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An extent of exposure study of the 1,3-butadiene (106990) polymer industry was conducted to determine the size of the exposed workforce, evaluate control technologies and personal protective equipment programs, and assess occupational exposure to the chemical. A new analytical method, sensitive to 0.1 micrograms per sample, was presented for 1,3-butadiene. A total of 17 polymer facilities were surveyed. A representative sample of 5 facilities was selected for in depth industrial hygiene surveys. These firms manufacture styrene-butadiene rubber, nitrile-butadiene rubber, adiponitrile, polybutadiene rubber or neoprene. For each job category personal sampling was carried out, for a total of 451 personal air samples. An additional 132 area air samples were obtained in the process area to determine the potential for exposure in general work environments. All worker exposures were well below the OSHA permissible exposure limit of 1000 parts per million (ppm). Exposures ranged from less than 0.006ppm to 209.6ppm; the average exposure was less than 2ppm. The American Conference of Governmental Industrial Hygienists threshold limit value for 1,3-butadiene was 10ppm; nineteen of the 451 samples exceeded this 10ppm level. Several recommendations were made: (1) to reduce the potential for occupational exposure it was recommended that quality control sampling be conducted with a closed loop, (2) all process pumps should be retrofitted with dual mechanical seals, (3) magnetic gauges should be used in the loading and unloading of rail cars, (4) engineering controls should be designed for the safe voiding of quality control cylinders.

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EXTENT-OF EXPOSURE STUDY:

1,3-BUTADIENE POLYMER PRODUCTION INDUSTRY

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February 1988

U.S. Department of Health and Human Services
Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Surveillance, Hazard Evaluations, and Field Studies
Cincinnati, Ohio

DISCLAIMER

NIOSH Project Officers: John M. Fajen and Dennis R. Roberts

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The NIOSH Project Officers for this study were John M. Fajen and Dennis R. Roberts. Other participants from NIOSH included R. Alan Lunsford, Yvonne T. Gagnon, and John Palassis of the Division of Physical Sciences and Engineering. This study was conducted under an Interagency Agreement with the U.S. Environmental Protection Agency (EPA), Office of Toxic Substances, Washington, D.C. PEI Associates, Inc. (PEI) was contracted by EPA on this study to conduct an occupational exposure analysis and control technology assessment for 1,3-butadiene (Contract No. 68-02-4248).

The cooperation of the companies that participated in the study is greatly appreciated. The review and comments provided by the companies were very helpful for this extent-of-exposure study.

PREFACE

The National Institute for Occupational Safety and Health (NIOSH) has been granted the authority and responsibility under the Occupational Safety and Health Act of 1970 to conduct field research studies in industry, evaluate findings, and report on these findings. Section 20(a)7 of this Act states that NIOSH shall conduct and publish industrywide studies of the effects of chronic or low-level exposure to industrial materials, processes, and stresses on the potential for illness, disease, or loss of functional capacity in aging adults. Section 22(e) provides the authority to enter into contracts, agreements, or other arrangements with appropriate public agencies or private organizations for the purpose of conducting studies relating to responsibilities under the Act. Under an Interagency Agreement with EPA, NIOSH, along with an EPA contractor, PEI Associates, Inc., performed an extent-of-exposure study of 1,3-butadiene in the 1,3-butadiene polymer production industry.

The predominant uses of 1,3-butadiene (C_4H_6) are in the manufacture of synthetic rubbers, plastics, and resins. Of the synthetic rubbers, styrene-butadiene rubber and polybutadiene rubber make up more than half the demand for 1,3-butadiene. Recent animal studies have indicated that 1,3-butadiene is carcinogenic to mice and rats at levels near the current Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) of 1000 parts per million (ppm). At the time of this report, OSHA had initiated new rulemaking action with respect to reducing worker exposures to 1,3-butadiene. Based upon reported animal carcinogenicity data, the American Conference of Governmental Industrial Hygienists (ACGIH) has included 1,3-butadiene as an "A2" industrial substance suspected of carcinogenic potential in man. A Threshold Limit Value (TLV) of 10 ppm has been assigned to 1,3-butadiene.

NIOSH recommends in its Current Intelligence Bulletin that 1,3-butadiene be regarded as a potential occupational carcinogen and teratogen and as a possible reproductive hazard. NIOSH has estimated that approximately 65,000 workers in the United States are potentially exposed to 1,3-butadiene during its manufacture, processing, and use. Historical industrial hygiene data on the extent of worker exposure to 1,3-butadiene suffer from the drawbacks of the sampling and analytical methods used. These procedures are susceptible to interference from C_4 compounds other than 1,3-butadiene and were developed for a standard of 1000 ppm.

This extent-of-exposure study of the 1,3-butadiene polymer industry was undertaken to determine the size of the exposed workforce, evaluate control technologies and personal protective equipment programs, and assess occupational exposures to 1,3-butadiene using a new sampling and analytical method for 1,3-butadiene developed by NIOSH. The new analytical method allows air volumes up to 25 liters (L) to be sampled, permitting quantitation of full-period exposures over a range of 0.4 to 10 ppm. The range may be extended up to 100 ppm by diluting desorbed samples. The limit of detection is about 0.2 ug per sample or 0.005 ppm for 25 L samples. This report contains a discussion of the sampling and analytical method, brief descriptions of the facilities surveyed, a discussion of the results, and recommendations based on the results. A study similar to this was previously conducted in the monomer industry and details the extent-of-exposure in that industry.

The polymer industry study was conducted in three phases: 1) a literature evaluation, 2) walk-through industrial hygiene surveys at 17 selected facilites, and 3) comprehensive in-depth industrial hygiene monitoring surveys at five facilites. After each phase, the information and data collected were reviewed and evaluated prior to progressing to the next phase. The new NIOSH analytical method for 1,3-butadiene was used to collect the field industrial hygiene samples.

ABSTRACT

Researchers from the National Institute for Occupational Safety and Health (NIOSH) conducted an extent-of-exposure study of the 1,3-butadiene polymer industry to determine the size of the exposed workforce, evaluate control technologies and personal protective equipment programs, and assess occupational exposure to 1,3-butadiene. A new analytical method was developed for 1,3-butadiene that increased the sensitivity and selectivity of the previous NIOSH methods. The new method is sensitive to 0.2 ug per 1,3-butadiene sample. Seventeen polymer plants were surveyed. From the 17 polymer plants a representative sample of 5 plants was selected for indepth industrial hygiene surveys. The 5 plants manufactured styrene-butadiene rubber, nitrile-butadiene rubber, adiponitrile, polybutadiene rubber or neoprene. Airborne exposure concentrations of 1,3-butadiene were determined for each job category using personal sampling. A total of 451 personal air samples were taken. An additional 132 area air samples were obtained in the process area to determine the potential for exposure in the general work environment. Sample results indicated that all worker exposures were well below the OSHA PEL of 1000 ppm. Exposures ranged from less than 0.006 ppm to 209.6 ppm. The average exposure for all samples was less than 2 ppm. The present ACGIH TLV for 1,3-butadiene is 10 ppm. Nineteen of the 451 personal samples collected by NIOSH were greater than 10 ppm (4.2%).

As a result of the environmental sampling several recommendations were made. To reduce the potential for occupational exposure it is recommended that quality control sampling be conducted with a closed loop. All process pumps should be retrofitted with dual mechanical seals. Magnetic gauges should be used in the loading and unloading of rail cars. Engineering controls should be designed for the safe voiding of quality control cylinders.

