INDUSTRIAL HYGIENE WALK-THROUGH SURVEY REPORT

of

DOW CHEMICAL U.S.A.
Texas Division
Freeport, Texas

SURVEY CONDUCTED BY:
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Industrial Hygiene Section
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Division of Surveillance, Hazard Evaluations and Field Studies
National Institute for Occupational Safety and Health
Centers for Disease Control
Cincinnati, Ohio

DISCLAIMER

Mention of company or product name in this report does not constitute endorsement by NIOSH.

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PURPOSE OF SURVEY:	To perform a walk-through industrial hygiene survey of a 1,3-butadiene monomer producing plant and determine the suitability for inclusion in an in-depth survey regarding this substance.
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STANDARD INDUSTRIAL CLASSIFICATION OF PLANT:	2869 (Industrial Organic Chemicals, not elsewhere classified)

ABSTRACT

A walk-through survey was conducted at the Texas Division of Dow Chemical U.S.A. in Freeport, Texas, on June 20, 1984. The purpose of the survey was to obtain information on the 1,3-butadiene monomer manufacturing process and the potential for occupational exposure to this chemical.

The plant, which opened in 1941, began producing 1,3-butadiene monomer in 1951. The ethylene coproduct process is used for the production of 1,3-butadiene. A fraction of the 1,3-butadiene produced is used at the plant for styrene-butadiene latex production.

The company has conducted extensive sampling for 1,3-butadiene over the last four years. Recent monitoring data for three different job categories show a mean 8-hour time-weighted average (TWA) of 3.5 ppm.

The company maintains accurate personnel records on all current and past employees.

INTRODUCTION

Inhalation exposure of rats and mice to 1,3-butadiene induced a carcinogenic response at multiple sites. Mammary fibroadenomas/carcinomas, uterine sarcomas, Leydig cell adenomas of the testes, thyroid follicular cell adenomas, exocrine tumors of the pancreas, and Zymbal gland carcinomas were identified in rats exposed at concentrations of 1,000 or 8,000 ppm of 1,3-butadiene. Mice exposed to 625 or 1,250 ppm of 1,3-butadiene developed a high incidence of malignant lymphomas; an increased incidence of other tumors, including hemangiosarcoma; and testicular and ovarian atrophy.[1,2]

The offspring of pregnant rats exposed to 1,3-butadiene at 8,000 ppm had major defects. In addition, fetal toxicity was observed when pregnant dams were exposed at 200 ppm, 1,000 ppm, and 8,000 ppm.[3]

Epidemiological studies of workers employed in facilities producing styrene-butadiene rubber indicated an increased, but not statistically significant, risk of mortality from neoplasms of the lymphatic and hematopoietic tissues and from leukemia.[4,5]

Based on these data, the National Institute for Occupational Safety and Health (NIOSH) recommends that 1,3-butadiene be regarded as a potential occupational carcinogen and teratogen and as a possible reproductive hazard.[6]

Due to the number of workers potentially exposed to 1,3-butadiene and the resulting potential health risk, NIOSH researchers are conducting an extent-of-exposure study and evaluating the feasibility of an epidemiological/genotoxicity study.

EXPOSURE EVALUATION CRITERIA

The current legally allowable air concentration enforced by the Occupational Safety and Health Administration for 1,3-butadiene is 1000 ppm for an 8-hour TWA. The American Conference of Governmental Industrial Hygienists (ACGIH), has included 1,3-butadiene in their Notice of Intended Changes for the 1984-85 Threshold Limit Values, based upon reported animal carcinogenicity data. The Intended Change identified 1,3-butadiene as an A2 industrial substance suspected of carcinogenic potential for man. A numerical TLV of 10 ppm was proposed in connection with the notice.[7]

NIOSH in their Current Intelligence Bulletin recommends that 1,3-butadiene be regarded as a potential occupational carcinogen and teratogen and as a possible reproductive hazard.[6]

HISTORY AND DESCRIPTION OF THE PLANT

The Texas Division of Dow Chemical U.S.A. began operations in 1941. Today, the complex covers approximately 3000 acres and consists of 77 processing facilities producing about 700 finished chemicals. Products manufactured

include chlorine, caustic, light hydrocarbons (e.g., ethylene, propylene), and resins (e.g., epoxy, polyethylene).

1,3-butadiene production began in 1951 by the ethylene coproduct process; cuprous ammonium acetate extraction was used between 1951 and 1982. In 1965, the plant began the concurrent use of acetrontrile extraction; this is the process still used. The facility's total nameplate capacity for 1,3-butadiene is 85 million pounds per year.

