INDUSTRIAL HYGIENE WALK-THROUGH SURVEY REPORT

of

Texas Petrochemicals Corporation
Houston, Texas
(formerly Petro Tex Chemical Corporation
Pasadena, Texas)

SURVEY CONDUCTED BY:
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Industrial Hygiene Section
Industrywide Studies Branch
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 names in this report does not constitute endorsement by NIOSH.

ACKNOWLEDGEMENTS

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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 walkthrough survey was conducted at the Texas Petrochemical Company in Pasadena, Texas on May 3, 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. It is important to note that the Texas Petrochemicals Company was reorganized on June 21, 1984. At the time of the survey the company operated under the name of Petro-Tex Chemical Corporation. Due to the reorganization much of the information on job descriptions have changed. The information in this walk-through survey is a compilation of the data collected on May 3, 1984.

The plant was built in 1943, and manufactured 1,3-butadiene by the Shell Process until 1965, although production was discontinued between World War II and the Korean War. The Houdry Process was added in 1957 and discontinued in 1977 due to high energy costs. The facility now manufactures butadiene using their own OXO-D process. It receives ethylene coproduct C_4 feed (40 to 60% 1,3-butadiene) from many major suppliers, and produces 1,3-butadiene of commercial quality.

The company has conducted personal monitoring of 1,3-butadiene between 1980 and 1983. The reported monitoring data for six different job categories showed a weighted (by number of samples) arithmetic mean time-weighted average (TWA) exposure of 7.8 ppm. The weighted geometric mean TWA for this data was 1.2 ppm.

The company maintains an index card file personnel record system on approximately 5,600 active and terminated employees. Presently, there are 12 employees/shift directly involved in 1,3-butadiene production.

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 have 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 workers potentially exposed to the 1,3-butadiene monomer.

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 Petro-Tex Chemical Company was owned and operated by Tenneco until June 21 1984. The company was purchased by Texas Olefins and renamed the Texas Petrochemicals Corporation. The plant was built and operated by the

U.S. Government from 1943-1955. Tenneco/FMC purchased the plant in 1955 and created Petro-Tex to operate the plant. Tenneco acquired FMC's 50% in 1978. 1,3-butadiene was manufactured by the Shell Process until 1965. The 1,3-butadiene process was discontinued between World War II and the Korean War. The Houdry Process was added in 1957 but discontinued in 1977 because of high energy costs. The company produces 1,3-butadiene feedstock by the OXO-D process and recovers 1,3-butadiene from crude ethylene coproduct C_4 streams obtained from many major suppliers. Approximately 700,000 lbs/day of 1,3-butadiene is produced. None of the 1,3-butadiene monomer is consumed at the plant. The monomer is shipped via pipeline, tank cars, barge, or trucks to outside customers for conversion to products such as neoprene and styrene-butadiene rubber.

The company also produces methyl tertiary butyl ether (MTBE) from the reaction of isobutylene (extracted from the C_4 streams) with methyl alcohol. Other byproducts include C_4 compounds such as isobutane, n-butane, isobutylene, and 1-butylene.

