INDUSTRIAL HYGIENE WALK-THROUGH SURVEY REPORT

of

Shell Chemical Company
Deer Park Manufacturing Complex
Deer Park, Texas

SURVEY CONDUCTED BY:
John M. Fajen

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Industrial Hygiene Section
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National Institute for Occupational Safety and Health
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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 walkthrough industrial hygiene survey of a 1,3-butadiene monomer producing plant and determine the suitability for inclusion in an in-depth exposure survey regarding this substance.
EMPLOYER REPRESENTATIVES CONTACTED:	Howard Kusnetz, Manager, Safety and Industrial Hygiene
	Sally Cowles, M.D., DPh, Medical Director, Epidemiology
	Phil Snyder, Senior Industrial Hygienist, DPMC
	Carolyn Phillips, Manager, Industrial Hygiene Services
	Donald Morman, Director, Industrial Hygiene Laboratory, Shell Development
	George Roe, Process Manager, BD/HT/IP, DPMC
	Jack Szymanowski, Manager, Health and Safety, Manufacturing and Technical
	John Rivard, Manager, Regulation and Safety Services
	Carl Russell, Industrial Hygiene Supervisor, DPMC
	Barry Kern, M.D., Medical Director, DPMC
EMPLOYEE REPRESENTATIVES CONTACTED:	Al Barnes, Deer Park Manufacturing Complex - Refinery, OCAW Local 4-367
	John Patterson, Deer Park Manufacturing Complex - Chemical, OCAW Local 4-367
STANDARD INDUSTRIAL CLASSIFICATION OF PLANT:	2869 (Industrial Organic Chemicals, not elsewhere classified)

ABSTRACT

A walkthrough survey was conducted at the Deer Park Manufacturing Complex in Deer Park, Texas on May 10, 1984. A preliminary survey meeting was held at the Shell Oil Company head office in Houston, Texas, on May 9, 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 world's first commercial-size 1,3-butadiene plant was built at Shell's Deer Park facility in 1942. Industrial hygiene information is available on 1,3-butadiene exposures. The geometric mean of the time-weighted average exposures for all job categories is 4.6 ppm for the period 1979 - 1983, based on Shell data. Accurate personnel records are maintained on all 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 skeletal 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 of the 1,3-butadiene producing industry.

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

Shell's Deer Park Manufacturing Complex (DPMC) is a refinery/chemical complex. The chemical plant was built in 1941. Shortly after this date, Shell built the world's first commercial size 1,3-butadiene plant. Two new extractive distillation units were built in 1978 and 1981. An older unit,

