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

NIOSH

Health Hazard Evaluation Report

HETA 87-252-1857
LTV STEEL, INDIANA HARBOR WORKS
EAST CHICAGO, INDIANA

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.

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LTV STEEL, INDIANA HARBOR WORKS
EAST CHICAGO, INDIANA
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I. SUMMARY

On April 21, 1987, the National Institute for Occupational Safety and Health (NIOSH) was requested to evaluate employee exposures to 1,1,1-trichloroethane at LTV Steel, Indiana Harbor Works, East Chicago, Indiana. The request was in response to employee concerns with the use of a cleaning solvent used in the Central Machine Shop. The solvent, "Gold Shield Perm-Ethane", was composed primarily of 1,1,1-trichloroethane, with a small amount of diethylene ether (dioxane) as a stabilizer.

In September 1987, NIOSH investigators conducted an initial and environmental survey. Personal and area air samples were collected for 1,1,1-trichloroethane and dioxane in the Central Machine Shop during the use of the solvent. In addition, ten employees who occasionally used the solvent were questioned about possible work related health problems.

Airborne concentrations of 15.3 and 36.0 parts per million (ppm) of 1,1,1-trichloroethane were found in two 15-minute personal air samples collected. These results are below both the NIOSH recommended exposure limit (REL) of 350 ppm and the American Conference of Governmental Industrial Hygienists (ACGIH) Short-Term Exposure Limit (STEL) of 450 ppm for a 15-minute period. Time-weighted average (TWA) concentrations of 13.2 ppm 1,1,1-trichloroethane in a personal sample, and 1.0 and 5.9 ppm in area samples were detected. These results are below the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) and ACGIH Threshold Limit Value (TLV) of 350 ppm as an 8-hour TWA. Dioxane was found to be above the level of analytical detection of 0.01 milligrams per sample in only one of the five air samples collected, but the the amount detected was less than the lower limit of quantitation (0.03 milligrams/sample) for the analytical method used.

Eight of the the ten employees interviewed during the survey did not report any health problems related to the use of the solvent in the machine shop. Two employees indicated that they had experienced health problems which they felt might be related to exposure to the solvent, but the nature of their reported problems was complex and would not normally be associated with the exposure levels found in this survey.

No exposures to 1,1,1-trichloroethane or dioxane above the evaluation criteria were found during this survey. Recommendations to further reduce employee exposures are contained in Section VIII of this report.

KEY WORDS: SIC 3312 (Steel Works), 1,1,1-trichloroethane, dioxane

II. INTRODUCTION

On April 21, 1987, NIOSH received a request from an authorized representative of the employees at LTV Steel Corporation, Indiana Harbor Works, East Chicago, Indiana for a health hazard evaluation. The request was in response to employee concerns with the use of a solvent containing 1,1,1-trichloroethane in the Central Machine Shop.

On September 10, 1987, an initial survey visit was conducted. An opening conference was held with representatives from LTV Steel and the United Steel Workers Local 1011. Background information related to the nature of operations in the Central Machine Shop -- in particular, the use of 1,1,1-trichloroethane, was obtained. Following this, a walk-through survey of the Central Machine Shop was conducted. On September 11, 1987, environmental samples were collected in the Central Machine Shop. The results of this survey were provided to company and union representatives by letter on December 16, 1987.

III. BACKGROUND

The Central Machine shop provides services plant wide. The shop employs approximately 148 workers over three shifts. On the day shift, this includes approximately 35 machinists, five floor hands, five millwrights, and five utilitymen. It was estimated that the length of service in this area ranged from 10 to 40 years, with roughly 20 years being the average. With the exception of the millwrights, the majority of the employees had been with the Machine Shop for the duration of their employment at the company.

The solvent being used in the Central Machine Shop was "Gold Shield Perm-Ethane" (Detrex Chemical Industries, Inc.). According to information supplied on the Material Safety Data Sheet, it is composed of approximately 96% 1,1,1-trichloroethane (methyl chloroform). The remaining ingredients which make up the balance of the mixture include; diethylene ether (dioxane), glycol methylene ether, and sec butanol.

The solvent is stored in a 1,000-gallon tank located inside the Machine Shop. A padlock was present on the tank's dispensing valve; however, the tank, reportedly, was not kept locked on a regular basis. It was estimated that 700 gallons of the material are used every three to four months. The primary use of the solvent is for cleaning electrical conductors and parts. An operation where welding dies are periodically cleaned was identified as being the job where the substance was used most frequently. Also, the solvent was, reportedly, used for miscellaneous cleaning of parts by the employees. One area where significant amounts of parts cleaning is done is in the tool crib area, where items such as pneumatic tools are repaired.