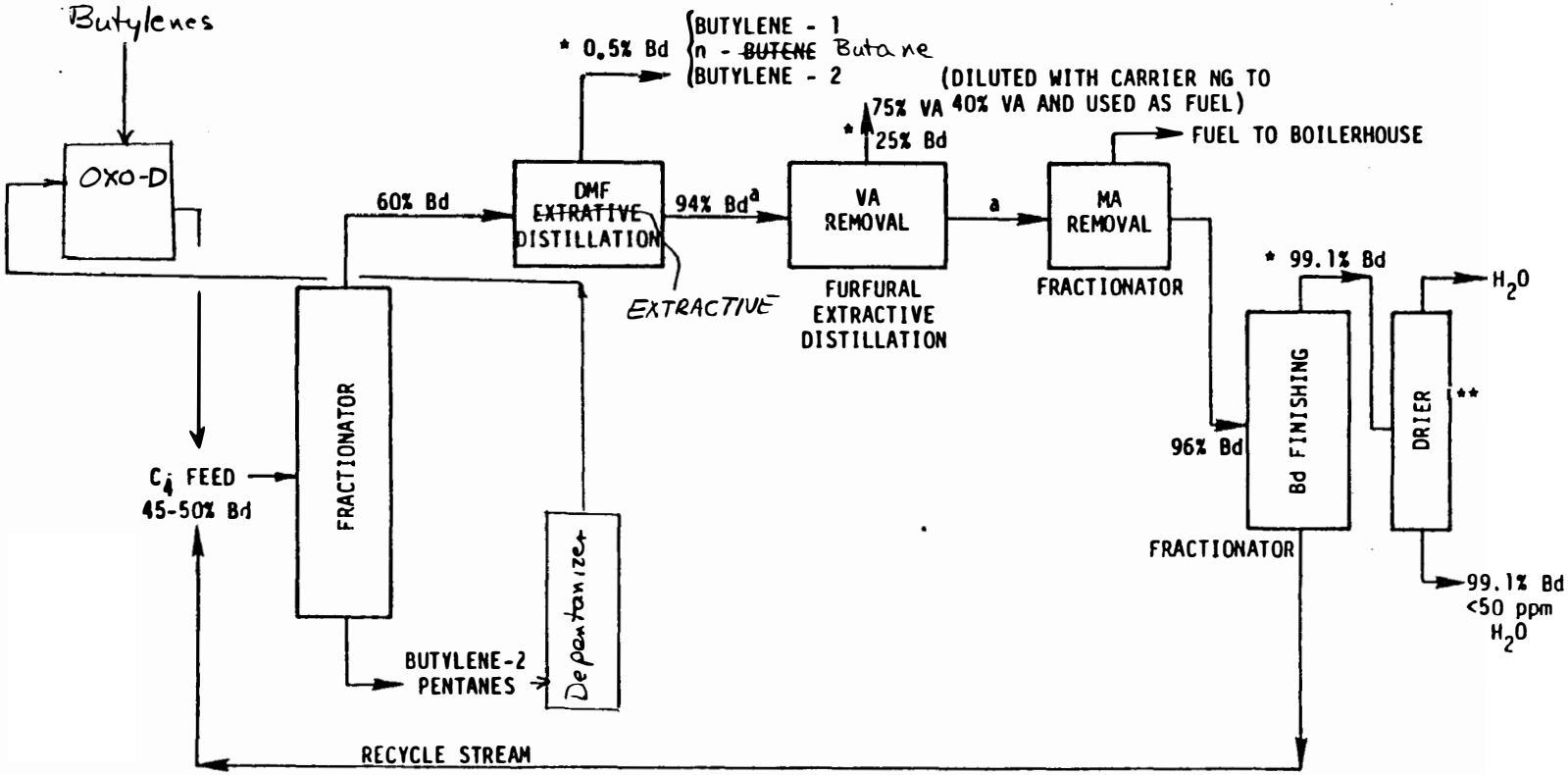
The plant covers approximately 200 acres. The process is monitored from 5 enclosed computerized control rooms. A large administration building which contains the cafeteria is located on the plant grounds. The company is located in Pasadena, Texas and is surrounded by other petrochemical manufacturing plants. The property abuts a facility that produces raw rubber and another facility that produces neoprene rubber.

The plant has ambient and refrigerated tanks for the storage of 1,3-butadiene monomer product. There are two ambient or pressure (35 to 40 psi) storage tanks each with a capacity of 6,000 barrels. 1,3-butadiene can be stored in these tanks on a short term basis only during the summer without degradation due to dimerization. In addition, there is one smaller pressurized tank of 2500 barrel capacity. The two refrigerated storage tanks each have a capacity of 50,000 barrels. Isobutane and n-butane are used as refrigerants. Tertiary butyl catechol (TBC) is used as an inhibitor in the refrigerated tanks.

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 OXO-D product and C_4 streams from off-site producers. The off-site feed is delivered via tank car, pipeline, and barge. The feedstocks range in composition from 20 to 70 percent 1,3-butadiene and are blended on-site to between 45 to 50 percent 1,3-butadiene.

The C_4 feed stream is fed to a fractionator where pentanes and some butylenes are removed as bottoms. The butylenes are depentanized and recycled as feed to the OXO-D unit. The enriched 1,3-butadiene stream from the fractionator, which contains approximately 60 percent 1,3-butadiene, is fed to extractive distillation towers which employ dimethyl formamide (DMF) as the solvent. Butylenes and n-butane are removed from the 1,3-butadiene



Bd - 1,3-BUTADIENE
DMF - DIMETHYL FORMAMIDE
VA - VINYL ACETYLENE
MA - METHYL ACETYLENE

* ON-LINE CHROMATOGRAPH LOCATION FOR QUALITY CONTROL

** ONLY REQUIRED WHEN 1,3-Bd IS TO BE CONVERTED TO NEOPRENE

[a] INTERMEDIATE STORAGE IN 12,000 bbl CAPACITY TANKS

Figure 1. Flow diagram showing process for recovery of 1,3-butadiene monomer from ethylene coproduct C_4 streams at Texas Petrochemical Facility, Pasadena, Texas

stream during extractive distillation; the isobutylene is subsequently converted to methyl tertiary butyl ether (MTBE), a gasoline blending stock. The product from the DMF extractive distillation towers (containing approximately 94 percent 1,3-butadiene) is fed to a vinyl acetylene (VA) removal unit and then to a methyl acetylene (MA) removal unit. Furfural is used as the extractive solvent for VA removal.