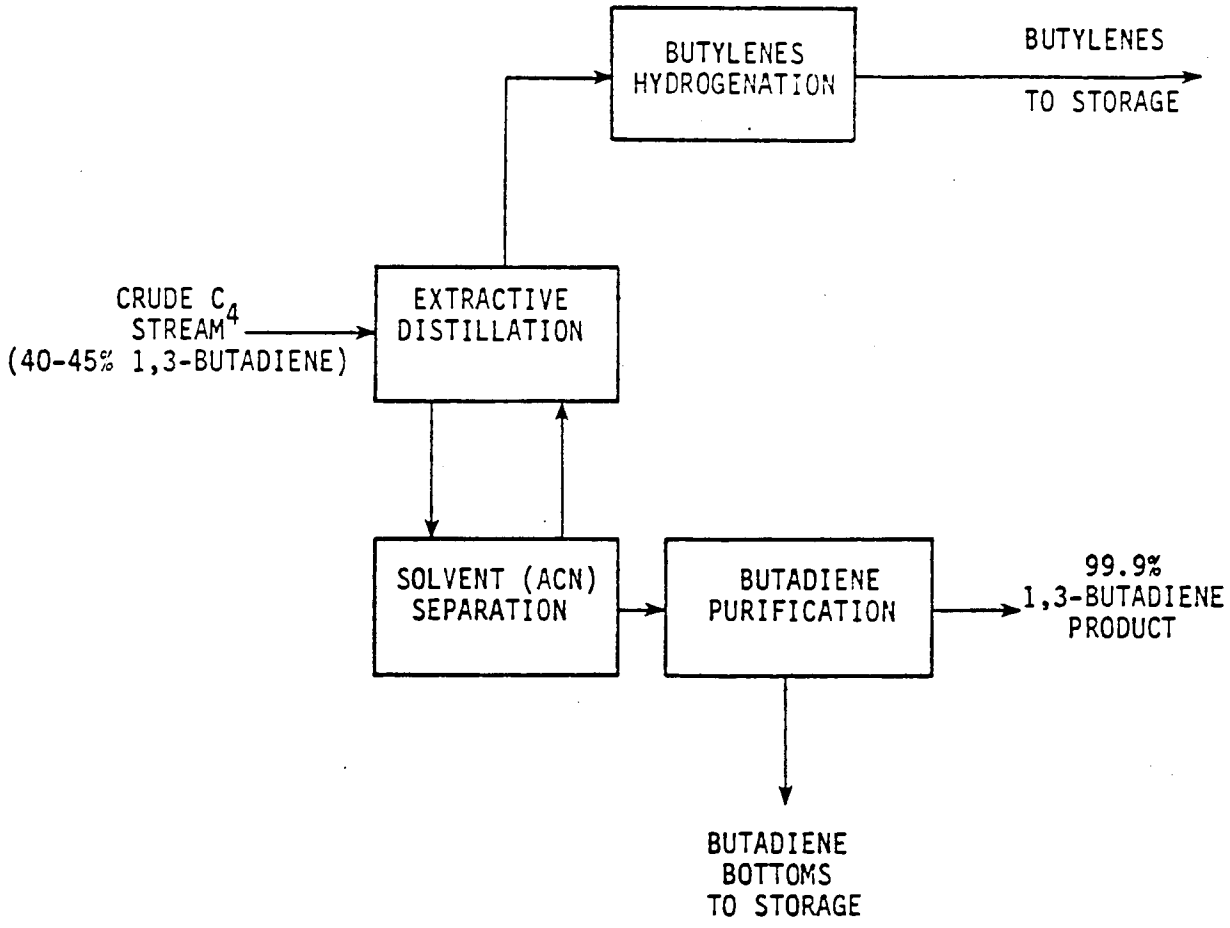

Figure 1. Block diagram for production of 1,3-butadiene monomer by ethylene coproduct process at Shell's Deer Park, Texas plant.

built in 1969, was mothballed in 1981. All 1,3-butadiene is produced as an ethylene coproduct. Shell currently uses acetonitrile as the extraction solvent.

Shell's total nameplate capacity for 1,3-butadiene is 780 million pounds per year. Over the 43-year history of the plant, it has expanded in size and product line. Currently, DPMC is the company's largest manufacturing location. The complex, which also includes the refinery, covers approximately 1500 acres. A variety of chemical, gasoline and petroleum products are produced at the facility.

Shell has the capability to ship 1,3-butadiene by rail car, tank truck, pipeline, marine vessel, or barge. To a limited extent, the marine movement is used for finished 1,3-butadiene as well as the receipt of crude butadiene. The Deer Park Complex does not consume the monomer.

PROCESS DESCRIPTION

Figure 1 is a block diagram of the 1,3-butadiene monomer production process. The crude ethylene coproduct C_4 feed to the process is produced in the Olefins area of the plant. The crude contains 40 to 45 percent 1,3-butadiene. The C_4 feedstock is fed to the extractive distillation unit where butylenes are removed. Acetonitrile (ACN) is used as the solvent for extraction of 1,3-butadiene. The extract from the ACN tower (containing 1,3-butadiene) is sent to a finishing tower which produces the final product containing 99.9 percent 1,3-butadiene and a butadiene bottoms byproduct. The finished product is pumped to one of three storage spheres prior to shipment by rail car, tank truck, pipeline, or marine vessel. This facility does not consume any of the 1,3-butadiene monomer on site. The process includes on-line gas chromatographs for quality control determinations. In addition, manual bomb samples are taken in a closed-loop system, with bomb contents recycled to the process and cleaned using a nitrogen purge.

DESCRIPTION OF THE WORKFORCE

As of May 1984, the Deer Park Manufacturing Complex employed a total of 3200 employees.

In the 1,3-butadiene production area, the department is divided into two areas of responsibilities: the BDIII-100 area and the BDIII-200/300/400 area. The department operates three 8-hour rotating shifts with six production employees on each shift. In the administrative area, there are four employees on the first shift and one supervisor on each of the second and third shifts for a total of 24 employees (not including maintenance personnel associated with the production of 1,3-butadiene).

The maintenance department in the Olefins unit is also responsible for the 1,3-butadiene unit. The maintenance department has 30 employees with approximately 4 to 6 employees assigned on the day shift to the 1,3-butadiene.

