

Environmental Health
Program A-2400, A-7000

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November 24, 1981

PURPOSE

The intent of this protocol is to document priorities established for the on-going industrial hygiene program in the Chlorinated Ethane Products plant. This document will also serve as a reference source for plant supervision and personnel responsible for the industrial hygiene programs. It is recognized that by definition an "on-going" program is one that is responsive and can easily be adjusted to changes in priorities. These may result from changes in process design, job procedures, the chemicals being handled as well as new toxicology data, exposure guidelines, or monitoring techniques.

GOALS

There are two basic goals the industrial hygiene program is designed to meet. They are:

- (1) To annually educate plant personnel on how overexposures to chemicals may occur, methods of reducing overexposure, potential adverse health effects of overexposure, primary information sources on health effects, and on the way in which the work done by various health related groups, within The Dow Chemical Company, help protect the health of employees.
- (2) To annually monitor and communicate the results to employees who have a potential for being overexposed to chemicals or physical agents in their work environment.

Meeting the Goals

1. Dow has established the goal of educating the employees on health related questions as a part of the corporate policy. It is recognized that an effective employee education program is one of the best methods for controlling workplace exposures to hazardous materials.

Three video tapes have been prepared for use by the plants to cover the basic aspects of the educational goals. The Environmental Health Team is a tape which summarizes the work of Toxicology, Industrial Hygiene, and Industrial Medicine functions. The second tape, How Overexposures May Occur and Methods of Controlling Overexposures reviews how various types of workplace stresses may occur and familiarizes the employee with various methods of exposure control. The last tape, Sources of Information, deals with how information on the toxicity of chemicals and physical agents is obtained.

Employees are educated in the potential adverse health effects of chemicals by a fourth aspect of the program where they are asked to read a general discussion of potential adverse health effects and review specific selected

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Meeting the Goals (continued)

Consequences of Overexposure To Toxic Amounts sheets and Toxicology Data Sheets incorporated into booklets. These booklets are distributed throughout the plant in easily accessible areas such as offices and control rooms.

The viewing of the video tapes and review of the booklets is documented and summarized each quarter to monitor the progress of the educational program. This documentation and summary of the progress is reported via the Index I form shown in Appendix I.

While use of the video tapes and hazard booklets will suffice for meeting the minimum Dow criteria, a successful employee education program will require attention throughout the year. It is recommended that all levels of supervision be actively involved in the presentation of the program.

2. The vehicle for establishing both educational and monitoring priorities is the Chemical and Physical Agent Inventory sheet. An inventory sheet for each job classification is prepared. The completed inventories for the CEP areas are contained in the following sections of this report. The inventory contains a complete list of the chemicals and physical agents that persons in a given job class have a recognized potential for exposure to while performing their normal job. An estimate of the degree of exposure is made based on job procedures, plant process design, and the quantity and physical properties of the material. Definitions for the ratings (1-4: Low-High) are given in Table 1. Based on these estimates of exposure potential and the toxicity of the compound, hazard ratings are assigned.

The hazard rating defines the necessary industrial hygiene action to be taken with respect to the two industrial hygiene goals. Definitions of the five hazard ratings are given in Table 2. The exposure and hazard ratings were assigned during and following discussions with various CEP supervisory personnel. Considerations concerning job procedures, how the chemicals are encountered or handled, the likelihood of being overexposed, previous monitoring results, toxicology data, and exposure criteria assisted in assigning hazard ratings. For those agents where the hazard rating indicates that monitoring is warranted, a monitoring program is effected and the results of this monitoring is communicated to the employees through supervision. The communication of the monitoring results is

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Meeting the Goals (continued)

documented and summarized each quarter to monitor the progress of the exposure communication effort. The documentation and summary of the progress is reported via the Index II form shown in Appendix I.