The product from the MA unit is sent to a finishing tower which produces the final product (commercial grade 1,3-butadiene) and a recycle stream which is returned to the initial C_4 feed stream.

There are on-line gas chromatographs for quality control. In addition, using open-loop sampling techniques, manual samples are also taken of the feed, intermediates, and products to ensure quality. Samples are taken using 150 cc stainless steel cylinder sampling containers.

DESCRIPTION OF THE WORKFORCE

As of May 1984, there were about 425 production and administrative employees at the plant. There are 9 employees in the 1,3-butadiene production area, and 6 employees in the shipping are a (tank trucks, rail cars, barge or pipeline) per shift. Three of the six workers in the shipping area are assigned to loading and unloading activities for the 1,3-butadiene operations. Therefore, 12 workers/shift are directly involved in 1,3-butadiene production. The average age of the employees is approximtely 50 years with average duration of employment at the plant being approximately 25 years. The average employment period in the 1,3-butadiene area is approximately 20 years. The workforce includes 6 women.

The employees at the time of the survey were represented by Local 4-277 of the Oil, Chemical and Atomic Workers (OCAW) Union.

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

Stillman	Most senior operating job. Takes written orders, oversees control rooms and does operating work as and when required. This job is accomplished by 3 employees per shift.
Assistant Stillman	Operates equipment. Responsible for housekeeping, control of process, and instrumentation in a specific area. Spends approximately four to eight hours outdoors for sampling, maintenance (decontamination), and quality control. This job is accomplished by 6 employees per shift.

Pumper	Monitors tank lines and pumps in tank farm areas. Logs the necessary information. Also takes quality control samples. This job is accomplished by 2 employees per shift.
Rackman	Responsible for hooking and unhooking tank trucks and tank cars which enter and leave the plant. This is an entry level job. This job is accomplished by 1 employee per shift.
Head Shift Tester	Analyzes quality control samples in the laboratory. This job is accomplished by 1 employee per shift.

DESCRIPTION OF PAST POTENTIAL WORKER EXPOSURES

Through the 41 years of 1,3-butadiene production at this facility, the production process has changed three times. These include the Shell Process (1943-1965); the Houdry Process (1957-1977); OXO-D (1965 to present) and the recovery of 1,3-butadiene from ethylene coproduct C_4 streams (1978-present). These changes have occurred as a result of changing economics.

Industrial hygiene personal sampling data are routinely collected for 1,3-butadiene, methanol, DMF, furfural, benzene, MTBE, and acrylonitrile. Area samples are taken for chlorinated compounds that are generated by the neighboring chemical company.

The company has collected personal 8-hour time-weighted average (TWA) samples for 1,3-butadiene during 1980-1983. Table 1 summarizes the results reported for several job categories.

The majority of the individual samples taken appear to be less than 10 ppm of 1,3-butadiene. The weighted (by number of samples) arithmetic mean TWA exposure for all job categories was calculated to be 7.8 ppm. The weighted geometric mean TWA exposure for this data was 1.16 ppm. The highest reported mean exposure is for the pumper; this appears to be due primarily to one very high measurement of 312.64 ppm. The company stated that there were interferences from n-butane in the NIOSH S91 method used for analyzing the samples.

The economics and fire hazards of the process require that the system be entirely closed (to the extent possible). However, there are several worker activities which could result in exposure to 1,3-butadiene. Quality control samples are manually taken at two locations in the process using open-loop sampling techniques. This could result in potential exposures to the assistant stillman or pumper collecting the samples. Major maintenance on the equipment occurs periodically when they are shut down for cleaning and

repairing. Maintenance workers in charge of these operations are potentially exposed to 1,3-butadiene. Tank truck and tank car rackmen are also potentially exposed during connection and disconnection of hoses to the trucks and rail cars.

Engineering Controls

Single mechanical seals are used on most pumps in the 1,3-butadiene production process. The more effective dual mechanical (tandem) seals are used on newer pumps in certain areas of the plant.

DESCRIPTION OF MEDICAL, SAFETY AND HYGIENE PROGRAMS

Medical Program

The company conducts pre-employment and annual physicals for all production workers. The plant has a physician on retainer who visits the plants every Tuesday for approximately one hour. All physicals are conducted off-site. Emergency medical care is available at a nearby hospital in Pasadena, Texas. A full-time registered nurse is on-site 5 days per week during the day shift. Selected employees are trained in first aid on every shift.