The production workforce is divided into two major job categories: the BDIII-100 operator and BDIII-200/300/400 operator. The job descriptions for these two operators are as follows:

BDIII-100 Operator	Operates feed preparation, extractive distillation, heavy ends removal sections, dropout and solvent sewer system, and degassing drum in BDIII unit. Assists the BDIII-200/300/400 operator (1 day/month). Cleans acetonitrile (ACN) pump suction screens (once/year). Prepares the sodium nitrite batch solutions (once/week). Collects routine quality control samples (ACN - 1/shift, BD-1/shift, nitrite solution - 1/shift). Unloads drums. 20 percent of time is spent in the unit. This is a 3-shift/day, 7 day/week position. Chemicals potentially exposed to are 1,3-butadiene, acetonitrile, sodium nitrite, and diethylhydroxylamine.
BDIII-200/300/400 Operator	Operates 1,3-butadiene finishing, acetonitrile recovery, and hydrogenation sections; nitrite/sulfite loop, oil mist generation, and distribution systems; and the steam generation/condensate recovery system in BDIII. Assists BDIII operator (once/month). Prepares sodium nitrite - cobalt catalyst and sodium sulfite batches. Collects routine quality control stream samples (ACN/water, 2 or 3/day and ACN/DB, 2/shift and 1/month). Operates caustic injection facility for pH control. Responsible for the tank farm. 20 percent of time is spent in the unit. This is a 3-shift/day, 7-day/week position. Chemicals potentially exposed to are 1,3-butadiene, butylene, sodium sulfite, acetonitrile, caustic soda, and sodium nitrite.

The administrative department is comprised of an operations supervisor, inspector, process chemist, and a technical supervisor. These people are generally not exposed to 1,3-butadiene. The number of workers in various job classifications is presented below:

JOB TITLE	NUMBER
Production	18
Administrative	7
Department Manager	1
Operations Supervisor	3
Process Chemist	1
Inspector	1
Technical Supervisor	1

DESCRIPTION OF PAST POTENTIAL WORKER EXPOSURES

During the 42 years of 1,3-butadiene production at DPMC, the process has been modified and a new unit built. The process evolved from the world's first commercial 1,3-butadiene plant in 1942 to the current extractive distillation process in the Olefins unit which uses acetonitrile as the extraction solvent.

There are two 1,3-butadiene recovery units at Deer Park. Unit I was constructed in 1969 and is presently mothballed. Unit II has been on line since 1978.

Table 1 presents Shell's monitoring data collected at three facilities during 1979-1983 on job categories with the highest potential for exposure to 1,3-butadiene. The facilities include Shell's 1,3-butadiene manufacturing plants in Deer Park, Texas, and Norco, Louisiana, and a 1,3-butadiene monomer-using location in Marietta, Ohio. More than 90 samples are represented in the table. The number of samples taken at each plant is not reported.

As seen from Table 1, exposure data for jobs with the highest exposure potential are well below the existing Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) of 1000 ppm. 1,3-butadiene process and laboratory technicians, who comprise the majority of the potentially exposed employees, have 8-hour TWAs below 6 ppm. For employees involved in tank car and tank truck operations, highest exposures range from 55 to 142 ppm, but with a substantially lower geometric mean of 4.3 to 8.3 ppm. Shell has identified approximately 60 employees at the Deer Park plant that have some potential for exposure to 1,3-butadiene.

In the area of hydrotreating there is potential for exposure to benzene.

Shell has a complete chemical inventory for the entire complex which lists approximately 2500 different chemicals. This list encompasses purchased

chemicals and products used throughout the complex, products sold by Shell Chemical and Shell Oil at Deer Park, and intermediates which are neither bought nor sold.

Steps have been taken by Shell to minimize the potential for occupational exposure to 1,3-butadiene by a combination of work practices and engineering controls. These steps are as follows:

1. Production occurs in a "closed system", designed and maintained to prevent emissions. The quality control samples are taken using a "bomb" in a closed-loop system. The bombs use snap lock connectors. The purged fluid from the bombs is recycled to the process at a point of lower pressure.

2. Collection systems are employed to capture any continuous emission of 1,3-butadiene resulting from production or loading operations. These collection systems route the material to recovery or to a flare.

3. The workforce is trained in the concept and practices of controlling workplace emissions.

4. Standard equipment decontamintion procedures are used which include washing with water or steam, and at times, nitrogen purging.

These controls are supplemented by an industrial hygiene monitoring program, with the results provided to the employees.

The decontamination procedures utilized at this plant result in the maintenance worker having a very low potential for exposure to 1,3-butadiene. The procedure for decontamination consists of the following steps:

1. Decontamination prior to any maintenance.
2. Padlocking "lockout" procedure to prevent decontamination from being performed on a live pump.
3. Nitrogen purging and steam cleaning.
4. Recycling of 1,3-butadiene to process and/or flare.
5. Tagging of equipment to identify decontaminated equipment.

DESCRIPTION OF MEDICAL, SAFETY AND INDUSTRIAL HYGIENE PROGRAMS

Medical Program

The company conducts pre-employment physicals on all its employees. Periodic physicals are voluntary and age dependent. The periodic physical is very comprehensive and records the department and job title of the employee. The pre-employment physical involves a detailed medical and smoking history as well as an exam.