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INTRODUCTION

Under the terms of the authority and responsibility given to the National Institute for Occupational Safety and Health (NIOSH) to develop needed information regarding potentially toxic substances in industry, NIOSH under an Interagency Agreement with the Environmental Protection Agency (EPA) initiated an industrial hygiene study of the extent-of-exposure to 1,3-butadiene in the 1,3-butadiene polymer producing industry. PEI Associates, Inc. (PEI) was a contractor to EPA on this study, concurrently conducting a control technology assessment for minimizing occupational exposures to 1,3-butadiene, including control costs and estimates of control effectiveness. Because of NIOSH's and EPA's common interest in determining the extent of occupational exposure to 1,3-butadiene in the polymer industry, NIOSH and PEI coordinated their efforts in this study. 1,3-Butadiene was selected for study because recent chronic oncology studies have shown that 1,3-butadiene is carcinogenic in rats and mice at levels near the current Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) of 1000 parts per million (ppm). Epidemiological studies of workers employed in facilities producing 1,3-butadiene and styrene-butadiene rubber, however, have not indicated a statistically significant increase in mortality from neoplasms of the lymphatic and hematopoeitic tissues or from leukemia.[1-3] At the time of this report, OSHA had initiated a new rulemaking process to reduce occupational exposures to 1,3-butadiene.

Limited published data exist on the extent of worker exposure to 1,3-butadiene. These data are highly suspect because they are based on analytical methods that do not adequately separate 1,3-butadiene from other C_4 hydrocarbons and were developed for a standard of 1000 ppm. It is believed that the historical monitoring results tend to overestimate exposure to 1,3-butadiene. The use of the existing exposure data in any risk assessment must be done with caution because of imprecision and error of the estimates of past exposure.

STUDY GOALS

The primary goal of this industrial hygiene study was to identify and document the potential for 1,3-butadiene exposure in the polymer production industry as it relates to various job descriptions of potentially exposed workers. A secondary goal was to identify individuals exposed to 1,3-butadiene who might be suitable for inclusion in other occupational health-related studies (e.g., genotoxocity study, epidemiology study).

STUDY OBJECTIVES AND SCOPE

To meet the study goals, the following objectives were established for this study:

- Identify job categories and describe specific tasks where exposures may occur at 1,3-butadiene polymer facilities.

- Describe current industrial hygiene and safety practices, including engineering controls, work practices, and administrative controls.

- Develop and validate a new NIOSH sampling and analytical method for 1,3-butadiene that is not susceptible to interference from other C_4 compounds, and is sensitive at lower concentrations.

- Measure 1,3-butadiene exposures at representative polymer producing facilities using the new NIOSH sampling and analytical method.

The 1,3-butadiene study was separated into three industry categories: the 1,3-butadiene monomer production industry, the 1,3-butadiene-based polymer (or chemical) production industry, and the polymer end-use industry. This report pertains only to the 1,3-butadiene polymer production industry.

The study of the polymer industry was conducted using a three-phased approach. The first phase consisted of a literature review (e.g., toxicity, previous sampling and analytical methods, process descriptions, identification of 1,3-butadiene containing polymers, historical monitoring data) pertaining to 1,3-butadiene; this was completed in early 1985.

The second phase consisted of industrial hygiene walk-through surveys at seventeen 1,3-butadiene polymer production plants. These visits, which were made in conjunction with PEI, were conducted from May to November 1985. Because polymers are further processed into finished products, it was one of the intentions of the walk-through surveys to analyze the polymer(s) produced at the survey site to determine the potential for release of 1,3-butadiene monomer at temperatures typical of various fabrication processes employed in the manufacture of finished products which use the polymer. Therefore, a bulk polymer sample was obtained at each site and analyzed for emission of free monomer at three predetermined temperatures.

The third phase of the study consisted of in-depth industrial hygiene exposure monitoring surveys (employing the new NIOSH sampling and analytical method) at five representative facilities. These surveys were conducted during the period of June to September 1986 in conjunction with PEI and Midwest Research Institute (MRI), a second EPA contractor. MRI evaluated for EPA another new sampling and analytical method (Grob Trap) for 1,3-butadiene that is sensitive at concentrations below 1 ppm. The results from Grob Trap monitoring are not included in this report.

STUDY LIMITATIONS

The industrial hygiene data collected during the polymer industry study represent evaluations of worker exposures to 1,3-butadiene at the facilities selected for the study. The five polymer plants were chosen to best represent the industry as a whole but may not cover all possible workplace scenarios. Accordingly, workplace exposures and exposure scenarios may be different in facilities that were not evaluated in the in-depth surveys. Exposures evaluated in this study may not necessarily reflect possible variations in exposure due to seasonal or operational changes. An attempt was made to evaluate exposures for each job category and associated work environment encountered during the surveys. No abnormal exposure situations were encountered; the reported exposure measurements are, therefore, considered to represent only those exposures associated with normal operating conditions.

BACKGROUND

CHEMICAL AND PHYSICAL PROPERTIES

1,3-Butadiene (C_4H_6) is a colorless gas at room temperature and atmospheric pressure. It is highly flammable and possesses a mild aromatic odor.[4] It is only slightly soluble in water, but readily soluble in organic solvents such as benzene, toluene, and cyclohexane. 1,3-Butadiene is stored in the liquid state, requiring pressurized or refrigerated vessels. Additional chemical and physical properties are listed in Table 1.

TOXICOLOGY AND EPIDEMIOLOGY STUDIES

Recent inhalation exposure studies of rats and mice to 1,3-butadiene reported induction of 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 adenomas were identified in rats exposed at concentrations of 1000 or 8000 ppm of 1,3-butadiene.[7] Mice exposed to 625 or 1250 ppm of 1,3-butadiene developed a high incidence of malignant lymphomas and an increased incidence of other tumors, including hemangiosarcomas of the heart. Testicular and ovarian atrophy were also observed in mice.[8]

The offspring of pregnant rats exposed to 1,3-butadiene at 8000 ppm had major skeletal defects. Pregnant rats exposed at 200, 1000, or 8000 ppm of 1,3-butadiene exhibited depressed body weight gain in all concentrations. In addition, fetal growth was significantly retarded among rats exposed at 8000 ppm.[9]

Occupational exposure at 2000, 4000, or 8000 ppm concentrations of 1,3-butadiene is reported to cause irritation of the skin, eyes, nose, and throat. Coughing, drowsiness, and fatigue have also been reported at higher, but unspecified, exposure concentrations. These physiological responses dissipated upon removal of the workers from the area where 1,3-butadiene had accumulated.[10-12] Dermatitis and frostbite may result from exposure to liquid and evaporating 1,3-butadiene.[11]

In the late 1970's, a retrospective cohort study was conducted at two styrene-butadiene rubber production facilities in the U.S. The combined cohorts consisted of 2756 white males who had an average length of employment of approximately 10 years. No historical exposure data were available. Environmental sampling conducted at the time of the study characterized the most likely chemical exposures to be 1,3-butadiene, styrene, and benzene. Average exposure concentrations of 1,3-butadiene in the two facilities were 1.24 ppm (range of 0.11 to 4.17 ppm) and 13.5 ppm (range 0.34 to 174 ppm).