The ethylene coproduct (C_4) feedstock for the 1,3-butadiene recovery unit is received via pipeline from two on-site ethylene plants. Annual 1,3-butadiene monomer production is a function of the C_4 stream production rates at the ethylene plants. Most of the monomer is shipped via rail tank cars to outside customers; a fraction is converted to styrene-butadiene latexes at the Texas facility.

PROCESS DESCRIPTION

Figure 1 is a flow diagram of the 1,3-butadiene production process. The crude C_4 feed to the process is a blend of C_4 streams from the two on-site ethylene plants, and contains 50 to 67 percent 1,3-butadiene. The C_4 feedstream is fed to a debutanizer from which a C_5 stream is removed. The C_4 cut goes through a series of wash towers which use caustic and water to purify the stream. After passing through a depropanizer, the C_4 stream is hydrogenated for removal of acetylenes and sent to a green oil tower for removal of an oil containing C_4 compounds. Acetonitrile (ACN) is used as the extraction solvent for further purification of 1,3-butadiene. The bottoms from the ACN tower is sent to a finishing tower which produces the final product containing 99 percent 1,3-butadiene, and a butadiene bottoms byproduct. Other byproducts include butylene and a green oil consisting of heavy organic compounds. Most of the 1,3-butadiene monomer product is loaded into a rail tank car and shipped to outside customers. The remainder is used on site for the production of styrene-butadiene latexes.

The process includes a number of on-line gas chromatographs (as shown in Figure 1) for quality control. In addition, manual samples are also taken of the feed, intermediates, and products to ensure quality. There is potential for worker exposure in the sampling and analytical activities.

DESCRIPTION OF THE WORKFORCE

As of June 1984, the Dow Texas Division had nearly 7000 employees. Research and development personnel are not included in this total.

In the 1,3-butadiene production area there are 8 operators and several supervisory personnel. The operators work an 8-hour shift with two operators on each shift.