Shell has 2 full-time physicians at DPMC. The plant also has 8 full-time nurses employed on the day shift. The remaining shifts have employees trained in first-aid.

The employees in the 1,3-butadiene department, who may also have potential exposure to benzene, are enrolled in the plant's benzene surveillance program.

Safety Program

The company has an organized safety program. The medical, industrial hygiene, and safety programs are all closely allied into an organized responsible program. The health and safety department at DPMC employs approximately 30 people. There is a safety supervisor who report to the manager of safety and industrial hygiene.

The personal protective equipment utilized at the complex is an additional factor in limiting exposure. Personal protection requirements are divided into job categories as follows:

I. Decontamination:

Rubber gloves (neoprene)
Air-supplied respirators
Rubber suits
Hard hats
Safety glasses/goggles
Covered shoes

II. All Others:

Gloves (if necessary)
Hard hats
Safety glasses/goggles
Covered shoes/pants

Showers and change areas are available but are reported not to be frequently used. All workers provide their own work clothes which are commonly worn home. Smoking is not permitted in the immediate production area because of the explosion hazard of 1,3-butadiene.

Specific work practices have been developed for each job or operation. The safety personnel oversee the safe work authorization program which involves safe work permits and hot work permits.

Industrial Hygiene Program

There are 30 health and safety employees at the Deer Park facility. The formal industrial hygiene program at the Shell facility began in 1974. This program is well organized and closely coordinates its activities and programs with the medical and safety departments.

Shell has its own corporate industrial hygiene laboratory, located at a central research facility and is accredited by the American Industrial Hygiene Association. All of the DPMC industrial hygiene samples are analyzed at this facility.

A computerized job exposure profile has been developed for each job title at DPMC. The data collected provide a detailed description of the work activity and the potential for chemical and physical agent exposure. This information can be tied to exposure data and thus gives detailed exposure data based on each job. The program has been operational since 1980.

Shell has developed a sampling program for jobs where employees are potentially exposed to 1,3-butadiene. The jobs identified by Shell which have a potential for 1,3-butadiene exposures are butadiene unit operators, tank truck/rail car loading operators, laboratory technicians, marine transfer operators, maintenance craftsmen, and light olefins operators.

DESCRIPTION OF PERSONNEL RECORD SYSTEM

The Shell Chemical Company maintains records on terminated as well as current employees. The company feels that follow-up on process employees is possible from 1970 to the present. Names of employees working in areas of potential exposure to 1,3-butadiene can be derived from department seniority lists which are kept to comply as a requirement of the union contract. The lists are generated quarterly and are believed to be accurate and complete. The records are maintained by Shell and verified by the Union.

From the seniority list the following information can be obtained:

1. Name
2. Badge number
3. Beginning and ending dates of working in a specific department
4. Date of employment

The recordkeeping system at Shell has evolved over the years. In the early 1970's, a conveyor filing system contained the personnel records of all current employees plus those terminated in the previous year. An alphabetical file called the "dead file" has records of personnel terminated in the last 10 years. Name, Social Security number, date of birth, sex, race, place of residence, and name and address of next of kin are available from the records.

The job exposure profile, which began in 1980, is a computerized program which defines each job title. This data base can be used to relate the exposure to the job history.

Shell also has a "job preference program" as DPMC. This program promotes job mobility based on seniority. An employee can bid for job opening in any part of the chemical plant that he or she is qualified for.

CONCLUSIONS

Shell Chemical Company 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 between 1979 and 1983. Mean TWA exposures to 1,3-butadiene for exposed job categories do not exceed 10 ppm. For employees involved in tank car and tank truck operations, the highest TWA exposures range from 55 to 142 ppm, but with a substantially lower geometric mean of 4.3 to 8.3 ppm.

Quality control samples are collected using a closed-loop sampling system which greatly lowers the potential for worker exposure.

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 SHELL'S MONITORING DATA FOR
1,3-BUTADIENE AT THREE PLANTS

Type of Facility/Location	Job Title	8-hour TWA* Exposures, ppm Range	Geometric Mean
1,3-butadiene monomer-producing plant/Deer Park, Texas	Process Technician	1**-6	1.2
	Tank Truck Operator	1 -55	4.3
	Tank Car Operator	1-142	8.3
1,3-butadiene monomer-producing plant/Norco, Louisiana	Process Technician	1	-
	Product Handler	1-146	1.5
	Laboratory Technician	1	-
1,3-butadiene monomer-using plant/Marietta, Ohio	Process Technician	1	-
	Laboratory Technician	1	-

* Time-weighted average
** Limit of detection