2.4%. No individual in this category had a post-shift COHb level greater than or equal to 5.0%, the criteria used in this report to indicate excessive absorption of methylene chloride during the work-shift.

For smokers the mean pre-shift COHb level of 7.1% declined to a mean post-shift level of 5.4%. The relatively high pre-shift levels represent the contribution of individuals' smoking habits to the COHb level. The decline in the COHb levels observed is probably due to the

less frequent use of smoking materials during the work-shift than prior to the work-shift. No individual who smoked had a COHb level in the toxic range greater than 20%.

The amounts of exhaled carbon monoxide directly paralleled the blood COHb levels, as shown in Table 11.

## VII. CONCLUSION

While medical data indicate employees were not absorbing excessive amounts of methylene chloride, environmental concentrations detected on the survey dates (June 1984 & November 1984) were in excess of the NIOSH recommended standards, the ACGIH-TLVs and STELs, and the OSHA ceiling limits. Additionally, carbon monoxide sampling showed that concentrations at some work stations were above 9 ppm with combined exposures to methylene chloride and carbon monoxide above the NIOSH recommendation for combined exposures, see Tables 7 and 8.

Employees were noted wearing disposable organic vapor cartridge respirators and unsupported Neoprene gloves while performing clean-up operations. NIOSH does not recommend the use of air purifying respirators when working with methylene chloride due to the lack of adequate warning properties. Additionally, neoprene gloves are not recommended for use with methylene chloride as neoprene has been shown to be permeable by methylene chloride. Due to the fact that employees are often required to wash laminator parts in 5-gallon buckets containing methylene chloride, skin absorption would be considered a major route of employee exposures.

The respirator program in effect at Sheldahl at the time of these surveys was insufficient. There was no written program and employees were not adequately trained in the proper use of respirators nor in the hazards of the chemicals with which they were working. Respirators were not properly selected for the chemical hazard (e.g. methylene chloride) from which they were to protect the employee and employees were quoted as saying that respirators being used were "replaced when they could smell methylene chloride."

Based on the responses to the questionnaires and the results of the biological monitoring for blood COHb levels, there appears to be no indication that workers surveyed were absorbing excessive amounts of methylene chloride nor experiencing symptoms related to methylene chloride or other solvents on the survey dates.

However, given the exposures to methylene chloride in excess of the NIOSH recommended standard, the potential exists for excessive bodily absorption of methylene chloride. Additionally, a review of the OSHA 200 logs for the years 1981-83 revealed seven reported illnesses in the Laminations Department #14 compatible with overexposure to methylene chloride or other solvents. Of these seven cases, four reported respiratory symptoms (difficult breathing, shortness of breath, or

bronchospasm), and three reported systemic and/or neurologic symptoms (nausea, dizziness, disorientation, or loss of consciousness).

Area and personal samples taken during the shifts when the medical evaluation was conducted indicate the potential for overexposure to methylene chloride. Appropriate engineering controls and/or respiratory protection and the avoidance of skin contact should limit the amount of individual worker absorption. However, given the recent evidence indicating that methylene chloride is an animal carcinogen, the goal should be to control worker exposures to the lowest feasible limit through effective engineering controls, good work practices, and proper maintenance procedures.

#### VIII. RECOMMENDATIONS

1. Substitution is the recommended method for controlling occupational exposures to toxic substances. The company should investigate the feasibility of substituting a less toxic substance for methylene chloride.
2. Engineering controls (improvements in the present local exhaust ventilation systems, where necessary) should be used to reduce excessive employee exposures to methylene chloride as well as other chemical substances used throughout the facility, and regularly scheduled maintenance of local exhaust ventilation systems should be adhered to.
3. A separate room equipped with an effective local exhaust ventilation system should be built and used for cleaning laminator parts. As noted in Table 8, one employee was shown to have a potential short-term exposure to methylene chloride of 1752 ppm while cleaning laminator parts in an closed room with no ventilation. Laminator parts should not be cleaned at the laminators or in closed rooms without proper ventilation.
4. The type of respirator selected for use should be based on the contaminant concentrations expected to be present and adequate warning properties should be taken into account when selecting respirators. Air purifying respirators are not recommended for use with methylene chloride due to the lack of adequate warning properties.
5. Personal protective equipment should be selected based on the chemical substance from which it is designed to protect employees. The use of unsupported neoprene gloves is not recommended for use as protection from methylene chloride. Polyvinyl alcohol (PVA) gloves should be used to properly protect the skin from absorbing methylene chloride. Additionally, aprons and any other protective clothing necessary to protect the employees from splashes and skin contamination should be used.