PROCESS DESCRIPTIONS, JOB DESCRIPTIONS, AND INVENTORIES

The CEP complex is located in the A-2400, A-1600 and A-7000 blocks. The major products of the unit are ethylene dichloride, vinylidene chloride, beta-trichloroethane, alpha-trichloroethane, alpha-dichloroethane, ethyl chloride, tetrachloroethane, and hydrochloric acid. Administratively the unit is broken down into the following areas: vinylidene chloride/ethyl chloride/beta-trichloroethane production, ethylene dichloride production, alpha-dichloroethane/alpha-trichloroethane production, CEP unit services, CEP Lab, and CEP maintenance. A total of approximately 145 full time employees work in these areas.

For each of the above areas a description of the process (where applicable), the associated job descriptions, and industrial hygiene inventories are given in the following appendices:

- Appendix II Vinylidene Chloride/Ethyl Chloride/Beta-Trichloroethane Production
- Appendix III Alpha-Dichloroethane/Alpha-Trichloroethane Production/THROX
- Appendix IV Ethylene Dichloride Production
- Appendix V CEP Maintenance
- Appendix VI CEP Unit Services
- Appendix VII CEP Lab

INDUSTRIAL HYGIENE MONITORING METHODS

A list of the compounds and physical agents which will require some degree of monitoring is given in Table 3. The methods used for performing the monitoring are referenced in the table and described below. The monitoring and analysis will be performed by CEP Lab personnel with the support and assistance of the plant industrial hygienist.

1. Charcoal Tube Monitoring

This method is to be used for determining both short term and 8-hour time-weighted average potential exposures. The method involves collection of the compounds on activated charcoal adsorption media and analysis by gas

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INDUSTRIAL HYGIENE MONITORING METHODS (continued)

chromatography via solvent desorption. Commercially available charcoal tubes containing one gram of PCB 20 X 40 mesh activated charcoal are used to collect organics from the sampled air. Personnel sampling pumps pull air through the tubes at known constant flow rates. The maximum flow rate and total sample volume criteria are established to ensure that no loss is occurring due to breakthrough. Recommended values for those compounds collected on activated charcoal are listed in Table 4. Where more than one of these compounds is to be collected on the same sample, the lowest recommended flow rate and total sample volume among the compounds to be monitored should be used. The recommended sample volumes and flow rates allow quantitative collection of the compounds. Flow rates may be increased for short term monitoring or periods less than 8 hours so that adequate sensitivity may be obtained. The total sample volumes, however, should not be exceeded.

Analysis of the samples should follow standard desorption with 10 ml of dry ice chilled carbon disulfide (or other solvents as necessary) and gas chromatographic analysis of the extract. Desorption efficiencies are reported in various references, however the values to be used in the calculations shall be determined by the CEP Lab by analysis of spiked samples. Reevaluation of desorption efficiencies should be done at least annually.

2. Peak Monitoring

This method is to be used to determine peak exposure to organics for personnel during very specific jobs such as sampling, breaking into equipment, entering vessels, and otherwise working on process equipment. A clean glass air tight syringe is taken to the job site and a sample of air is taken in the breathing zone of the worker by pumping the piston in and out several times and then slowly drawing the air into the cylinder. The syringe is closed securely to prevent air leaks and taken to the laboratory for analysis by injection into a gas chromatograph as soon as possible. A gas chromatograph dedicated for this type of analytical work should be used. The gas chromatograph should be standardized with known air samples at regular intervals.

3. Colorimetric Indicator Tubes

Exposures to chlorine, hydrochloric acid, and ammonia will be evaluated using Dräger direct reading colorimetric indicator tubes. Pursuant

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INDUSTRIAL HYGIENE MONITORING METHODS (continued)

4. Membrane Filters

Silica dust exposures will be determined by collection on PVC membrane filters (Millipore®, 0.6 micron, 47 mm) at calibrated flow rates of 1.5-2.0 liters per minute and analyzed by X-ray diffraction. Validation of the analytical procedure is reported in Analytical Services report TC-566.

Welding fume exposures will be evaluated by collection on Millipore membrane filters (GSHP, 0.2 microns, 47 mm) using a calibrated 10-15 liters per minute) high volume sampling pump. Analysis of the samples will be done by atomic absorption analysis.