Table 1. Chemical and physical properties of 1,3-butadiene[4-6]

Chemical identity	1,3-Butadiene
Synonyms	Biethylene, bivinyl, butadiene, buta-1,3-diene, alpha-gamma-butadiene, divinyl, urethrene, NCI-C50602, pyrrolylene, vinyl ethylene
Molecular weight	54.10
Molecular formula	C_4H_6
Structural formula	$CH_2:CHCH:CH_2$
Boiling point	−4.41°C (at 760 mm Hg)
Freezing point	−108.9°C
Heat of vaporization, J/g (cal/g), 25°C	389 (93)
Explosive limits, vol % 1,3-butadiene in air	
Lower	2.0
Upper	11.5
Vapor pressure	2 atm at 15.3°C 5 atm at 47.0°C
Recognition (odor) threshold	1.3 ppm

No statistically significant excesses in total or cause-specific mortality were observed for the total worker populations of either facility. However, a subgroup of workers from one had a statistically non-significant excess mortality rate for cause-specific categories of cancer of the lymphatic and hematopoietic tissues.[3]

A 1985 report of a cohort study at a 1,3-butadiene production plant showed a significantly increased standardized mortality ratio (using U.S. population rates for comparison) for lymphosarcoma and reticulum cell sarcoma in the total cohort, and a significantly increased standardized mortality ratio (using Texas Gulf Coast rates for comparison) for stroke in the non-routinely exposed group. Neither the corresponding local standardized mortality ratio nor the national standardized mortality ratio was statistically significant. In addition, consistently elevated, though nonsignificant, increases in other lymphohematopoietic cancer were noted in each of the eight subcohorts examined.[2]

APPLICABLE STANDARDS AND RECOMMENDED LIMITS.

Based on the 1968 Threshold Limit Value (TLV) of the American Conference of Governmental Industrial Hygienists (ACGIH),[13] OSHA promulgated a standard for occupational exposure to 1,3-butadiene of 1000 ppm (2200 mg/m^3) determined as an 8-hour time-weighted average (TWA) concentration.[14] The TLV of 1000 ppm was based on the absence of significant progressive injury to rats and guinea pigs exposed at 600, 2300, or 6700 ppm of 1,3-butadiene during an 8-month daily exposure period and on the occurrence of only mild irritation experienced by human subjects exposed at 8000 ppm.[13] At the time of this report, OSHA had initiated new rulemaking action with respect to reducing worker exposures to 1,3-butadiene.

Based upon reported animal carcinogenicity data, the ACGIH has included 1,3-butadiene as an "A2" industrial substance suspected of carcinogenic potential in man.[15] A numerical TLV of 10 ppm has been assigned to 1,3-butadiene.

NIOSH, in its Current Intelligence Bulletin, recommends that 1,3-butadiene be regarded as a potential occupational carcinogen and teratogen and as a possible reproductive hazard.[16]

PRODUCTION AND USE

The total U.S. demand for 1,3-butadiene in 1985 was 3.25 billion pounds, of which about 2.45 billion pounds was domestically produced.[17] The predominant uses of 1,3-butadiene are in the manufacture of synthetic rubbers, plastics, and resins. It is also used to a lesser degree as a chemical intermediate in the manufacture of various other products such as fungicides and industrial solvents. Of the synthetic rubbers, styrene-butadiene rubber and polybutadiene rubber make up more than half of the demand for 1,3-butadiene; these rubbers are used primarily in the tire industry.[18,19]

The use of 1,3-butadiene is thus primarily affected by rubber and tire demand. Table 2 shows the present domestic usage profile for 1,3-butadiene. There has been a significant decline in demand in recent years, with domestic production dropping from 3.6 billion pounds in 1979 to 2.5 billion pounds in 1984.[24,25] This decline in demand has been accompanied by only a slight decrease in industry capacity.

Table 2. Usage profile for 1,3-butadiene[17]

Product		Percentage of total consumption
Styrene-butadiene rubber (SBR)		37
Polybutadiene rubber (PBR)		22
Adiponitrile		13
Styrene-butadiene copolymer latexes		9
Neoprene		7
Acrylonitrile-butadiene-styrene (ABS) resins		6
Nitrile rubber (NBR)		3
Miscellaneous (pesticides, solvents, etc.)		3
	Total	100

STUDY DESIGN

Site Selection Criteria

To determine the sites for the in-depth industrial hygiene surveys it was first necessary to identify the different 1,3-butadiene polymers or products produced in the United States. Twenty-three polymers or products were identified and are listed in Table 3.

Table 3. 1,3-Butadiene Polymers or Products Produced in the United States

1. Styrene-Butadiene Rubber
2. Styrene-Butadiene Rubber Latex
3. Butadiene Rubber
4. Neoprene
5. Nitrile
6. Adiponitrile
7. Chloroprene
8. Polystyrene Butadiene Rubber
9. Butadiene-Vinylpyridine Latex
10. Acrylonitrile-Butadiene Styrene
11. Liquid Polybutadiene Styrene Resins
12. Vinyl Polybutadiene Resins
13. Liquid Polybutadiene Resins
14. Butadiene Dimer
15. Captan
16. Sulfolene
17. Butadiene Acrylonitrile Latex
18. Tetrahydrophthalic Anhydride
19. 1,4-Hexadiene
20. 1,5-Hexadiene
21. Butadiene Furfural Cotrimer
22. Liquid Polybutadiene
23. R-11

Twenty-four polymers were identified and 17 plants were randomly chosen to cover all 23 polymers. Consideration was given to location so that more than 1 plant could be visited during a field trip. Walk-through surveys were conducted at 17 production plants that represented all 23 polymers or products. The site selection criteria for an in-depth survey were based on the information acquired during the walk-through surveys. The final site selection for the in-depth surveys was based on the following key criteria:

1. Five plants should be selected.
2. The selected plants should include the largest 1,3-butadiene polymer producing plants.
3. The selected plants should have a large number of employees potentially exposed.
4. Each of the types of polymerizaton processes should be included (emulsion and solution).

The information obtained during each of the five in-depth industrial hygiene monitoring surveys is discussed in subsequent sections titled "FACILITIES SURVEYED" and "NIOSH INDUSTRIAL HYGIENE SAMPLING RESULTS". During the in-depth surveys, considerable additional information was collected on the nature of the process operations, workforce, work practices, potential routes of exposure, engineering and administrative controls, and personal protective equipment. In addition, industrial hygiene air sampling for 1,3-butadiene was conducted. Both personal and area monitoring samples were taken at controlled and uncontrolled process operations in an effort to determine employee exposure and to assess the efficacy of the engineering controls in use at the time of the survey. These results represent a unique body of exposure information because improved sampling and analytical techniques not previously available to industry or government were used for their collection.

