

INDUSTRIAL HYGIENE WALK-THROUGH SURVEY REPORT

of

Mobil Chemical Company
Olefins/Aromatics Plant
Beaumont, Texas

SURVEY CONDUCTED BY:
John M. Fajen

DATE OF SURVEY:
May 11, 1984

DATE OF REPORT:
April 2, 1985

REPORT NUMBER:
147.11

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 name in this report does not constitute endorsement by NIOSH.

ACKNOWLEDGEMENTS

This report was prepared in cooperation with PEDCo Environmental, Incorporated. Principal authors from PEDCo were Radha Krishnan and Les Ungers. Their responsibilities were completed under the scope of work of Contract Number 68-02-3938, Task 7 with the Environmental Protection Agency.

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.

EMPLOYER REPRESENTATIVES
CONTACTED:

Fred Schneider, Manager, Manufacturing

Lester Ryall, Plant Manager

Dennis Bruce, Loss Prevention
Supervisor

Charles Ferraro, Corporate Industrial
Hygienist

Mike Carlozzi, Safety and Loss
Prevention Manager

Robert Nash, 1,3-Butadiene
Superintendent

Dan Beckert, Production Manager

Pat Mullin, Environmental
Supervisor

Sam Jeansonne, Production
Superintendent

Dr. Paul Andreini, Medical Director,
Beaumont Facility

EMPLOYEE REPRESENTATIVES
CONTACTED:

Employees Not Unionized

STANDARD INDUSTRIAL
CLASSIFICATION OF PLANT:

2869 (Industrial Organic Chemicals,
not elsewhere classified)

ABSTRACT

A walk-through industrial hygiene survey was conducted at the Mobil Chemical Company in Beaumont, Texas, on May 11, 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, constructed in 1960, produces 1,3-butadiene by the ethylene coproduct process. The company has conducted personal monitoring using charcoal tubes on 5 different job categories. The mean of their 8-hour time-weighted (TWA) average exposures to 1,3-butadiene was 3.5 ppm. Exposures ranged from 0.20 - 17.60 ppm for all job categories.

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 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 This change will be considered for formal adoption in 1985.

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 Mobil Chemical Company's Olefins/Aromatics Plant was constructed in 1960 on 43 acres. The 1,3-butadiene complex covers approximately 1 acre.

1,3-butadiene has always been produced at this facility by the ethylene coproduct process using furfural as the extraction solvent. For a number of years the company purchased the ethylene coproduct C₄ feedstock from other ethylene plants.

The major chemicals manufactured are benzene, butylenes, ethylene, propylene, toluene, and 1,3-butadiene. In addition, polyethylene resins are also produced. The ethylene plant supplies approximately 1000 barrels/day of C₄ feedstock to the butadiene plant. Annual production of 1,3-butadiene is a function of the feed rate from the ethylene plant. Presently, production averages about 40 million pounds per year.

PROCESS DESCRIPTION

Figure 1 is a flow diagram of the 1,3-butadiene production process. The crude C₄ (butadiene concentrate) feed to the process comes from the on-site ethylene plant. For a number of years, however, the company purchased the C₄ feedstock. The feedstock contains 60 to 65 percent 1,3-butadiene and is stored in one of two feedstock spheres. The C₄ feedstock is fed to the primary absorber where furfural is used as the extraction solvent to separate the 1,3-butadiene stream from the mixed butenes stream. A secondary absorber continues this extraction process, with the furfural/1,3-butadiene stream fed to a stripper for separation of the 1,3-butadiene from the furfural. The furfural is cleaned to remove undesirable polymers that are formed, and then recycled to the primary absorber.

The 1,3-butadiene stream removed from the stripper is fed to primary and secondary fractionators to produce a butadiene bottoms byproduct and a 99+ percent 1,3-butadiene product. The product is treated in a carbonyl scrubber prior to storage in one of two 1,3-butadiene product spheres. Most of the 1,3-butadiene is transferred by pipeline to a large consumer in the Beaumont area. Small quantities are shipped to other consumers by rail car.

Historically, quality control samples were taken by hand using bombs which were vented to the atmosphere. At present two closed loop systems are on line which vent to the flare. The entire system will be in closed loop at the end of 1985.

DESCRIPTION OF THE WORKFORCE

As of May 1984, there were a total of 350 Mobil employees and 100 to 150 contract employees at the Beaumont Olefins/Aromatics Plant. In the 1,3-butadiene production and storage area, there are approximately 15 employees. The production employees work a rotating 12-hour day, 42-hour week. The storage area is operated on one 8-hour shift per day.