Prior to use, the solvent is dispensed from the storage tank into safety cans, which then are taken to the work area for use. In the work area, the solvent usually is manually applied with brushes or rags, or the

part is immersed in the solvent. When the solvent becomes excessively contaminated with dirt and oil, the cans are taken to the back of the shop and dumped into a large settling/disposal tank. Protective gloves are made available to the employees using the solvent. A NIOSH/MSHA approved half-face piece respirator with organic vapor cartridges (TC23C-151) also had been recently made available to the individual who was responsible for the cleaning of welding dies. Periodic training on the safe use of solvents is presented to the employees during safety meetings. A placard which states the health hazards of the solvent along with recommended personal protection and work practices is present on the front of the storage tank.

IV. MATERIALS AND METHODS

On September 11, 1987, air samples were collected to assess employee exposures during use of the solvent in the Central Machine Shop . This included personal samples collected near the employee's breathing zone, as well as general area samples. Since the solvent was being used on a limited basis, all operations where the solvent was in use were monitored. This included two short-term personal samples collected on employees engaged in brief activities with the greatest potential for solvent exposure; the dumping and filling of a solvent container and the cleaning of welding dies. A long-term personal sample was collected during the routine repair activities of a tool crib employee who was periodically using the solvent throughout the day. In addition, two area air samples were collected at fixed locations to reflect the airborne concentration of solvent in the vicinity of the storage tank.

Samples were collected using battery-powered pumps operating at approximately 200 cubic centimeters of air per minute. The pumps were attached via Tygon tubing to a charcoal tube collection media. The tubes were later analyzed by gas chromatography for 1,1,1-trichloroethane and dioxane, using NIOSH methods 1003 and 1602.[1] A complete listing of the sample locations and other pertinent data is located in Table 1.

In addition to the charcoal tube samples, instantaneous or "grab" samples were collected during select operations involving the use of the solvent. These samples were collected using Drager detector tubes (Trichloroethane 50/D) and a Drager hand pump in accordance with the manufacturer's instructions. Sample results, based on visual observation of the length of stain indicator on the tubes, were determined immediately .

During the period of sample collection, brief interviews were conducted with eight Central Machine Shop employees who were identified as periodic users of the solvent. The purpose of the interviews was to determine if any of these employees were experiencing health problems related to the use of the solvent. Also, two additional Central Machine Shop employees who reportedly used the solvent were contacted by phone for this information.

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 preexisting 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 becomes 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 exposure limits, 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 brief discussion of the toxicity and evaluation criteria for the substances evaluated during this survey is provided as follows.

A. 1,1,1-Trichloroethane

1,1,1-Trichloroethane or methyl chloroform was the primary constituent of the Perm-Ethane solvent being used in the Machine Shop. Liquid 1,1,1-trichloroethane can cause dermatitis upon repeated skin contact, and may cause irritation if splashed in the eyes. The vapor of 1,1,1-trichloroethane is a narcotic. In controlled human exposures to 500 ppm, no effects other than slight transient eye irritation were noted; at 1000 ppm, mild eye irritation was experienced by all subjects, and some became dizzy. Above 1700 ppm, minor disturbances of equilibrium have been observed, with complaints of headache and lassitude. An exposure to concentrations in excess of 1000 ppm for 15-minutes, or 2000 ppm for 5-minutes, can be expected to produce a disturbance of equilibrium in the majority of adults. A five minute exposure to 5000 ppm can be expected to cause marked incoordination and anesthesia. At very high concentrations, unconsciousness, irregular heart-beat, and death may occur, and a number of human fatalities related to industrial exposure in confined spaces have been reported.[2] The odor threshold for 1,1,1-trichloroethane is in the range of 20 to 100 ppm.[2] Currently, 1,1,1-trichloroethane is not classified as a carcinogen by NIOSH, ACGIH, the International Agency for Research on Cancer (IARC), or the National Toxicology Program (NTP).[3]

The current OSHA standard for 1,1,1-trichloroethane is 350 ppm as an 8-hour time-weighted average (TWA).[4] The NIOSH recommended exposure limit is 350 ppm averaged over a 15-minute period.[2] The ACGIH recommends 350 ppm as an 8-hour TWA, and 450 ppm as a short-term exposure limit (not to be exceeded during any 15-minute period).[5]

B. Dioxane

Dioxane, is commonly used as a stabilizer in 1,1,1-trichloroethane, and was listed as being present as a minor ingredient on the material safety data sheet for Perm-Ethane. Overexposure to dioxane may cause irritation of the eyes, nose, and throat. In sufficient concentrations, it may also cause dizziness, loss of appetite, headache, nausea, vomiting, stomach pain, and liver and kidney damage. Prolonged skin exposure to the liquid may cause drying and cracking. Dioxane has been shown to induce tumor formation in experimental animals.[2] Presently, dioxane is classified as a suspect human carcinogen by NIOSH, the IARC, and NTP.[3]