SAMPLING AND ANALYTICAL METHOD

The major limitation at the start of the study was the sensitivity and selectivity of the then current analytical method for 1,3-butadiene (NIOSH Method S-91[26]). This method was developed to meet compliance monitoring needs associated with the current OSHA standard of 1000 ppm (2200 mg/m^3); therefore, the S-91 method was validated over a limited range of concentrations: 481 to 2237 ppm (1065 to 4950 mg/m^3). Because of new animal test data indicating toxicity at much lower concentrations, it was necessary for NIOSH to develop and validate an analytical method that had a lower detection limit. The NIOSH Method S-91 recommends a 6-m x 3.2-mm outer diameter stainless steel column packed with 10 percent Free Fatty Acid Phase (FFAP) on 80/100-mesh Chromosorb® [acid washed-dimethyldichlorosilane treated (AW-DMCS)] for the gas chromatographic analysis of 1,3-butadiene. The column provides a convenient separation of 1,3-butadiene from the extraction solvent (carbon disulfide), but 1,3-butadiene and other light hydrocarbons, being non-polar, are poorly retained by the highly polar liquid phase, and consequently are poorly separated from each other. Methods using columns which do not adequately separate the four carbon chain (C_4) hydrocarbons and other potential interferences probably overestimate the 1,3-butadiene content of the sample. To improve the resolution of the C_4 hydrocarbons, NIOSH researchers selected a 50-m x 0.32-mm inner diameter fused silica, porous layer open tubular column coated with Al_2O_3/KCl, and used methylene chloride as the extraction solvent. The applicable range of the new NIOSH method is approximately 0.4 to 10 ppm for a 25 liter (L) sample. The range may be extended up to 100 ppm by diluting the desorbed samples. Below 0.4 ppm, the desorption efficiency falls below 75 percent and allowances should be made for the decreased accuracy. The limit of detection is about 0.2 ug per sample or 0.005 ppm for 25 L samples. A more detailed description of the new NIOSH method is provided in Appendix A.

During the in-depth surveys both personal and area sampling were performed. Samples were collected by drawing a known volume of air from a worker's breathing zone or work area through a sampler by means of an SKC Model 224® or Gillian Model HFS-113A-UT® portable low-flow air-sampling pump. Samples were collected on tandem solid sorbent tubes. The forward tube contained 400 mg of coconut charcoal and acted as the primary collection medium. The backup tube contained 200 mg of charcoal and acted to quantify the level of breakthrough. The charcoal tubes were connected to the pumps with plastic Tygon® tubing. Samples were collected with low-flow pumps at a flow rate of 0.05 to 0.5 liters per minute (Lpm). Sample air volumes were limited to a minimum of 1 L and a maximum of 25 L. Sampling pumps used during the survey were checked for significant air-flow deviation (greater than 5 percent) after each sampling period.

To assure the quality of results, sample blanks and quality assurance spikes were generated, analyzed, and reported in accordance with NIOSH Quality Assurance and Quality Control procedures.[27] Field samples were refrigerated during shipment and storage. Samples are known to remain stable for at least 21 days when kept at -4°C.

At the laboratory, each personal sample was prepared for analysis by desorbing the collected material with 4 ml of methylene chloride for 30 minutes. The resulting solutions were analyzed by gas chromatography with flame ionization detection, a technique which separates the various chemicals and provides responses that are proportional to the amounts present. Each set of samples was analyzed along with 1) calibration standards prepared by desorbing sampling media that had been spiked with known amounts of selected chemicals (analytes) expected to be in the samples, 2) similar solution standards spiked directly, and 3) blank solutions prepared by desorbing blank sampling media. Compounds in the samples were tentatively identified (based by their chromatographic retention times) and quantitated (based on their observed detector responses) by comparison with the retention times and response observed for the known analytes in the calibration standards.

At the lower range of an analytical method, it may not be possible to confidently attribute an instrument response to the substance in question. The point at which instrument response can confidently be attributed to the contaminant being measured is called the "limit of detection" (LOD). If an instrument response is attributed to the contaminant, it may be present at such low levels that the confidence interval for the results reported may be excessive. The point at which the range of possible values are within acceptable limits is called the "limit of quantitation" (LOQ).

The reported LOD and LOQ differed slightly for different analytical runs. For this study, the LOD for 1,3-butadiene was 0.3 micrograms per sample (ug/sample) and the LOQ ranged from 1.0 to 1.1 ug/sample. These limits were calculated from the statistics of the calibration curve. Treatment of less-than-detectable results for computing both the means and the geometric standard deviation was accomplished by using the numerical value halfway between zero and the reported LOD. This approach should provide an accurate measure of the means and standard deviations since only 15 percent of the total data set was below the LOD.

SAMPLING STRATEGY

Each of the five in-depth surveys was planned and scheduled to obtain full-shift (8-hour) sampling during normal production conditions. The job categories identified during the walk-through surveys as having any potential for exposure to 1,3-butadiene were sampled. Area samples covered the major work environments as well as points along the plant perimeter. Both long-and short-term samples were collected. Short- and long-term samples in this study were defined respectively, to be of less than 120 minutes duration and of greater than 120 minutes duration (usually 8 hours), respectively. The number of individuals sampled within a given job category was based on the total number of employees in that category and reflected a 95 percent confidence level ($p = 0.05$), so that the highest and lowest exposed individuals would be included in the sampling(29).

At least one worker in each job category was monitored for a full shift. During each in-depth survey, the survey team monitored for a total of three shifts over the course of three work days. Auxiliary jobs in the production area, in which exposure to 1,3-butadiene was intermittent, or thought to be nonexistent, were also monitored. Nonproduction jobs involving maintenance and laboratory workers were also evaluated to determine their potential for exposure. The area sources and personal sampling included the following operations: 1) quality control sampling activities, 2) laboratory analysis, 3) production, 4) packaging, 5) tank farm operations, and 6) transportation vehicle loading activities.

FACILITIES SURVEYED

Walk-through surveys were conducted at 17 U.S. facilities that produced 1,3-butadiene based polymers or products. In-depth industrial hygiene monitoring surveys were conducted at five of these facilities. These five facilities, designated as Plants A, B, C, D, and E in this report, are described in this section. For each plant, information is presented on plant history, process description, workforce, engineering controls, past worker exposure, medical, safety and industrial hygiene programs and personnel recordkeeping.

SITE DESCRIPTION

Plant A

Plant A located in Louisiana manufactures styrene-butadiene rubber (SBR) by the emulsion process and nitrile (acrylonitrile)-butadiene rubber (NBR). The production facilities, which were originally constructed in 1943, cover approximately 65 acres.

The government constructed the plant to produce SBR for the war effort. In 1948, batch polymerization temperatures were reduced from 130°F to 45°F as part of a conversion to production of "cold" SBR. The polymer production capacity of the plant at that time was rated at 30,000 tons per year. In 1958, the polymerization process was converted to a continuous process, and the annual polymer capacity was increased to 33,200 tons. The company began manufacture of NBR in 1967. SBR currently accounts for 97 percent of polymer production. The production rates of SBR and NBR are 465 million pounds per year and 15 million pounds per year, respectively. NBR production is block-operated three to four times per year. The company also operated a 1,3-butadiene monomer manufacturing plant from 1951 to 1982.

The plant produces approximately 50 different grades of SBR and NBR varying in physical properties (e.g., viscosity) according to the formulation of the raw materials utilized in the process. The products are sold for use in the manufacture of a wide variety of tire and rubber goods.

Plant B

Plant B is located in southeast Texas. The plant was constructed on 750 acres in 1946; the adiponitrile (ADN) process, which consumes 1,3-butadiene, was built in 1971. The plant has a capacity to produce 490 million pounds/year of ADN. ADN is captively used in the production of hexamethylene-diamine (HMDA), which is a principal ingredient in the production of Nylon-66.

Other products manufactured at the facility include HMDA, adipic acid, ethylene, high and low density polyethylenes, and ethylene copolymers.