The maintenance of the 1,3-butadiene area is handled by 6 personnel: 2 millwrights, 2 pipefitters, a boiler maker, and an instrument man.

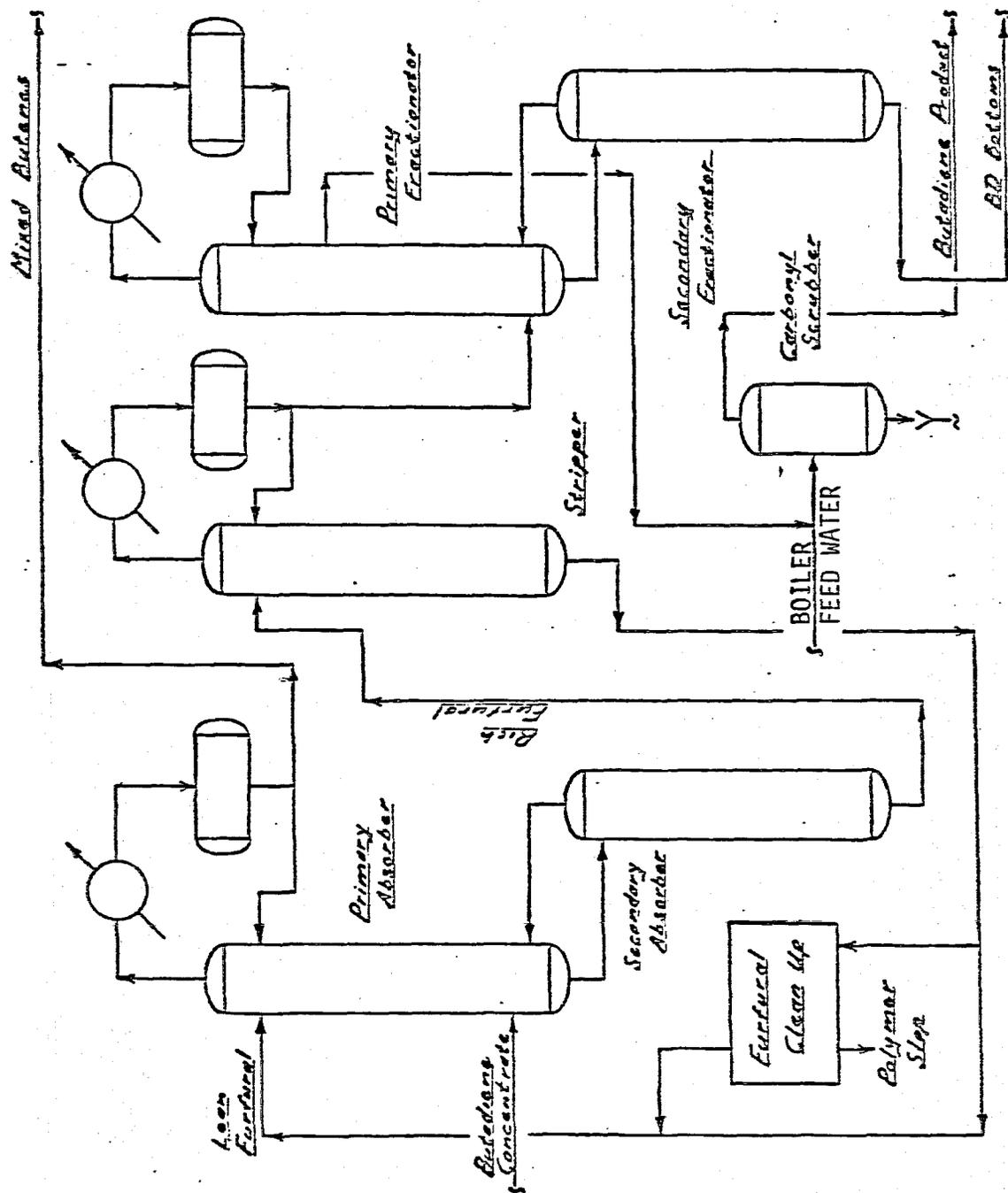


Figure 1. Flow diagram for production of 1,3-butadiene by ethylene coproduct process at Mobil Chemical's Olefins/Aromatics plant in Beaumont, Texas.

The 1,3-butadiene production unit is located within the ethylene facility. It is difficult to differentiate and assign all employees to either of the two units because many of the workers have overlapping responsibility for both the ethylene unit and the 1,3-butadiene unit. However, the process operators are specifically assigned to the 1,3-butadiene unit.