The current OSHA standard for dioxane is 100 ppm as an 8-hour time-weighted average (TWA).[4] The NIOSH recommended exposure limit is 1 ppm averaged over a 30-minute period, and NIOSH recommends that dioxane be treated as a potential occupational carcinogen.[2] The ACGIH recommends 25 ppm as an 8-hour TWA for dioxane exposure.[5]

VI. RESULTS

The results of the charcoal tube air samples collected during the use of the solvent are shown in Table 1. Airborne concentrations of 15.3 and

36.0 ppm of 1,1,1-trichloroethane were found in the two 15-minute personal air samples collected. These results are below both the NIOSH recommended exposure limit of 350 ppm for a 15-minute ceiling and the ACGIH STEL of 450 ppm for a 15-minute period. In addition, the employee involved in the cleaning of the welding dies was wearing an organic vapor respirator during this procedure. If properly fitted and maintained, this employee's actual exposure would be expected to be substantially less than the concentration measured in the air sample (36 ppm).

A TWA concentration of 13.2 ppm 1,1,1-trichloroethane was found in the personal air sample collected during the routine repair activity performed in the tool crib. Assuming that the solvent would be used in a similar manner throughout the workshift, this sample would be well below the OSHA and ACGIH 8-hour TWA's of 350 ppm.

The remaining area samples collected in the vicinity of the solvent storage tank showed TWA concentrations of 1.0 and 5.9 ppm 1,1,1-trichloroethane. Therefore, employees present in this area for either brief or extended periods of time would not be expected to be exposed to 1,1,1-trichloroethane above either the ceiling or TWA evaluation criteria.

Dioxane was found to be below the level of analytical detection of 0.01 milligrams per sample in four of the five air samples collected (Table 1). Dioxane was detected in the long-term personal sample collected in the tool crib; however, the amount detected was less than the lower limit of quantitation (0.03 milligrams/sample) for the analytical method used. Although the exact concentration of dioxane in this sample could not be accurately determined, based on the sensitivity of the method, the airborne concentration of dioxane would be expected to be below the NIOSH recommended exposure limit of 1 ppm by a factor of at least 5.

The results of the detector tube samples for 1,1,1-trichloroethane are presented in Table 2. During the cleaning of welding dies, instantaneous concentrations of 50 and 100 ppm were found in the immediate vicinity of the welding die being cleaned. In measurements taken during the dumping and filling of a solvent container, the concentrations of 1,1,1-trichloroethane detected were less than 50 ppm (the lowest gradation on the detector tube). In a sample collected directly above the steam pit drain where the solvent was alleged to have been dumped on occasion, no detectable quantity of 1,1,1-trichloroethane was found. While these instantaneous concentrations can not be applied directly to any environmental criteria, they do indicate that even during peak exposures, no excursions above the limits for 1,1,1-trichloroethane were found.

The majority of the ten employees interviewed during the survey did not report any health problems related to the use of the solvent. One employee did report a previous episode where he had experienced symptoms of overexposure while using the solvent in a poorly ventilated area in another section of the plant. Two employees indicated that they had

experienced or currently were experiencing health problems which they felt might be related to exposure to the solvent. The nature of their reported problems was complex, and each of these employees was seeing an occupational health physician in order to determine if their health problems were potentially work-related.

During the interviews, several of the workers expressed concern over the possible misuse of the solvent by their co-workers. They described incidents where they felt excessive amounts of solvent were being used to clean machines and work areas, creating unnecessary exposure to employees in neighboring areas. Plastic buckets without lids also were reported to be used frequently around the shop as containers for the solvent. This would contribute to the amount of solvent vapor in the general shop area. In addition, several employees reported that they did not regularly wear gloves when working with the solvent.

VII. DISCUSSION AND CONCLUSIONS

As evidenced by the results of the environmental samples collected during this survey, the airborne concentrations of 1,1,1-trichloroethane and dioxane were below the evaluation criteria. Although only a limited amount of solvent use occurred during the period of the survey, the job tasks monitored were reported to be representative of those which would be expected to represent normal usage.

However, based on the information obtained during the employee interviews, it appears that increased emphasis on the proper use of the solvent is necessary. While no overexposures to the solvent components would be expected during the routine types of activities that were monitored, ongoing efforts should be focused toward the prevention of unnecessary exposure. Limiting exposure to the solvent will help reduce the likelihood that an employee might suffer adverse health effects because of a preexisting condition, hypersensitivity, or the combined effects of exposure to another substance. In addition, since the solvent contains dioxane, a suspect carcinogen, limiting the overall exposure to the mixture correspondingly will decrease the potential exposure to dioxane. This would be considered a prudent precaution when dealing with substances which are potentially carcinogenic.