Plant C

Plant C began operation in 1943 in Louisiana, producing styrene-butadiene rubber (SBR) by an emulsion process. This SBR emulsion operation has been shut down since February, 1983. The plant currently produces three polymers from 1,3-butadiene: SBR and polybutadiene rubber (PBR) via solution polymerization, and vinyl pyridine latex (VPL) via emulsion polymerization. Current production processes are: A SBR/PBR solution process which came on-line in 1968, and a VPL emulsion process installed in 1981. The facility occupies 79.2 acres and is capable of producing 120,000 metric tons of SBR/PBR and 1,800 metric tons of VPL annually. The plant has not been operating at capacity over the 12-month period prior to the survey (June 1985 to June 1986).

Plant D

Plant D, located in southeast Texas covers approximately 27 acres. The plant, built by the government during World War II, originally produced SBR as part of the Rubber Recovery Program. The plant began producing maleic anhydride in 1961 and began neoprene rubber production in 1970.

Plant D produces neoprene and tetrahydrophthalic anhydride (THPA). Neoprene (or polychloroprene) is produced at a rate of 50 million pounds per year. Neoprene is produced in the form of a latex. The latex can be drummed for shipment or proceeded further to form a polymer "chip". Neoprene latex is used to dip shoeboards and as an additive in paints. Solid polymer neoprene chips represent a synthetic rubber with properties such as oil resistance and durability. THPA production commenced in 1963. THPA, synthesized from maleic anhydride and 1,3-butadiene, is made in batches when ordered. Production usually occurs once a month for several days; total production ranges from 2 million to 5 million pounds per year. THPA is sold as a curing agent for epoxy resins.

Plant E

Plant E is located in southeast Texas. The plant, which is located on 130 acres, produces styrene-butadiene rubber (SBR), and acrylonitrile-butadiene rubber (NBR) using an emulsion polymerization process. Styrene-butadiene (SB) latex is an intermediate product in the SBR manufacturing process. The plant began production in 1943.

The nameplate capacity of the plant to produce synthetic polymers is 960 million pounds per year.

PROCESS DESCRIPTION

Plant A

Plant A uses a "cold" emulsion polymerization process to produce SBR and NBR. The 1,3-butadiene monomer for the SBR and NBR processes is received principally by pipeline but can also be received by rail tank car. Approximately 10 million pounds of the monomer are received each month at the facility. There are six storage spheres (260,000 gallons each) for storing 1,3-butadiene. A 30,000-gallon storage tank in the rubber tank farm is charged with 1,3-butadiene from the spheres and supplies fresh 1,3-butadiene to the processes. The fresh 1,3-butadiene is blended in the 30,000 gallon storage tank with recycled 1,3-butadiene from the recovery area.

Figures 1 and 2 illustrate the processes for "cold" emulsion polymerization of SBR and NBR at Plant A. Both processes use similar equipment and chemicals except for the use of styrene (SBR) and acrylonitrile (NBR). For production of each polymer, blended 1,3-butadiene is mixed with other charge chemicals and fed to the reactor chains. For production of SBR there are two chains, one with 15 reactors and one with 14 reactors; for NBR there is one chain with 14 reactors. The NBR production process was not operational at the time of the survey, and SBR was being produced in both reactor chains.

In each of the chains there are two reactors with a capacity of 6,000 gallons each, and twelve other reactors (13 in one of the SBR chains) that have a capacity of 3,300 gallons each. The appropriate number of reactors is utilized in the chain to provide the desired production rates. After polymerization in the reactor the latex product is surged in cold blowdown tanks and pumped to hot blowdown tanks.

In the recovery area for the SBR process, latex from the hot blowdown tank goes to the pressure (2 to 4 psig) flash tank, and then to the vacuum (22 to 23 in. Hg) flash tank, which releases greater than 99 percent of the unreacted 1,3-butadiene to the vacuum knockout tank (which is part of the absorber/desorber system). Final stripping of the 1,3-butadiene occurs in the latex stripping columns from which 1,3-butadiene is added back to the vacuum knockout tank. Vacuum pumps discharge 1,3-butadiene from the knockout tanks to the 1,3-butadiene compressors which then feed it to the 1,3-butadiene recycle tower. The 1,3-butadiene recycle tower also scrubs out styrene. The 1,3-butadiene is then condensed and returned to the recycle 1,3-butadiene tanks in the tank farm. The absorber/desorber unit purges air from the recycle 1,3-butadiene tanks, where it goes into a vapor stream which returns to the compressors. The vapor stream from this unit averages 6 percent 1,3-butadiene and is burned in the boilers. All reactor and recovery vessels, coolers, etc. have relief valves vented to the flare system. Recovery of the 1,3-butadiene from NBR production is similar to the SBR recovery systems except that an acrylonitrile recovery tower separates 1,3-butadiene from acrylonitrile before 1,3-butadiene re-enters the NBR recovery system at the compressor suction.