The workforce in the production and storage area is variable but broken down into the following job descriptions:

JOB TITLE	STORAGE AREA	PROCESS AREA
Process Operator/Supervisor	1	2
Maintenance		(1 to 4)
Pumper	1	0
Meterman	1	1
Engineer	1	1

DESCRIPTION OF PAST POTENTIAL WORKER EXPOSURES

During the 24 years of 1,3-butadiene production at the Beaumont Facility, the ethylene coproduct process using furfural as the extraction solvent has been employed.

The final products produced at the plant are: benzene, 1,3-butadiene, butylenes, ethylene, propylene, and toluene.

Mobil has collected industrial hygiene data on 1,3-butadiene, benzene, toluene, and xylene. Table 1 presents the Mobil monitoring data for 1,3-butadiene exposures. The mean 8-hour TWA over all job titles was calculated to be 3.5 ppm, with the highest exposed individual being the butadiene process operator (reported exposure range: 10.1 to 17.6 ppm).

The final product is transferred by underground pipeline to a large consumer of 1,3-butadiene in the Beaumont area. On a very limited basis, 1,3-butadiene is shipped in rail cars. Transfer by pipeline reduces the potential for worker exposure when compared to the other methods of transportation, i.e. rail, truck, or barge. The employees who transfer/ship chemicals spend approximately 20% of their time transferring 1,3-butadiene. The remaining time is spent shipping other final products.

Because of the location of the 1,3-butadiene unit within the ethylene facility, there is a potential for multiple exposures to a variety of chemicals manufactured at the complex. Of particular importance is the employees' potential for exposure to benzene from the ethylene unit.

Historically, quality control samples for the 1,3-butadiene unit were obtained by the process operator using a manual open loop sampling system. The sample bomb was screwed into a fitting in the 1,3-butadiene line, filled, then purged to the atmosphere and refilled. However, while the operator was removing the bomb, small amounts of 1,3-butadiene were released

to the atmosphere. This procedure was performed to release pressure in the bomb before sending it to the laboratory. After gas chromatographic analysis in the laboratory, the partially empty bomb was sent back to the production operator who then manually vented the bomb directly to the atmosphere by opening the bomb at arms length upwind. The aforementioned sampling related procedures thus appear to be sources of (potentially) significant exposures to 1,3-butadiene.

Mobil supplied NIOSH investigators with engineering diagrams (see Figure 2 for composite) for a closed-loop sampling train that limits potential exposure to 1,3-butadiene when obtaining quality control samples. This type of sampling train has recently been installed in the ethylene unit. Closed-loop sampling systems are being considered for the 1,3-butadiene unit.

The process operator is responsible for decontamination of the pumps and process equipment, while maintenance personnel perform the actual repair operations. Mobil has a defined procedure for equipment decontamination and maintenance. The defective unit is blocked off and the process material contained in the unit is vented to a flare (if it is 1,3-butadiene) or to a sump (if it is a solvent). Nitrogen purge and steam cleaning are performed on the major vessels only; there is no purge or steam cleaning of pumps or small lines. The pumps and small lines are washed with water. After purging/cleaning the necessary maintenance is performed on the equipment. At the completion of work the equipment is again purged with nitrogen before being recommissioned.

DESCRIPTION OF THE MEDICAL, SAFETY AND INDUSTRIAL HYGIENE PROGRAMS

Medical Program

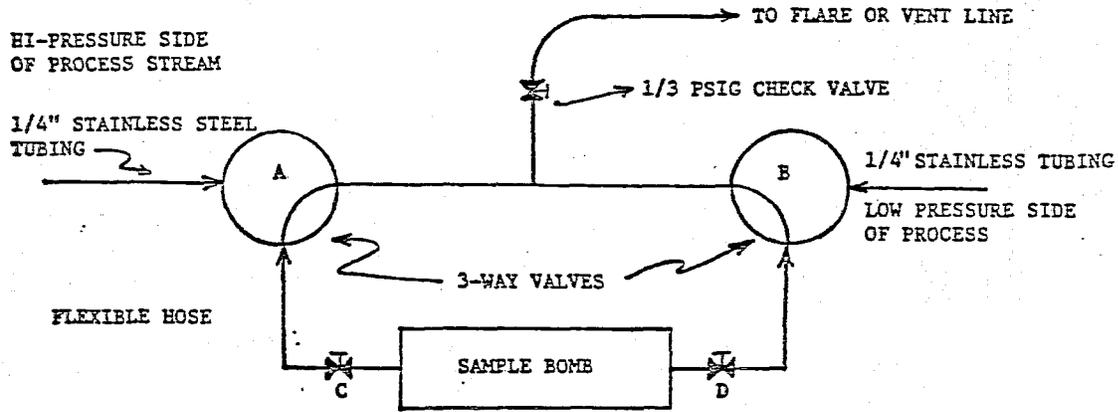
The company conducts pre-employment physicals on all its employees. Periodic physicals are voluntary and age dependent. Physicals are offered every 3 years for employees less than 50 years old and every 2 years for those over 50. A surveillance program, which is not age dependent, is also being conducted which requires certain job categories to participate in an annual physical examination.