VIII. RECOMMENDATIONS

Based on the information collected during the evaluation, the following recommendations are made in order to further reduce employee exposures. Although many of these recommendations are currently in place, ongoing attention is needed to ensure that they are practiced regularly. If necessary, the NIOSH "criteria for a recommended standard....occupational exposure to 1,1,1-trichloroethane" should be consulted for more detailed information in each of these areas.[6]

1. Protective gloves should be worn in order to avoid skin contact with the solvent. This is particularly necessary since the dioxane, which

is contained in the solvent, can penetrate the skin readily. Furthermore, during many machining operations, employees' skin also may also come into contact with oils, machining fluids, and other substances which can increase the likelihood of dermatitis.

2. Splash-proof safety goggles should be worn whenever the possibility of solvent contact with the eyes exists. If the solvent contacts the eyes, they should be washed with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, the individual should seek medical attention.

3. Hands or other skin surfaces coming into contact with the solvent should be promptly washed with soap or mild detergent and water. Clothing or shoes which become wet with the solvent should be removed and the underlying skin washed thoroughly. The solvent should not be used to clean hands or clothing.

4. Avoid unnecessary use of the solvent. The water soluble cleaner available in the shop should be used whenever practical to clean parts and machinery.

5. The solvent should be stored in properly designed and labelled containers with attached, closeable lids. Open containers of solvent should not be left in the work area.

6. Emergency spill and leak procedures should be prepared. These procedures should describe the appropriate personal protective equipment and clothing and solvent collection and disposal methods. Such procedures should address both large spills and leaks (e.g., from the bulk storage tank) as well as smaller spills which might occur in the work area.

7. To avoid the formation of phosgene, hydrochloric acid or other toxic decomposition products, care should be taken to avoid contact of the solvent liquid or vapor with flames or red-hot surfaces.

8. The solvent should never be used in any enclosed or poorly ventilated area without appropriate supervision and the use of specially prepared confined space work procedures.

IX. REFERENCES

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4) Occupational Safety and Health Administration. Code of federal regulations, 29:1900-1910. Washington D.C.: U.S. Department of Labor, Occupational Safety and Health Administration, 1980.

5) American Conference of Governmental Industrial Hygienists. Threshold Limit Values and Biological Exposure Indices for 1987-1988. Cincinnati, Ohio: American Conference of Governmental Industrial Hygienists, 1987.

6) National Institute for Occupational Safety and Health. Criteria for a Recommended Standard....Occupational Exposure to 1,1,1-Trichloroethane. Cincinnati, Ohio: National Institute for Occupational Safety and Health, 1976. [DHEW (NIOSH) Publication No. 76-184].

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XI. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

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A. LTV Steel Corporation, Indiana Harbor Works, East Chicago, Indiana
B. United Steel Workers of America, Local 1011
C. Requestor
D. U. S. Department of Labor, OSHA - Region V
E. NIOSH Regional Offices/Divisions

TABLE 1
Results of Environmental Samples Collected for 1,1,1-Trichloroethane and Dioxane
LTV Steel, Indiana Harbor Works, East Chicago, Indiana
Samples collected September 11, 1987

Sample Type	Sample Location/ Description	Sample Duration (minutes)	Sample Volume (Liters)	TWA Concentration 1,1,1-Trichloroethane (ppm)	TWA Concentration Dioxane (ppm)
Personal	Tool Crib Employee/ Emptying & Refilling Solvent Can	15	3.6	15.3	< LOD
Personal	Tool Crib Employee/ Repair of Pneumatic Tools	148	30.4	13.2	Trace (between LOD & LOQ)
Personal	Welder Die Repairman/ Cleaning Welding Die	15	3.2	36.0	< LOD
Area	On Ice Machine/ 3 Feet from Rear of Storage Tank	180	38.7	1.0	< LOD
Area	On Ledge/ 5 Feet from Front of Storage Tank	180	40.3	5.9	< LOD
NIOSH Recommended Exposure Limit				350 (15-min ceiling)	1 (30-min ceil.)
OSHA Permissible Exposure Limit				350 (8-hour TWA)	100 (8-hour TWA)
ACGIH Threshold Limit Value				350 (8-hour TWA) 450 (15-min Ceiling)	25 (8-hour TWA)

Abbreviations and Key
TWA - Time-weighted average concentration (results expressed as TWA's for the duration of sample collection).
ppm - parts of contaminant per million parts of air.
< LOD - Less than the analytical limit of detection of 0.01 milligrams per sample.
< LOQ - Less than the analytical limit of quantitation of 0.03 milligrams per sample.