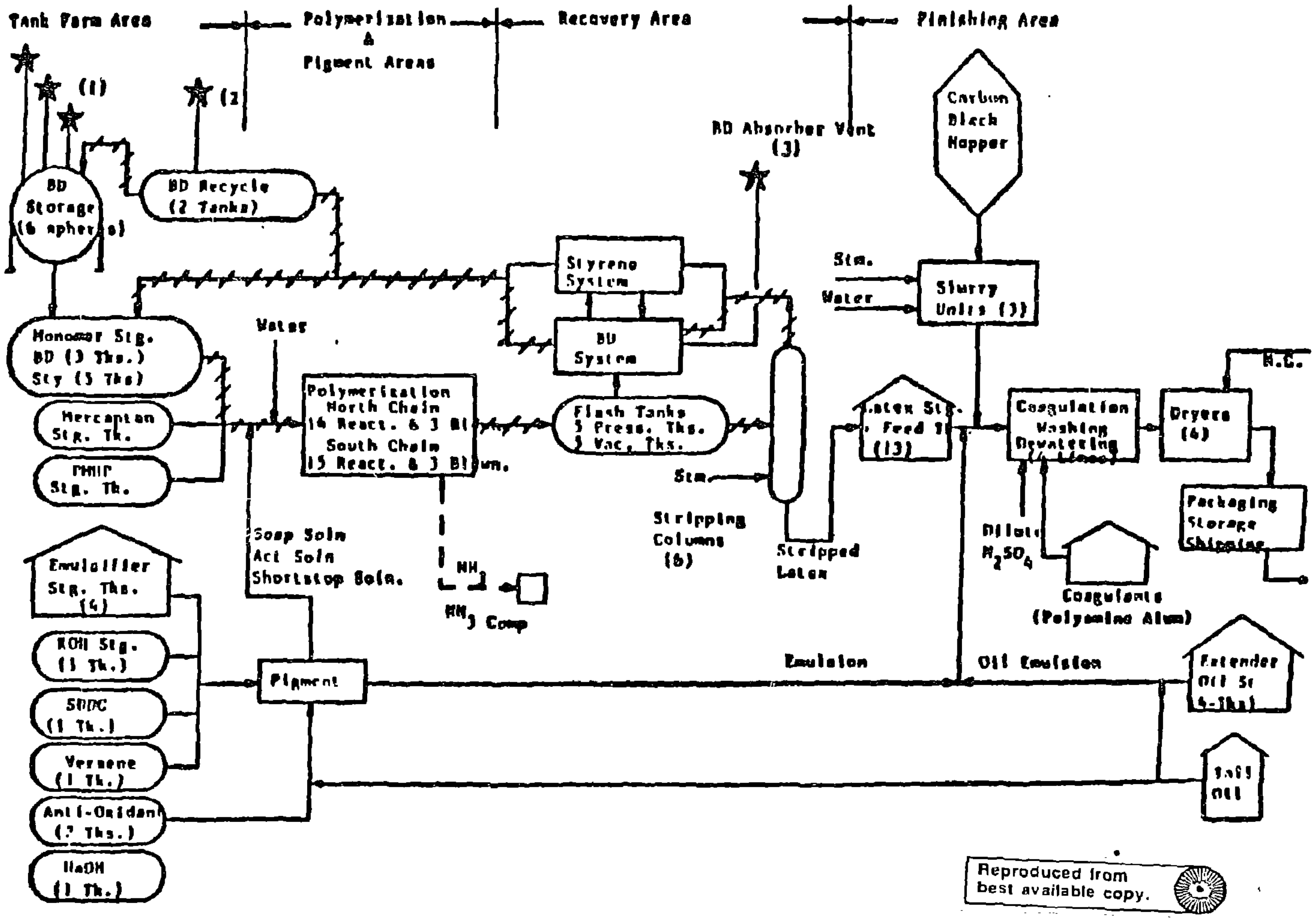

Figure 1. Process flow diagram for production of SBR at Plant A.

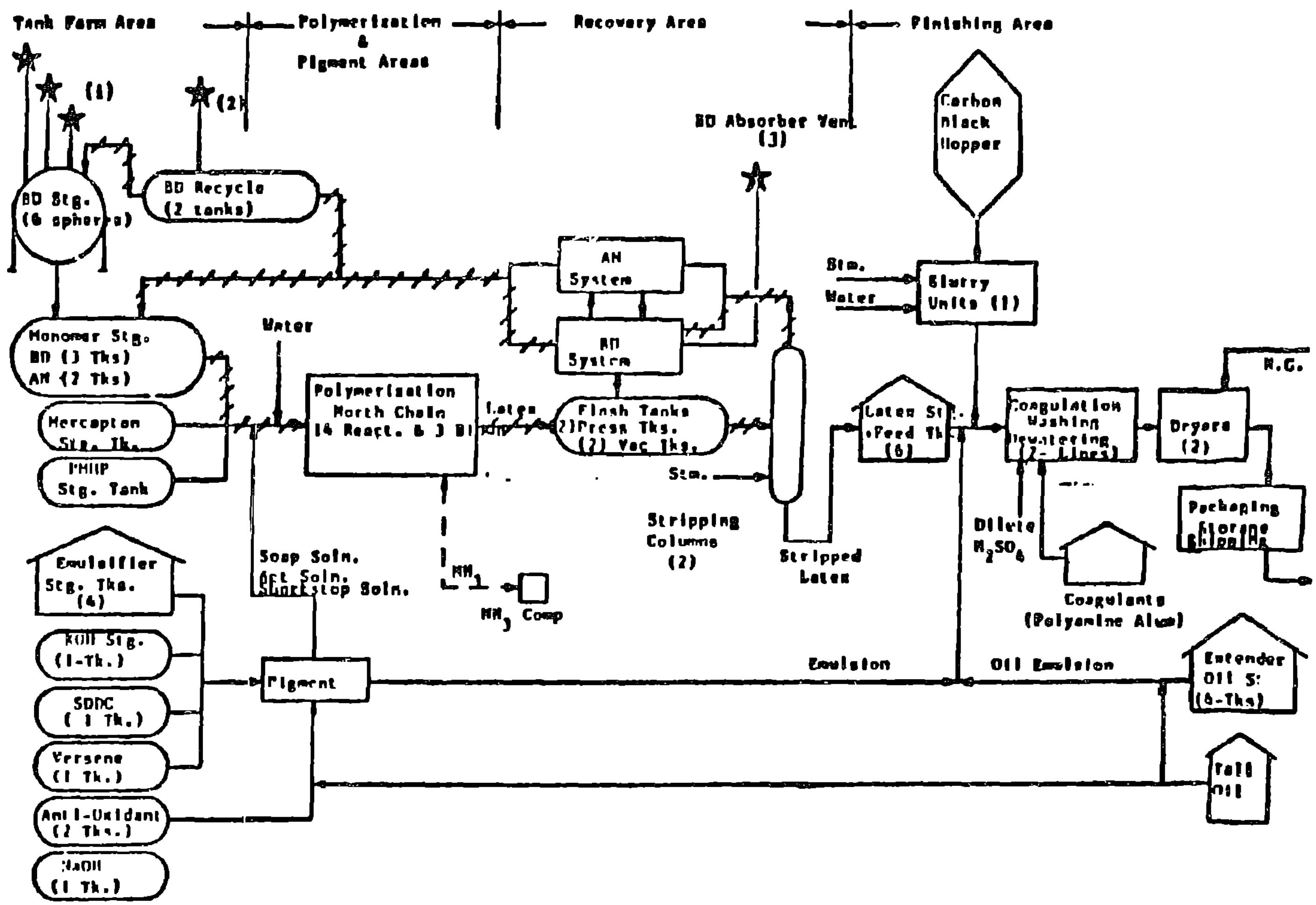

Figure 2. Process flow diagram for production of NBR at Plant A.

In the finishing process area, the stripped latex is temporarily stored in surge tanks prior to entry into the final finishing processes. In the finishing area, latex, oil, carbon black, and antioxidant are blended and coagulated to form a product in crumb form. The crumb rubber is dewatered mechanically before being sent to thermal dryers for complete water removal. The product is then pressed into 90-pound bales and crated for shipment. The SBR product constitutes approximately 43 weight percent reacted 1,3-butadiene, whereas the NBR product contains approximately 40 weight percent reacted 1,3-butadiene.

The products are stored in either onsite or offsite warehouses. Transportation to the customer is by ship, rail, truck, air or United Postal Service.

Plant B

Figure 3 is the process flow diagram for production of adiponitrile. The 1,3-butadiene monomer is received by barge and pipeline. It is dried using molecular sieves and continuously fed to the pentenenitrile synthesis unit were it is reacted with hydrogen cyanide (HCN) and reportedly totally consumed. The resulting pentenenitriles contain parts-per-million concentrations of residual 1,3-butadiene at this point. The pentenenitriles may be sold commercially or refined further on-site. On-site processing begins with distillation for use in the next reaction, dinitrile synthesis. In the dinitrile synthesis unit, the mononitriles are further hydrocyanated for conversion to dinitriles. The resulting mixture of 6-carbon dinitriles is refined by distillation. The final product, ADN, a colorless liquid with the viscosity of water, is stored in tanks and then pumped via pipeline to the HMDA unit for hydrogenation.

Most of the byproducts produced are burned in a boiler due to their fuel value. One of the mononitrile byproducts is sold as a commercial product. 1,3-butadiene content of this material is reported by the plant to be non-detectable by standard laboratory analysis which has a limit of detection of 200 to 400 ppm by weight.

All ADN produced at the plant is stored in nitrogen-padded storage tanks equipped with both conservation and emergency vents. Normal operating pressure is 4 inches of water. All process equipment is totally enclosed; process vapors are exhausted to a flare stack for burning.