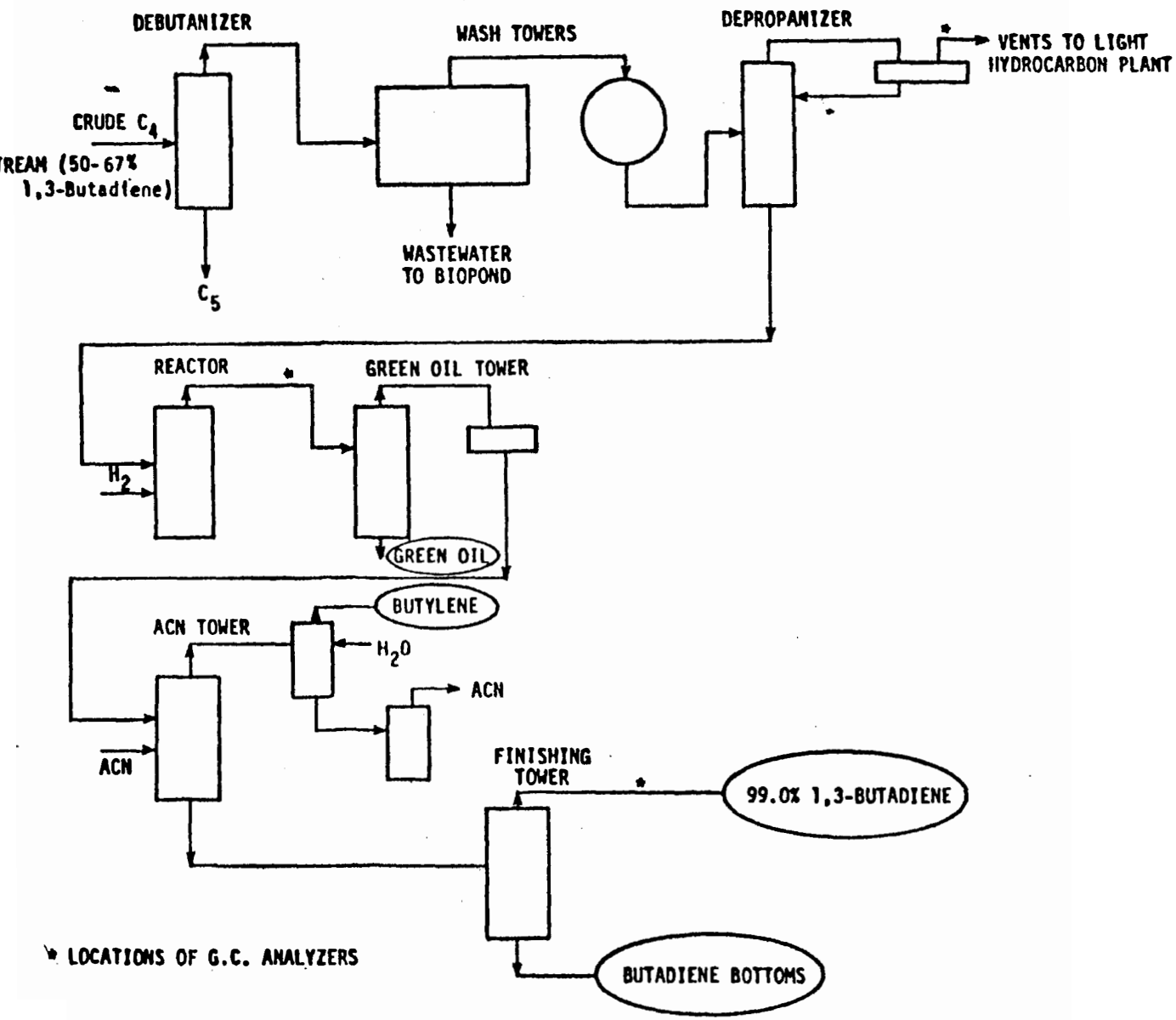

Figure 1. Flow diagram for production of 1,3-butadiene by ethylene coproduct process at Dow's Freeport, Texas Plant.

There are two employees associated with the loading and storage areas. One operator, either on the day shift or on the evening shift, is responsible for day-to-day operations. These operators spend 40 to 50 percent of their time loading 1,3-butadiene. Other compounds which they handle include butylenes, pentanes, isoprene and dicyclopentadiene.

The maintenance department for the combined butadiene, aromatics, and dienes production facility consists of 4 full-time Dow craftsmen (3 pipefitters and 1 machinist), 1 foreman, and 5 outside contractors (4 craftsmen and 1 insulator). These employees work an 8-hour day shift. Approximately, one-third of the maintenance personnel's time is allocated to maintenance activities in the 1,3-butadiene production area.

The job descriptions for the 1,3-butadiene production, handling, and loading activites are as follows:

Control A Operator - spends approximately 90 percent of his time inside the control room. Oversees control room activities and conducts periodic inplant supervision.

Control B/Control C Operator - spends 75 to 80 percent of his time outdoors. Duties include obtaining quality control samples, decontamination of process equipment, and switching product tanks (Control B classification has recently been eliminated).

Special Relief Operator (SRO) - fills in for Control A, Control B and Control C operators as and when required.

Lab Technician - analyzes quality control samples and voids sample bombs following completion of analyses.

Control C Loading Operator - loads rail tank cars.

The Control B/Control C and Control C Loading Operators have the highest potential for exposure to 1,3-butadiene. The number of operators in each job category is presented below:

JOB TITLE	NUMBER
Control A	4
Control C	3
SRO	1
Lab Technician	2
Control C-Loading Operator	2

The employees are represented by two separate unions.

DESCRIPTION OF PAST POTENTIAL WORKER EXPOSURES

During the 33 years of 1,3-butadiene production, the Freeport, Texas complex has used the ethylene coproduct process.

Dow industrial hygiene data on 1,3-butadiene is available from two sampling surveys. The first major sampling survey was conducted by Dow in 1981, and the second survey (which was ongoing at the time of the NIOSH survey) was initiated in 1984. Other chemicals that have been sampled in the 1,3-butadiene area include benzene and dicyclopentadiene. Tables 1 and 2 present the 1,3-butadiene monitoring data for 1981 and 1984, respectively. The mean 8-hour TWA's for all job categories are below 10 ppm for both the 1981 and 1984 data. Mean 8-hour TWA exposures above 5 ppm are observed for the Control B operator in the 1981 survey and for the Control C-Loading Operator in the 1984 survey.

The sampling method for the Dow surveys consisted of collection in 1 gram charcoal tubes at a flow rate of 90 cc/min; the analytical procedure comprised desorption with carbon disulfide and analysis by flame ionization gas chromatography.