Safety Program

The company maintains an organized safety program. The company has a joint management/union safety committee that stresses the philosophy that safety is a line organization responsibilty. The company operates the Safety Training and Observation Program (STOP) developed by DuPont. Area and shop supervisors inspect the plant for approximtely 20 minutes twice per week to evaluate safety procedures associated with the work practices.

The only personal protective equipment required by the company are safety glasses, goggles, and hard hats. Additional protection such as respirators, gloves, and face shields are specified for particular areas or job tasks. Showers and clothing change areas are available but reportedly not in frequent use. All workers provide their own work clothing which is commonly worn home. Smoking is not permitted in the production area because of the explosion hazard of the hydrocarbons processed.

Industrial Hygiene Program

The company has performed periodic industrial hygiene air sampling for many years. However, due to the high OSHA Standard of 1000 ppm for 1,3-butadiene, extensive monitoring was deemed to be unwarranted for this chemical.

The Corporate Manager of Environmental Control develops the sampling strategy for the plant. The company uses an analytical method which is

analogous to the NIOSH S91 Method. The organic vapor monitors used for sampling are desorbed with 1.5 ml carbon disulfide and analyzed using a gas chromatograph with a flame ionization detector.

DESCRIPTION OF PERSONNEL RECORD SYSTEM

The company maintains personnel records on past and present employees. Some of the personnel records were purged a few years ago; however, an index card is available on all employees.

The personnel file for each employee consists of the application for employment and the employee's personnel records. An employee's personnel record contains the following information:

1. Name
2. Employee's No.
3. Department Employed In
4. Date of Employment
5. Date and Place of Birth
6. Education
7. Marital Status
8. Prior Experience
9. Work History - date, salary, job classification and department

An alphabetical index card file is maintained for all employees. Each card lists the following information:

1. Name
2. Badge Number
3. Social Security Number
4. Date and Place of Birth
5. Job History - Department
6. Badge Number
7. Job description, salary
8. Sex
9. Date employed
10. Date Terminated
11. Education

The cards are maintained in 8 index file drawers and contain information on approximately of 5,600 active and terminated employees.

Medical records are maintained on all employees and are updated regularly. These records do not contain a work history of the individual employees.

CONCLUSIONS

Texas Petrochemical currently recovers 1,3-butadiene from crude C_4 ethylene coproduct streams using dimethylformamide (DMF) as the extraction solvent. The production occurs in a closed system, tightly maintained for economic and fire hazard reasons.

Due to the high current OSHA Standard for 1,3-butadiene, industrial hygiene data for the chemical has been collected by the company only since 1980. The reported results showed a weighted (by numbers of samples) arithmetic mean TWA exposure of 7.8 ppm for all job categories. The weighted geometric mean TWA exposure for this data was 1.16 ppm. TWA exposures ranged from 0.02 to 312.64 ppm.

Texas Petrochemical uses both on-line gas chromatographs and manual open-loop sample bombs for quality control determinations. Single mechanical seals are used on most pumps for leak prevention; newer pieces of equipment have dual mechanical (tandem) seals.

On the basis of information gathered and observations made during this survey, this facility is suitable for consideration as a possible in-depth survey site.

RECOMMENDATIONS

Since there appears to be potential for exposure to 1,3-butadiene during quality control sampling, consideration should be given to installation of a closed looped sampling system that would reduce the potential for 1,3-butadiene exposure from this source.

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TABLE 1

SUMMARY OF TEXAS PETROCHEMICAL'S AIR MONITORING RESULTS
FOR 1,3-BUTADIENE, 1980-1983

JOB TITLE	8-hour TWA, ppm* RANGE	ARITHMETIC MEAN**	GEOMETRIC MEAN**
Stillman	0.02 - 8.99	2.27(6)	0.24(6)
Assistant Stillman (includes helper)	0.02 -43.60	3.36(31)	0.68(31)
Lab Tester, QC Laboratory (includes head shift tester and lab special tester)	0.60 - 2.37	1.44(4)	1.21(4)
Pumper, Tank Farm Storage Areas	0.50 -312.64	22.27(15)	0.88(15)
Tank Truck Rackman, Loading/Unloading Dock	3.66 -13.96	8.61(3)	7.49(3)
Tank Car Rackman, Loading/Unloading Dock	0.75 - 7.84	3.64(5)	2.28(5)

* Time-Weighted Average
** Number of samples averaged is shown in parenthesis.