Mobil Chemical Company has 2 full-time physicians available at the adjacent refinery who are responsible for the plant's medical program. In addition, the company employs 4 licensed nurses, one part-time audiometric technician, and one part-time x-ray technician. The support staff are all on the first shift. The remaining shifts have employees trained in emergency first aid.

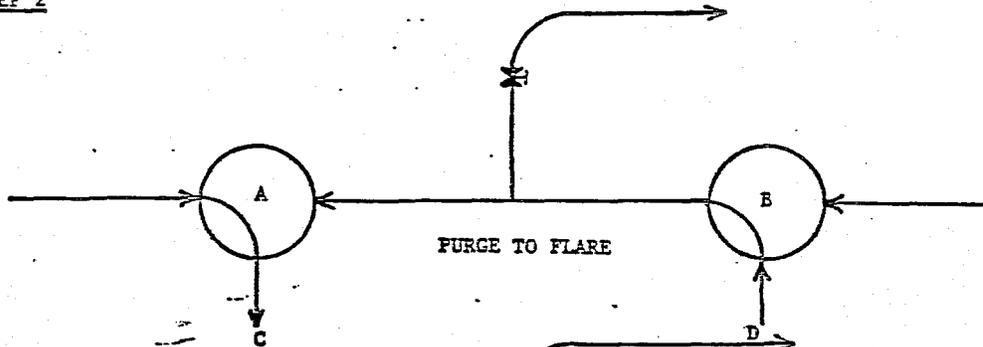
Safety Program

The company has an organized safety program. There is a full-time safety manager for the entire complex. A central safety committee meets monthly to discuss safety problems and to review training and operating procedures. Each department has a follow-up safety meeting to discuss safety work

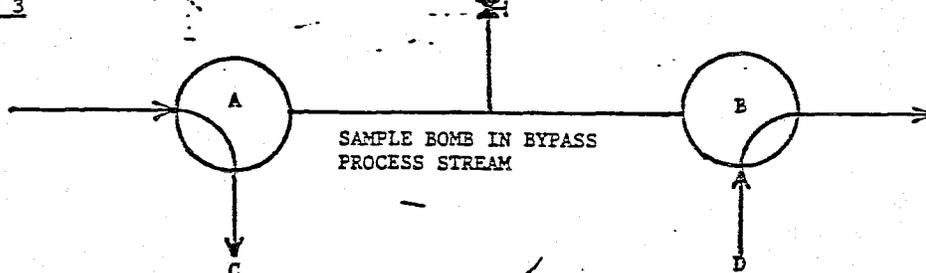
STEP 1



STEP 2



STEP 3



SAMPLING PROCEDURE - BOMB

Step 1 is the static "setup". Valves A&B open to the flare line with the check valve keeping the air out. Depressure bomb by opening valves C&D then purge to flare line by turning valve A to process (Step 2). Next turn valve B to process (Step 3).

To Sample: Close valve D then C. Return valves A&B to flare. "Crack" valve D to release hydraulic pressure on bomb, then close immediately. Secure hoses in notches provided for them pointing away from operator.

Figure 2. Closed-loop sampling train.
(Supplied by Mobil Chemical Corp.)

practices and to implement programs developed by the central safety committee.

Under normal operating conditions the personal protective equipment required by the company are safety glasses and hard hats. Respirators and other protective clothing are required for specific jobs such as the maintenance personnel and rail tank car loaders if a potential for exposures is suspected. Respirators are available to all employees throughout the plant. Showers and clothing change areas are available but reported not to be in frequent use. All workers provide their own work clothes which are commonly worn home. Smoking is not permitted in the production area because of the explosion hazard of 1,3-butadiene.