Prior to 1981, the method used for obtaining quality control samples was the old method of attaching a sample bomb to the process release valve using a screw type fitting, and releasing the 1,3-butadiene through the bomb to the atmosphere. Since 1981, a closed-loop sampling system has been implemented which circulates the 1,3-butadiene from the process through the bomb and back to the process. Thus, the potential for worker exposure during sampling is greatly reduced. Exposures to the lab technician are very low (see Table 1). This is attributed to good ventilation design and prudent work practices. Dilution ventilation in the laboratory is accomplished at the rate of 12 air changes per hour. The laboratory is also equipped with 3 Class A hoods with minimum face velocities of 150 linear feet per minute. When performing analysis for 1,3-butadiene, the sample bomb is screwed directly on to the gas chromatograph (GC); for wet tests, a small volume of the sample is released from the bomb into a beaker under one of the laboratory hoods. Five to ten samples per day are subjected to GC analysis; wet tests are performed daily on two to three samples. Compounds analyzed for in the wet tests include inhibitor (tertiary butyl catechol), nonvolatiles and 1,3-butadiene peroxide. Following analysis, the bombs are voided by the lab technician by purging to a flare.

Monitoring of the rail tank car loading process is performed with magnetic gauges. The magnetic gauge is a completely sealed metering system which prevents the release of 1,3-butadiene from the tank cars and hence eliminates the potential for worker exposure. Loading of a car takes approximately 2 to 3 hours. Quality control samples are taken from each car on the load line.

The Control C operator is responsible for decontamination of pumps and process equipment, while maintenance personnel perform the actual repair operations.

Engineering Controls

Dual mechanical (tandem) seals are used on all pumps in the 1,3-butadiene production process. These seals provide additional protection during leakage by releasing the seal liquid to the atmosphere first before allowing the release of 1,3-butadiene.

DESCRIPTION OF THE MEDICAL, SAFETY AND INDUSTRIAL HYGIENE PROGRAMS

Medical Program

The company conducts pre-employment physicals on all its employees. Dow offers a physical examination on a two year basis and encourages participation by all employees. Employees involved in loading 1,3-butadiene are part of a benzene surveillance program because they also handle material from an adjacent aromatics plant; a complete blood count is done on a biannual basis.

Dow has 5 full-time physicians at the Freeport, Texas plant. The plant also employs 12 full-time and 3 part-time licensed nurses. The full complement of doctors and nurses work during the day shift. During the remaining shifts, one nurse is present and a physician is on call. All employees are trained in first aid.

Safety Program

The company has an organized safety program. The safety department at the Texas Division has a full-time safety director and 72 full-time safety personnel. The safety department is responsible for conducting safety audits, collecting data and developing safety programs for the plant. A safety committee consisting of 22 people meets every other week to formulate policies and training activities. This committee also meets weekly to discuss reported accidents or problems. The safety committee is designed to respond to the specific needs of the plant's employees. The safety department has made an application to the Occupational Safety and Health Administration (OSHA) for the STAR program.

The personal protective equipment required by the company includes: fire-retardant clothing, safety glasses with side shields, hard hats, and R722-type respirators for protection from the neighboring chlorine and amines manufacturing facilities. Showers and change areas are available but are not reported to be in frequent use. Smoking is not permitted in the production area because of the explosion hazard of 1,3-butadiene.

Industrial Hygiene Program

The company has a staff of 8 industrial hygienists who are responsible for the various plants in the Texas Division. The industrial hygiene program, which has been in place for about 10 years, is implemented via a line management responsibility philosophy. The main elements of the industrial hygiene program are as follows:

1) The industrial hygiene inventory is updated and reviewed on an annual basis. An assessment is made of how each chemical and physical stress is encountered by all plant personnel.

2) Degree of exposure is given an ordinal ranking of 1 to 4.

3) An educational program and a surveillance monitoring program are implemented; inclusion in a program is based on the hazard indices for a particular chemical and job classification.

Industrial Hygiene sampling was conducted for 1,3-butadiene, benzene and dicyclopentadiene in 1981-82. This included short term and 8-hour time-weighted average (TWA) personal and area samples. A second sampling study for 1,3-butadiene was initiated in 1984. This study was still in progress at the time of the survey, and only a limited amount of data was available (see Tables I and II).

DESCRIPTION OF PERSONNEL RECORD SYSTEM

Dow Chemical U.S.A. maintains personnel records on terminated as well as current employees. Since 1941, 48,000 people have worked at the plant. The personnel records are maintained on standard forms for each employee, and provide the following information:

1. Name
2. Social Security Number
3. Date of birth
4. Date of employment
5. Date of termination or retirement
6. Work history - department and job classification

A new entry is made in the personnel file every time the wage or the job classification of an employee changes. There is considerable mobility of employees between different plants in the company.