Potential asbestos exposures will be evaluated using standard NIOSH procedures (Method No. P & CAM 239). Samples are collected on 0.8 micron, 37 mm Millipore® cellulose acetate filters at calibrated flow rates of 2.0-2.5 liters per minute. Asbestos fibers are counted using phase contract microscopy.

5. Continuous Air Monitor

The continuous air monitor in place in the A-2400 block will be used for the purpose of identifying problems in the process area which could lead to potential exposures to chemicals. When the continuous air monitor data indicates a high level of airborne chemical concentration, consideration of this data will be used to determine necessary steps to reduce potential exposures. The continuous air monitor data will not, however, be used to calculate individual doses.

EVALUATION CRITERIA

Personnel monitoring is performed to determine potential exposure levels both as a daily time-weighted average and short term exposure. The results of the monitoring are compared with the recommended exposure guidelines given in Table 1. Also listed in the table is the source of the recommended standard. These values are based on reliable toxicology data and industrial experience. It is believed that nearly all workers will tolerate exposure to these levels without adverse health effects.

The exposure guidelines represent the acceptable time-weighted average exposures for a normal 8-hour work day, 40 hours per week. Short Term Exposure Limits (STEL's) represent the maximum

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EVALUATION CRITERIA (continued)

concentration for a 15 minute exposure. The STEL should be considered a maximum or ceiling concentration that should not be exceeded unless other criteria state otherwise. Further, no more than four excursions per day are acceptable. At least 60 minutes must elapse between exposure periods, and the time-weighted average (TWA) should not be exceeded.

As a group, the chlorinated hydrocarbons exhibit similar consequences of overexposure. Among these are systemic effects to the liver and kidney from chronic overexposure and central nervous system depression from acute overexposure. Due to this similarity and the likelihood that potential exposures will occur to more than one of the chlorinated hydrocarbons during the work day, it is necessary to give primary consideration to the combined, rather than individual, effect of the compounds when evaluating the monitoring results. The additive effect of different compounds is accounted for by calculating the sum of the ratios of observed exposure concentration to the exposure guide for each compound. If this sum exceeds unity then the combined exposure is in excess of acceptable limits. An example calculation is given in Table 6.

In addition to personnel sampling, grab sampling with gas tight syringes should be performed to evaluate potential peak exposures. This sampling should be job task oriented involving those routine tasks that result in a high potential for exposure. These include process sampling, connecting and disconnecting loading lines, breaking into process equipment, tank gauging, and any open transfers of materials. The results of this monitoring will be evaluated relative to the STEL's given in Table 5.

Employees shall be informed of the results of all monitoring and the significance of the data. All informing of employees on exposure data is to be documented.

RECOMMENDED MINIMUM MONITORING REQUIREMENTS

As stated earlier, monitoring is warranted for those agents indicated by the hazard rating on the industrial hygiene inventory sheets as described in Table 2. The industrial hygiene inventories have been reviewed and the recommended monitoring requirements are outlined below. Given in the outline are the job classifications and chemicals for which monitoring should be done. The outline is broken down into specific operations and service areas although some job classification might overlap.

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VINYLDENE CHLORIDE PRODUCTION

Chemicals

Job Classifications

Vinyl Chloride
Vinylidene Chloride
1,1,2-Trichloroethane
Syn-Tetrachloroethane
Unsym-Tetrachloroethane

Engineer
Shift Foreman
Control A Operator
Control C Operator

ETHYL CHLORIDE PRODUCTION

Vinyl Chloride
Ethyl Chloride
1,1-Dichloroethane
Ethylene Dichloride

Engineer
Shift Foreman
Control A Operator

BETA-TRICHLOROETHANE PRODUCTION

Ethylene Dichloride
Vinyl Chloride
1,1,2-Trichloroethane
Sym-Tetrachloroethane
Unsym-Tetrachloroethane
Pentachloroethane
Hexachloroethane

Engineer
Shift Foreman
Control A Operator
Control C Operator

ALPHA-DICHLOROETHANE PRODUCTION

Vinyl Chloride
Ethylene Dichloride
Sym-Tetrachloroethane
Unsym-Tetrachloroethane
Pentachloroethane
Hexachloroethane