Industrial Hygiene Program

The plant does not have an industrial hygienist on location. However, an industrial hygiene technician is available on-site to implement industrial hygiene programs and sampling strategies developed by the Corporate industrial hygiene department. At the Corporate level, the job description and chemical exposure profile for production workers are maintained in a computerized data file.

Industrial hygiene sampling is routinely done for benzene, toluene, xylene and, most recently, 1,3-butadiene. Noise surveys also are conducted at the plant.

DESCRIPTION OF PERSONNEL RECORD SYSTEM

Mobil maintains personnel records on terminated as well as current employees. The records contain a work history of each employee. The plant is not unionized; there are, therefore, no union membership records.

CONCLUSIONS

Mobil Chemical Company manufactures 1,3-butadiene at the Beaumont site using the ethylene co-product process, with furfural as the solvent for extractive distillation. The production occurs in a closed system, tightly maintained for both economic and fire hazard reasons.

The company has conducted industrial hygiene sampling for 1,3-butadiene in 1983. The mean of the 8-hour TWA exposures to 1,3-butadiene for all job categories is 3.5 ppm. Exposures ranged from 0.20 - 17.60 ppm for all job categories.

Mobil historically employed a manual sampling system for obtaining quality control samples for the 1,3-butadiene unit. The sampling procedure involves purging and venting of sample bombs containing 1,3-butadiene directly to the atmosphere which posed a significant exposure to 1,3-butadiene during the sampling procedure. However, with the design of the closed looped the potential for exposure has been significantly reduced.

In an ongoing attempt to eliminate quality control sampling as a source of exposure, closed-loop sampling trains have been installed in the ethylene unit.

RECOMMENDATIONS

At the present, Mobil is switching over to a closed loop sampling system. The design of the system should significantly reduce the potential for exposure to 1,3-butadiene. However, to determine the effectiveness of the system, Mobil should continue to monitor worker exposure to 1,3-butadiene.

REFERENCES

1. Owen PE: The toxicity and carcinogenicity of butadiene gas administered to rats by inhalation for approximately 24 months. Final Report. Volumes 1-4, Addendum. Unpublished report submitted to the International Institute of Synthetic Rubber Producers, Incorporated by Hazelton Laboratories Ltd, Harrogate, England (November 1981).
2. Powers M: Board Draft of NTP technical report on the toxicology and carcinogenesis studies of 1,3-butadiene (CAS No. 106-99-0) in B6C3F₁ mice (inhalation studies). NTP-83-071/NIH Publication No. 84-2544. U.S. Department of Health and Human Services, Public Health Service, National Institute of Health, National Toxicology Program (October 28, 1983).
3. Owen PE, Irvine LFH: 1,3-Butadiene: Inhalation teratogenicity study in the rat. Final Report. Unpublished report submitted to the International Institute of Synthetic Rubber Producers, Inc. by Hazelton Laboratories Ltd, Harrogate, England (November 1981).
4. Meinhardt TJ, Lemen RA, Crandall MS, et al.: Environmental epidemiologic investigation of the styrene-butadiene rubber industry: Mortality patterns with discussions of the hematopoietic and lymphatic malignancies. Scan J. Work Environ Health 8:250-359 (1982).
5. Matanoski GM, Schwarts L, Sperrazza J, et al.: Mortality of workers in the styrene-butadiene rubber polymer manufacturing industry: Final report. Unpublished report submitted to The International Institute of Synthetic Rubber Producers, Inc. by John Hopkins University School of Hygiene and Public Health, Baltimore, Maryland (June 1982).
6. Current-Intelligence Bulletin No. 41 - 1,3-Butadiene. U.S. Department of Health and Human Services, Public Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health DHHS (NIOSH) Publication No. 84-105 (February 9, 1984).
7. American Conference of Governmental Industrial Hygienists: TLVs^R Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment and Biological Exposure Indices with Intended Changes for 1984-85. ACGIH, Cincinnati, Ohio (1984).

TABLE 1

SUMMARY OF MOBIL'S MONITORING DATA RESULTS FOR 1,3-BUTADIENE

JOB TITLE	NO. OF SAMPLES	8-hour TWA* CONCENTRATIONS, PPM	
		RANGE	MEAN
Butadiene process operator	5	10.10 - 17.60	12.7
Pumper	4	0.20 - 2.49	1.3
Loading rack operator	2	1.40 - 3.98	2.7
Lab technician	3	0.36 - 2.98	0.5
Ethylene process operator	2	0.20 - 0.40	0.3

*Time-weighted average