The medical department keeps death certificates on deceased employees, based on information received from the benefits department. This practice was initiated in the 1970's. The personnel records system at the plant is being improved via development of a vital status registry.

CONCLUSIONS

Dow Chemical U.S.A. manufactures 1,3-butadiene by the ethylene coproduct process, using acetonitrile as the solvent for extractive distillation. The production occurs in a closed system, tightly maintained for both economic and safety reasons.

The company has conducted industrial hygiene sampling for 1,3-butadiene in 1981 and 1984. Mean TWA exposures to 1,3-butadiene for all job categories are below 10 ppm.

Dow employs a number of controls to reduce worker exposure during various activities. Quality control samples are collected using a closed-loop sampling system, the laboratory is equipped with local exhaust ventilation systems, monitoring of the rail tank car loading is accomplished via sealed magnetic gauges, and tandem seals are used for prevention of leaks from pumps.

RECOMMENDATIONS

On the basis of information gathered and observations made during this walk-through survey, no recommendations were considered necessary at this time.

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TABLE 1

SUMMARY OF DOW'S MONITORING RESULTS FOR 1,3-BUTADIENE, 1981

JOB TITLE	DATE	SHIFT	8-hour TWA* (ppm)	Range of peak exposures**(ppm)
Control A Operator	5/7/81	Day	3.07	1.6 - 542
	5/18/81	Graveyard	14.63	4.4 - 199
	6/18/81	Day	2.18	0.40 - 66
	7/20/81	Graveyard	2.53	--
	8/16/81	Graveyard	5.05	1.7 - 749
		Average	4.17***	
Control B Operator	5/7/81	Day	1.50	0.21 - 10.2
	5/18/81	Graveyard	8.77	0.17 - 204
	6/18/81	Day	4.90	0.50 - 568
	7/20/81	Graveyard	7.37	--
	8/16/81	Graveyard	11.77	3.3 - 1176.0
		Average	5.21	
Control C Operator	5/7/81	Day	0.97	--
	5/18/81	Graveyard	8.23	--
	6/18/81	Day	6.84	9.75 - 12.75
	7/20/81	Graveyard	3.34	--
	8/16/81	Graveyard	4.34	4.6 - 75.2
		Average	4.32	
Control C-Loading Operator	5/7/81	Day	0.50	--
	5/18/81	Graveyard	3.28	--
	6/18/81	Day	0.51	0.56
	7/20/81	Graveyard	4.62	1.26 - 9240
	8/16/81	Graveyard	0.45	--
		Average	1.24	
Lab Technician	5/7/81	Day	0.19	0.17 - 8.20
	5/18/81	Day	0.58	0.21 - 15.8
		Average	0.39	

* Time-weighted average

** Based on samples of less than one minute duration

*** The average 8-hour TWA exposure was calculated as follows:

Day (and Evening)		Graveyard	
5/7/81	3.07	5/18/81	14.63
6/18/81	2.18	7/20/81	2.53
		8/16/81	5.05

Therefore:

Day & Evening average 2.62 (represents 2/3 day)

Graveyard average 7.40 (represents 1/3 day)

Average 8-TWA = (0.33)(7.40)+(.67)(2.62)=4.17

A similar calculation technique was used for averages of the Control B,C, and C-Loading Operators.

TABLE 2

SUMMARY OF DOW'S MONITORING RESULTS FOR 1,3-BUTADIENE, 1984

JOB TITLE	DATE	SHIFT	8-hour TWA* (ppm)	Range of peak exposures**(ppm)
Control A Operator	5/10/84	Day	1.0	--
	6/07/84		2.1	--
	5/16/84	Graveyard	0.2	--
			Average***1.1	
Control C Operator	5/10/84	Day	6.2	0.9 - 963.3
	6/07/84		2.4	126.5 - 133
	5/16/84	Graveyard	1.0	0.9 - 469
			Average 3.2	
Control C-Loading Operator	6/7/84	Day	6.2	2.8 - 334.7

* Time-weighted average
** Based on samples of less than one minute duration

*** The average 8-hour TWA exposure was calculated as follows:

	Day (and Evening)		Graveyard
5/10/84	1.0	5/16/84	0.2
6/07/84	2.1		

Therefore:
Day & Evening average 1.55 (represents 2/3 day)
Graveyard average 0.2 (represents 1/3 day)
Average 8-TWA = (0.67)(1.55)+(0.33)(0.2)=1.10
A similar calculation technique was used for the average of the Control C operator.