Plant C

Production of SBR and PBR is carried out on the same process line; the major difference is that PBR production does not use styrene. The 1,3-butadiene is received via pipeline from barge loading docks. In the production process (see Figure 4), 1,3-butadiene and the solvent (a paraffinic hydrocarbon) are purified in fractionating columns, then blended with styrene and polymerized in the presence of a catalyst in a reaction vessel. After a reaction period, the resulting slurry (cement) may be treated with an extender oil depending on

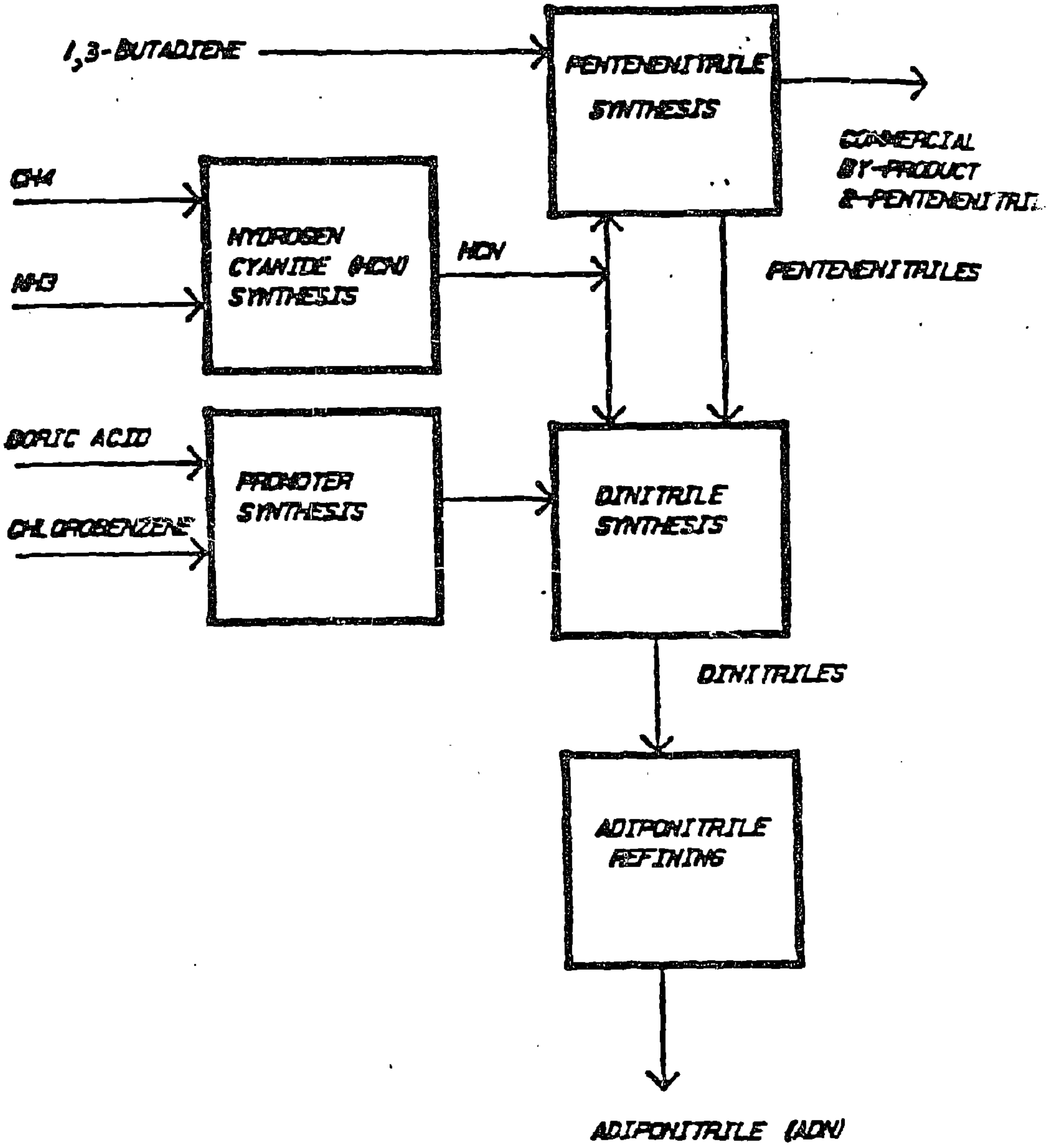

Figure 3 Process flow diagram for production of adiponitrile at Plant B.

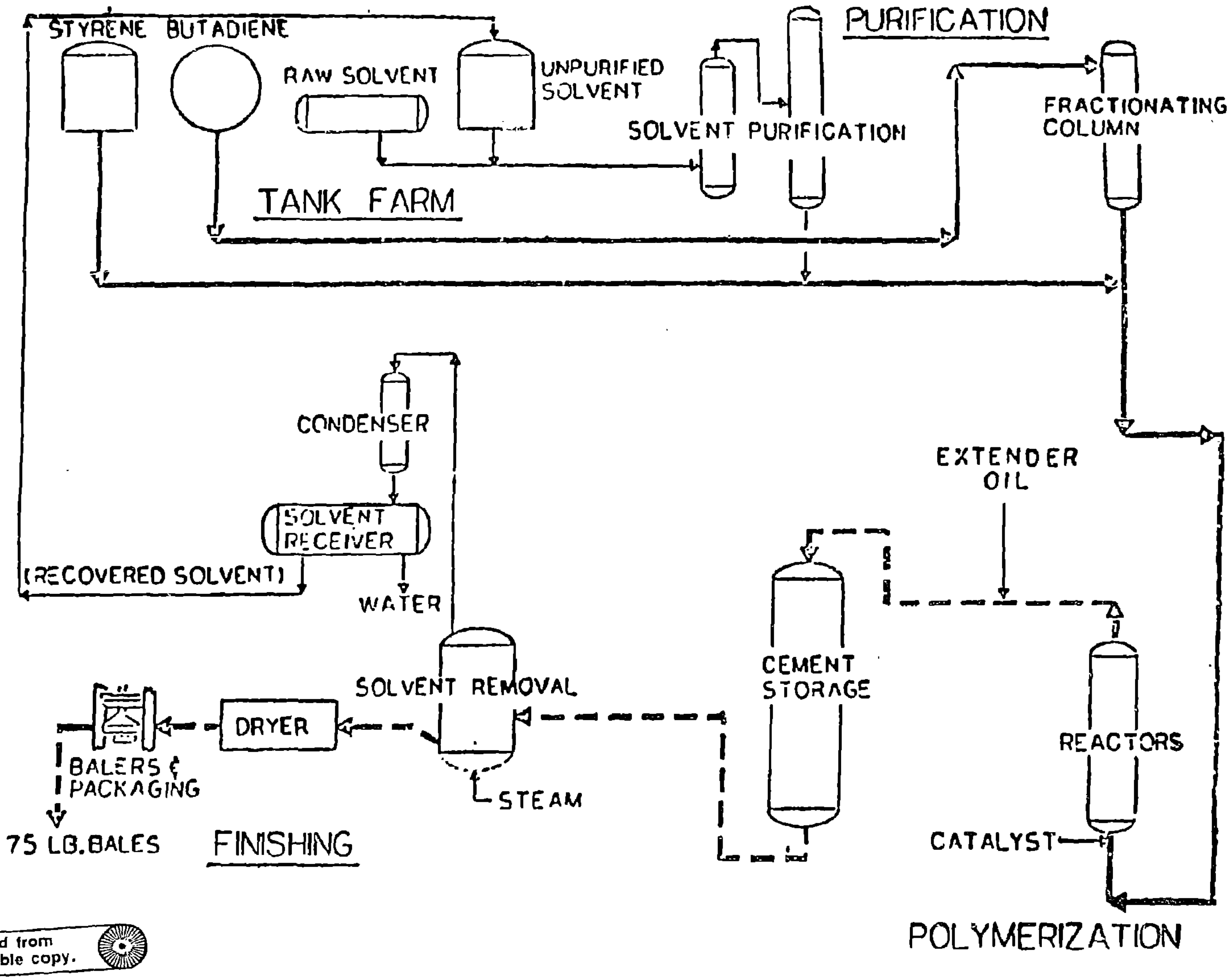

Figure 4 Process flow diagram for production of SBR at Plant G.

the desired end product. In the solvent recovery area, the paraffinic hydrocarbon solvent is driven off by steam and recovered. The rubber cement product is sent to finishing where it is dried into a crumb, and compressed into 75-pound bales, wrapped in film and crated for shipping.