6. A comprehensive respiratory protection program addressing all areas of an effective respirator program in accord with the Code of Federal Regulations (29 CFR 1910.134) should be established and strictly enforced and should include the following at a minimum: selection, medical evaluations of employees required to wear respirators, respirator use, fit testing, procedures for cleaning, disinfecting, storing, inspecting, repairing, and maintaining respirators, emergency use, training of supervisors and respirator wearers, and procedures for regularly evaluating the effectiveness of the program.

7. Solvent soaked rags used for cleaning laminator parts should be placed in trash containers with sealable lids, in order to prevent the escape of vapors into the general workroom environment.

8. A complete inventory of all chemical substances used in this facility should be completed. Any changes in chemical substances used should be discussed with those individuals responsible for industrial hygiene and safety to be certain that proper safety and health precautions are implemented before using.

9. A review of personal protective equipment should be undertaken. All personal protective equipment should be of the type that provides adequate protection for the user from the chemical in use.

10. Employees should be educated about the hazards of the chemicals they will be working with, any special precautions that must be taken when working with these substances, and proper maintenance and care of personal protective equipment.

11. Personal breathing-zone air monitoring of workers potentially exposed to methylene chloride should be conducted on a routine basis and employees should be advised of the results.

12. A medical monitoring program capable of detecting methylene chloride induced health effects should be implemented and should include the following:<sup>2</sup>

- a) Comprehensive preplacement and annual medical examinations should be made available to all workers subject to methylene chloride exposure, unless a different frequency is indicated by professional medical judgment based on factors such as emergencies, variations in work periods, and preexisting health status of individual workers.
- b) Examinations should include, but should not be limited to:
  - 1) A comprehensive or interim medical and work history to include but not be limited to the occurrence of headache, dizziness, fatigue, pain in the limbs, and irritation of the skin and eyes.
  - 2) A comprehensive medical examination including at least blood counts (hemoglobin or RBC). In addition, clinical impressions of autonomic and pulmonary function should be noted and follow-up measurements should be made where indicated.

- 3) An evaluation of the workers ability to wear respiratory protection.
  - 4) Such a medical program could also provide the opportunity for advising the worker of the increased hazards of methylene chloride exposure due to CO from tobacco smoking.
  - 5) It is recommended that COHb values be determined at the end of the workday on a quarterly basis and that this coincide with environmental monitoring. If COHb values in excess of 5% in nonsmokers and 10% in smokers are found, an investigation of the source of COHb should be instituted, and if appropriate from this investigation.
- c) Medical records should be maintained for persons employed one or more years in work involving methylene chloride. All medical records with supporting documents shall be maintained at least 30 years after the individual's employment is terminated.

#### IX. REFERENCES

1. National Institute for Occupational Safety and Health. NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards. Cincinnati, Ohio: National Institute for Occupational Safety and Health, 1981. (DHHS (NIOSH) publication No. 81-123).
2. National Institute for Occupational Safety and Health. Criteria for a recommended standard--occupational exposure to methylene chloride. Cincinnati, Ohio: National Institute for Occupational Safety and Health, 1976. (DHEW publication No. (NIOSH) 76-138).
3. DiVincenzo GD, Kaplan CJ: Uptake, metabolism and elimination of methylene chloride vapor by humans. *Tox Appl Pharm* 59:130;1981a.
4. DiVincenzo GD, Kaplan CJ: Effect of exercise or smoking on the uptake, metabolism and excretion of methylene chloride vapor. *Tox Appl Pharm* 59:141;1981b.
5. Stewart RD, Hake CL: Paint-remover hazard. *JAMA* 235:398;1976.
6. Putz VR, Johnson BL, Setzer JV: A comparative study of the effects of carbon monoxide and methylene chloride on human performance. *J Environ Pathol Toxicol* 2:97;1979.
7. Mennear, JH: NTP Technical Report on the Toxicology and Carcinogenesis Studies of Dichloromethane (Methylene Chloride)(CAS No. 75-09-2) In F344/N Rats and B6C3F<sub>1</sub> Mice (Inhalation Studies). U.S. Department of Health and Human Services, Public Health Service, National Institutes of Health, NIH Publication No. 85-2562, Draft Report, February, 1985.