Engineer
Shift Foreman
Control A Operator
Control B Operator

ALPHA-TRICHLOROETHANE PRODUCTION

1,1-Dichloroethane
1,1,1-Trichloroethane
Sym-Tetrachloroethane
Unsym-Tetrachloroethane
Pentachloroethane
Hexachloroethane

Production Foreman
Control A Operator
Control C Operator

THROX

Vinyl Chloride

Shift Foreman
Control C Operator

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ETHYLENE DICHLORIDE PRODUCTION

Chemicals

Ethylene Dichloride
1,1,2-Trichloroethane
Sym-Tetrachloroethane
Unsym-Tetrachloroethane

CC Classifications

Shift Foreman
Control A Operator
Control C Operator

CEP MAINTENANCE

Ethylene Dichloride
1,1-Dichloroethane
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Vinyl Chloride
Vinylidene Chloride
Ethyl Chloride
Sym-Tetrachloroethane
Unsym-Tetrachloroethane
Pentachloroethane
Hexachloroethane

Electricians
Machinists
Pipefitters

CEP UNIT SERVICES

Vinyl Chloride
Vinylidene Chloride
1,1,2-Trichloroethane
Ethylene Dichloride
Sym-Tetrachloroethane
Unsym-Tetrachloroethane
Ethyl Chloride
Perchloroethylene

Asst. Production Supt.
Loading Supervisor
Control B Operator

CEP LAB

Vinyl Chloride
Vinylidene Chloride
1,1-Dichloroethane
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Ethylene Dichloride
Sym-Tetrachloroethane
Unsym-Tetrachloroethane
Ethyl Chloride

Production Chemist
Chemical Technologist
Chemical Technicians

Sr. Asst. Chemist Class B

PLR/bbs

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TABLE 1

DEGREE OF EXPOSURE

1. No contact----- Sources of exposure are isolated from the work area.
2. Minor contact----- Work performed in areas where the material is handled or processed in closed systems. Exposures are passive in nature, not direct result of work activities.
3. Occasional/daily contact-- Some work tasks result in direct contact with the material. Examples are: process sampling, breaking into process equipment, manually gauging tanks, loading and unloading tank trucks.
4. Gross contact likely---- Prolonged amount of time spent in an area of high concentration or performing tasks resulting in large exposures.

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TABLE 2
INDUSTRIAL HYGIENE HAZARD RATING

The rating indicates the necessary industrial hygiene actions to be taken for each chemical

<u>HAZARD RATING</u>	<u>ACTION REQUIRED</u>
1	More frequent than annual monitoring (usually defined by law, e.g. vinyl chloride). Include in annual education program.
2	Annual monitoring is required as a minimum. Include in annual education program.
3	Some monitoring may be required. Include in annual education program.
4	No monitoring necessary, but should be included in annual education program.
5	No action required.

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Not to be Produced Pursuant

to E.O. 12327

Exemption

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TABLE 3

COMPOUNDS AND PHYSICAL AGENTS REQUIRING MONITORING

<u>COMPOUND OR PHYSICAL AGENT</u>	<u>MONITORING METHOD</u>
Vinyl Chloride	1,2,5
Ethyl Chloride	1,2,5
Methylene Chloride	1,2
Vinylidene Chloride	1,2,5
1,1-Dichloroethane (Alpha-di)	1,2,5
1,2-Dichloroethane (EDC)	1,2,5
1,1,1-Trichloroethane (Alpha-tri)	1,2,5
1,1,2-Trichloroethane (Beta-tri)	1,2,5
Perchloroethylene (Perchlor)	1,2
1,1,1,2-Tetrachloroethane (Unsym-tet)	1,2
1,1,2,2-Tetrachloroethane (Sym-tet)	1,2
Pentachloroethane	1,2
Hexachloroethane	1,2
Hydrochloric Acid *	3
Chlorine *	3
Silica *	4
Asbestos *	4
Welding Fumes *	4

1. Charcoal tube
2. Gas tight syringe
3. Colorimetric indicating tube
4. Membrane filter
5. Continuous area monitor

* monitoring to be done as special plant circumstances dictate

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