X. AUTHORSHIP AND ACKNOWLEDGEMENTS

## Report Prepared by:

Daniel Almaguer  
Industrial Hygienist  
NIOSH - Region V  
Chicago, Illinois

Paul Seligman, M.D.  
Medical Officer  
Medical Section  
Hazard Evaluation and Technical  
Assistance Branch  
Division of Surveillance, Hazard  
Evaluations, and Field Studies

## Environmental Assistance:

Richard S. Kramkowski  
Regional Consultant for OS&H  
NIOSH - Region V  
Chicago, Illinois

## Field Assistance:

Ruth Rondinelli  
Medical Officer  
Medical Section  
Hazard Evaluation and Technical  
Assistance Branch  
Division of Surveillance, Hazard  
Evaluations, and Field Studies

## Originating Office:

Division of Surveillance, Hazard  
Evaluations & Field Studies  
Hazard Evaluation and  
Technical Assistance Branch  
Cincinnati, Ohio

## Laboratory Analysis:

Utah Biomedical Laboratory  
Salt Lake City, Utah



XI. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report are currently available upon request from NIOSH, Division of Standards Development and Technology Transfer, Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days the report will be available through the National Technical Information Services (NTIS), Port Royal Road, 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 the following:

- A. Amalgamated Clothing and Textile Workers Union (ACTWU), Local #1481
- B. ACTWU, Minneapolis
- C. Sheldahl, Inc.
- D. U.S. Department of Labor, OSHA - Region V
- E. NIOSH, Region V

For the purposes of informing the affected employees, copies of the report should be posted in a prominent place accessible to the employees, for a period of 30 calendar days.

Table 1

## Sampling and Analysis Methodology

Sheldahl Incorporated  
Northfield, Minnesota  
HETA 84-214

Substance	Collection Media	Flowrate	Analysis	Detection Limit	NIOSH Reference Method
Methylene chloride	Charcoal Tube	10-200 ccpm	Gas Chromatography	0.01 mg	P&CAM 127
Toluene	Charcoal Tube	200 ccpm	Gas Chromatography	0.01 mg	P&CAM 127
Ethyl acetate	Charcoal Tube	200 ccpm	Gas Chromatography	0.01 mg	P&CAM 127
2-ethoxyethanol acetate	Charcoal Tube	200 ccpm	Gas Chromatography	0.02 mg	P&CAM 127
Petroleum naphtha	Charcoal Tube	200 ccpm	Gas Chromatography	0.1 mg	P&CAM 127
Methyl ethyl ketone	Charcoal Tube	200 ccpm	Gas Chromatography	0.01 mg	P&CAM 127
2-butoxy ethanol	Charcoal Tube	110-115 ccpm	Gas Chromatography	0.01 mg	S-76
Carbon Monoxide	Direct Reading Detector Tube	20 ccpm	Length of stain		NA
Toluene-2,4-diisocyanate (TDI)	Amine treated glass wool tube	1.0 lpm	High Pressure Liquid Chromatography	0.3 ug	P&CAM 326
Methylene bisphenyl isocyanate (MDI)	Impreganted glass fiber filter	1.0 lpm	High Pressure Liquid Chromatography	0.4 ug	P&CAM 347
Sulfur acid	Washed Silica Gel tube	100-200 ccpm	Ion Chromatography	10 ug	7903
Ammonia	Silica Gel tube with 37 mm cellulose ester membrane pre-filter	180-200 ccpm	Ion Chromatography	6 ug	S347

Abbreviations: NA - not applicable

mg - milligrams

ug - micrograms

ccpm - cubic centimeters per minute

lpm - liters per minute

Table 2  
Air Concentrations of Methylene Chloride

Sheldahl, INC.  
Northfield, Minnesota

June 12, 1984

Job Classification or Location	sample time (minutes)	sample vol. (liters)	Methylene Chloride (ppm)
Operator, Lam. #1†	32	6.4	256*
Operator, Lam. #1	136	1.4	197
Operator, Lam. #1	294	1.7	47
			8-hour TWA = $\frac{85}{}$
Operator, Lam. #4	335	3.6	103
			8-hour TWA = $\frac{72}{}$
Area Sample, Lam. #4	323	21.0	122*
			8-hour TWA = $\frac{82}{}$
Blank	-0-	-0-	<LOD
Blank	-0-	-0-	<LOD
Blank	-0-	-0-	<LOD

\* - greater than 30% of reported concentration found on B section of charcoal tube. These values should be considered minimum concentrations since breakthrough of the sampler may have occurred.

† - sample showed 19 ppm methyl ethyl ketone in addition to methylene chloride

Laboratory limit of detection: 0.01 mg/sample for methylene chloride

Abbreviations:

<LOD - Less than laboratory limit of detection  
ppm - parts of contaminant per million parts of air  
NA - not applicable

Environmental Criteria:

NIOSH - 75 ppm, 8-hour TWA; 500 ppm, ceiling limit  
ACGIH-TLV - 100 ppm, 8-hour TWA; 500 ppm, STEL  
OSHA-PEL - 500 ppm, 8-hour TWA; 1000 ppm, ceiling limit

Table 3

## Personal Breathing Zone/General Area Air Concentrations of Anhydrous Ammonia

Sheldahl, Inc.  
Northfield, Minnesota

June 13, 1984

Job Classification or Location	sample time (minutes)	sample vol. (liters)	Ammonia (ppm)
Operator	170	34.0	3.7
"	23	4.6	4.3
			8-hour TWA = 1.5
Area samples collected across aisle from etcher	169	32.1	8.5
	23	4.4	6.7
			8-hour TWA = 3.3
Area sample collected at feed end next to time clock	177	32.7	3.6
	20	3.7	3.4
			8-hour TWA = 1.5
Blank	-0-	-0-	<LOD
Blank	-0-	-0-	<LOD

Laboratory limit of detection: 6 micrograms (ug) ammonia per sample

## Abbreviations:

<LOD - Less than laboratory limit of detection  
ppm - parts of contaminant per million parts of air

## Environmental Criteria:

NIOSH - 50 ppm, 5 minute ceiling concentration  
ACGIH-TLV - 25 ppm, 8-hour TWA; 35 ppm, STEL  
OSHA-PEL - 50 ppm, 8-hour TWA

Table 4

## Personal Breathing Zone/General Area Air Concentrations of 2-butoxyethanol (2-BE)

Sheldahl, Inc.  
Northfield, Minnesota

June 13, 1984

Job Classification or Location	sample time (minutes)	sample vol. (liters)	2-BE (ppm)
Operator, fan belt lose	115	13.1	7.7
" fan belt tightened	239	27.2	2.3
			8-hour TWA = 3.0
Operator, short term	22	2.5	5.8
fan belt lose	16	1.8	6.9
Operator, short term	24	2.7	2.3
fan belt tightened	56	6.4	1.9
	12	1.4	1.5
Area samples taken (lose)	168	18.6	7.6
across aisle from (tight)	254	28.2	1.5
dip tank			8-hour TWA = 3.5
Blank	-0-	-0-	<LOD
Blank	-0-	-0-	<LOD

Laboratory limit of detection: 0.01 milligrams of 2-butoxyethanol per sample

## Abbreviations:

<LOD - Less than laboratory limit of detection  
ppm - parts of contaminant per million parts of air

## Environmental Criteria:

ACGIH-TLV - 25 ppm, 8-hour TWA; 75 ppm, STEL; SKIN  
OSHA-PEL - 50 ppm, 8-hour TWA

Table 5

## Personal Breathing Zone Air Concentrations at Laminator #2

Sheldahl, Inc.  
Northfield, Minnesota

June 12, 1984

Job Classification or Location	sample time (minutes)	sample vol. (liters)	ethyl acetate (ppm)	toluene (ppm)
Operator, Lam. #2	270	54.0	10.3	2.4
"	164	32.8	16.1	3.2
Blank	-0-	-0-	<LOD	<LOD

Laboratory limit of detection: 0.01 milligrams ethyl acetate per sample  
0.01 milligrams toluene per sample

## Abbreviations:

<LOD - Less than laboratory limit of detection  
ppm - parts of contaminant per million parts of air

## Environmental Criteria: ethyl acetate

ACGIH-TLV - 400 ppm, 8-hour TWA  
OSHA-PEL - 400 ppm, 8-hour TWA

## Environmental Criteria: toluene

NIOSH - 100 ppm, 8-hour TWA; 200 ppm ceiling limit  
ACGIH-TLV - 100 ppm, 8-hour TWA; 150 ppm STEL  
OSHA-PEL - 200 ppm, 8-hour TWA; 300 ppm ceiling limit

Table 6

## Personal Breathing Zone/General Area Air Concentrations at Laminator #10

Sheldahl, Inc.  
Northfield, Minnesota

June 12, 1984

Job Classification or Location	sample time (minutes)	sample vol. (liters)	2-EEA (PPM)	Pet. Naphtha (mg/M <sup>3</sup> )	MEK (PPM)
Lam. #10, Operator	252	50.4	0.15	2.0	0.20
" Asst.	253	50.6	0.15	<LOD	0.14
" Asst.	163	32.6	0.17	<LOD	0.21
Lam. #10, Asst.	10	2.0	<LOD	<LOD	3.40
Blank	-0-	-0-	<LOD	<LOD	<LOD
Blank	-0-	-0-	<LOD	<LOD	<LOD

Laboratory limit of detection: 0.02 milligrams 2-ethoxyethyl acetate per sample  
 0.01 milligrams petroleum naphtha per sample  
 0.01 milligrams methyl ethyl ketone per sample

## Abbreviations:

<LOD - Less than laboratory limit of detection  
 mg/M<sup>3</sup> - milligrams of contaminant per cubic meter of air  
 ppm - parts of contaminant per million parts of air  
 2-EEA - 2-ethoxy ethyl acetate  
 MEK - methyl ethyl ketone

## Environmental Criteria: 2-ethoxy ethyl acetate

ACGIH-TLV - 5 ppm, 8-hour TWA  
 OSHA-PEL - 100 ppm, 8-hour TWA

## Environmental Criteria: petroleum naphtha

NIOSH - 350 mg/M<sup>3</sup>, 8-hour TWA  
 OSHA-PEL - 2000 mg/M<sup>3</sup>, 8-hour TWA

## Environmental Criteria: methyl ethyl ketone (MEK)

NIOSH - 200 ppm, 8-hour TWA  
 ACGIH-TLV - 200 ppm, 8-hour TWA  
 OSHA-PEL - 200 ppm, 8-hour TWA

Table 7

Total Combined exposures of Methylene Chloride (MC) &amp; Carbon Monoxide (CO)

Sheldahl Inc.  
Northfield, Minnesota

Operator Job/ Dept. #	Sample Time	MC/TWA Conc. (ppm)	Sample Time	CO/TWA Conc. (ppm)	Combined Exposure
11/14/84					
Tape machine Dept. 12	477 min.	132*	475 min.	10.2	2.05
Laminator #1 Dept. 14	415 min.	63*	417 min.	6.9	----
11/15/84					
Laminator #3 & 4 Dept. 14	447 min.	65*	438 min.	21.0	1.47
Laminator #1 Dept. 14	436 min.	38*	438 min.	8.3	----
Adhesive mixer Dept. 14	196 min.	26*	196 min.	11.0	0.27
Tape machine Dept. 12	451 min.	59*	376 min.	23.0	1.45
Laminator #4 Dept. 14	419 min.	33*	420 min.	2.6	----
Mixing room emp. employee, Dept. 14	318 min.	87*	318 min.	30.0	2.02
11/16/84					
Laminator #1 Dept. 14	192 min.	25*	377 min.	8.0	----
39" laminator Dept. 12	359 min.	105*	333 min.	18.0	1.91

\* These values should be considered minimum values since breakthrough of the sampler may have occurred.

Environmental Criteria: NIOSH - 75 ppm MC, 35 ppm CO, <1 for combined exposures  
ACGIH-TLV - 100 ppm MC, 50 ppm CO  
OSHA-PEL - 500 ppm MC, 50 ppm CO



Table 8

## Short-term/Personal Breathing Zone Air Concentrations of Methylene Chloride

Sheldahl Inc.  
Northfield, Minnesota

Job/Dept. #	Sample Time (minutes)	Sample Volume (liters)	PPM
November 15, 1984			
Operator, laminator #3 & #4 Employee cleaning, wearing resp.	10	2.2	122*
Employee cleaning parts in room with no ventilation Employee wearing resp.	14	3.0	1752*
Employee mixing adhesives wearing respirator Dept. 12	12	2.5	164*
November 16, 1984			
Operator cleaning 39 inch laminator, wearing resp. Dept. 12	26	5.2	731*
Operator cleaning tape machine, wearing respirator Dept. 12	31	6.6	505*
Employee cleaning "tunnel" of laminator #10, wearing resp. Dept. 14	31 69	6.4 14.4	445* 268*

\* These values should be considered minimum values since breakthrough of the sampler may have occurred.

Short-term environmental criteria: NIOSH - 500 ppm  
ACGIH - 500 ppm  
OSHA - 1000 ppm

TABLE 9

DEMOGRAPHIC DATA

SHELD AHL INC., NORTHFIELD, MINNESOTA  
NOVEMBER, 1984

Departments 12 and 14

	<u>Mean + 1 S.D.</u>	<u>Range</u>
Age	34.3 + 11.4 years	22.5 - 60.4
Length of employment at Sheldahl	8.3 + 6.0 years	0.8 - 22.0
Length of employment in laminations	6.4 + 6.5 years	0.8 - 21.5
Race	White, not Hispanic origin	19 (95%)
	American Indian	1 (5%)
Sex	Male	14 (67%)
	Female	7 (33%)
Current smokers		12/21 (57%)
Uses respirator		17/21 (81%)
	Half-mask	10/17 (59%)
	Full-mask	3/17 (18%)
	Air-supplied	4/17 (23%)

TABLE 10

PREVALENCE OF SYMPTOMS

SHELD AHL INC., NORTHFIELD, MINNESOTA  
NOVEMBER, 1984

I - Respiratory/mucous membrane irritation

Symptom

Nose irritation	3/21
Eye irritation	2/21
Cough	2/21
Shortness of breath	2/21
Wheezing	1/21
Chest pain	1/21

II - Skin rash

Rash	2/21
------	------

III - Central Nervous System symptoms

Headache	2/21
Numbness	1/21
Giddiness	1/21
Nausea	1/21
Chills	1/21
Dizziness, episodes of confusion, weakness, muscle cramping, slurred speech, diarrhea, stumbling, loss of balance, difficulty walking	0/21

TABLE 11  
CARBOXYHEMOGLOBIN LEVELS (COHb) and EXHALED CARBON MONOXIDE (CO)  
SHELDAHL INC., NORTHFIELD, MINNESOTA  
NOVEMBER, 1984

<u>Smoking Status</u>	<u>COHb (%)</u>					
		<u>Pre-shift</u>		<u>Post-shift</u>		
	<u>#</u>	<u>Mean + 1 SD* (Range)</u>		<u>#</u>	<u>Mean + 1 SD* (Range)</u>	
Non-smoker	6	1.9 + 0.3 (1.6 - 2.1)		6	2.4 + 1.1 (0.7 - 3.8)	
Smoker	10	7.1 + 2.7 (3.1 - 10.4)		5	5.4 + 2.5 (1.9 - 7.7)	
=====						
	<u>CO (ppm)</u>					
		<u>Pre-shift</u>		<u>Post-shift</u>		
	<u>#</u>	<u>Mean + 1 SD* (Range)</u>		<u>#</u>	<u>Mean + 1 SD* (Range)</u>	
Non-smoker	7	9.1 + 2.6 ( 7.0 - 14.0)		7	16.1 + 4.3 ( 8.0 - 22.5)	
Smoker	10	30.6 + 10.7 (15.5 - 46.0)		10	29.0 + 8.5 (18.0 - 40.5)	

\*SD - standard deviation