In the production of vinyl pyridine latex (VPL) (see Figure 5), styrene, 1,3-butadiene catalyst, and soap solution are combined with vinyl pyridine monomer in a reaction vessel. After the reaction period, the unreacted 1,3-butadiene is flashed off and recovered, and the VPL production stabilized for storage. Shipment of latex is either by tank truck or rail tank car.

Plant D

Figure 6 is a process diagram for the production of chloroprene, the monomer used to produced polychloroprene rubber. In the production of chloroprene, 1,3-butadiene and chlorine are heated and combined in a vapor phase reactor to produce dichlorobutenes (DCB). Two DCB isomers, 1,4-dichloro-2-butene (1,4-DCB) and 3,4-dichloro-1-butene (3,4-DCB) are produced in the reaction. Unreacted 1,3-butadiene is removed in a degassing column and the DCB mixture is sent to an isomerization separator where it is converted to the 3,4-DCB isomer. Unit operations through the 3,4-DCB isomer separation step represent the dry end of the chloroprene monomer production process. In the next reactor, 3,4-DCB isomer is treated with caustic solution (NaOH), undergoing dehydrohalogenation (removal of HCl) to chloroprene. This represents the wet end of the monomer production process. Figure 7 shows a process flow diagram for the polymerization and finishing of neoprene rubber. Chloroprene, or 2-chloro-1,3-butadiene, goes through emulsion polymerization to form polychloroprene or neoprene. At this point, the polychloroprene latex can be drummed as a product for subsequent use in coatings or the latex can be finished by coagulation, drying, and roping to produce neoprene polymer chips, which are used in automotive, industrial, and mechanical goods. Approximately 10 different grades of neoprene are produced at Plant D. The neoprene production process consumes an estimated 38 million pounds of 1,3-butadiene per year.

In the production of THPA (Figure 8), liquid 1,3-butadiene is pressure fed to a vaporizer where it is converted to a vapor. Vaporized 1,3-butadiene is pressurized to the reactor where reaction with molten maleic anhydride occurs. Maleic anhydride is consumed over a period of 6 to 10 hours. Residual 1,3-butadiene vapors in the head space of the reactor are vented to the atmosphere; the actual amount of 1,3-butadiene emitted is reported to be minor, since the reaction occurs in a stoichiometric manner. The product, molten THPA, is crystallized onto a chill roller at the bagging operation. Solidified THPA is cut from the roller by a doctor blade into a weighed container, either a bag or a drum.

Plant E

Plant E produces SBR, SB latex, and NBR by emulsion co-polymerization. The same process equipment is used for the manufacture of the three products.

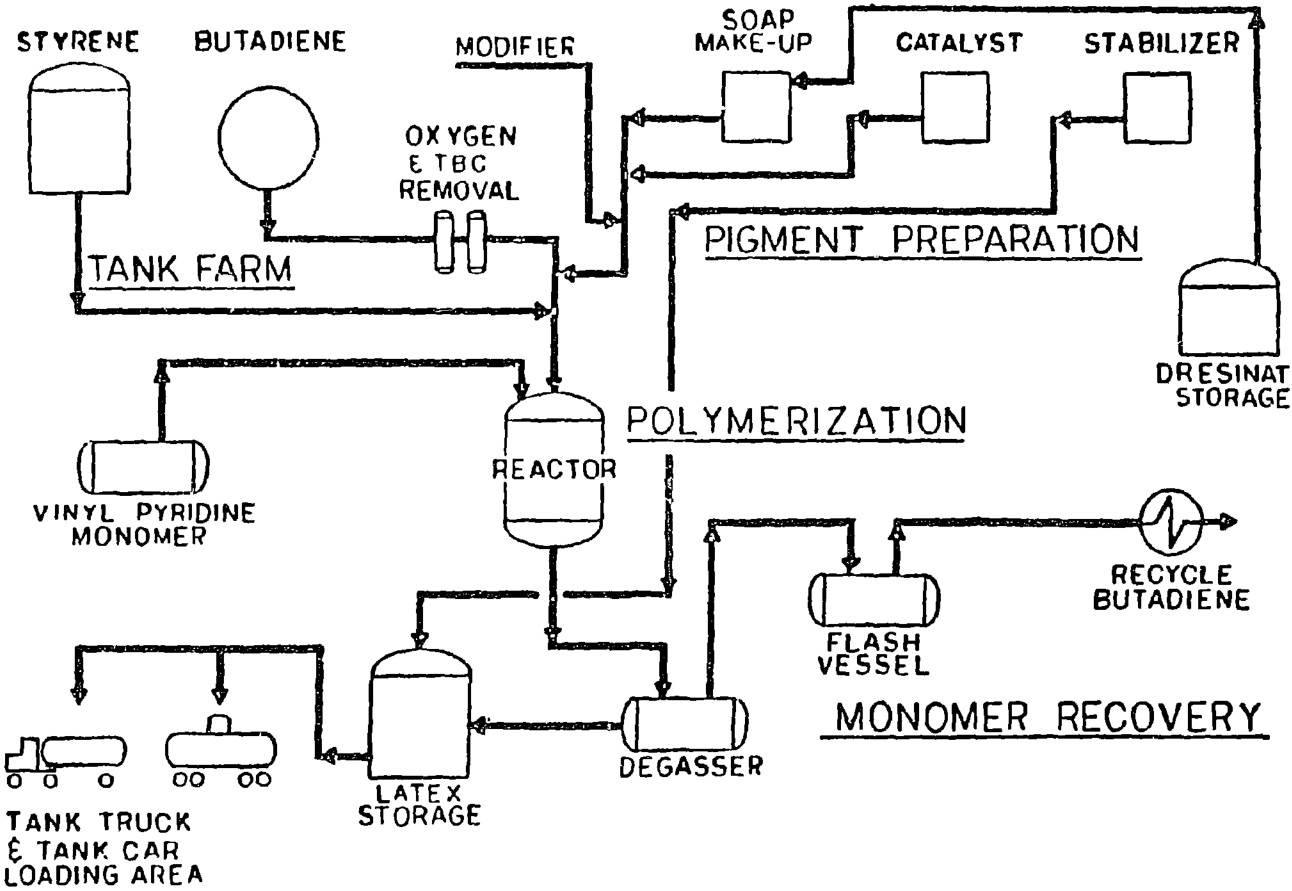

Figure 5 Process flow diagram for production of vinyl pyridine latex Plant C.

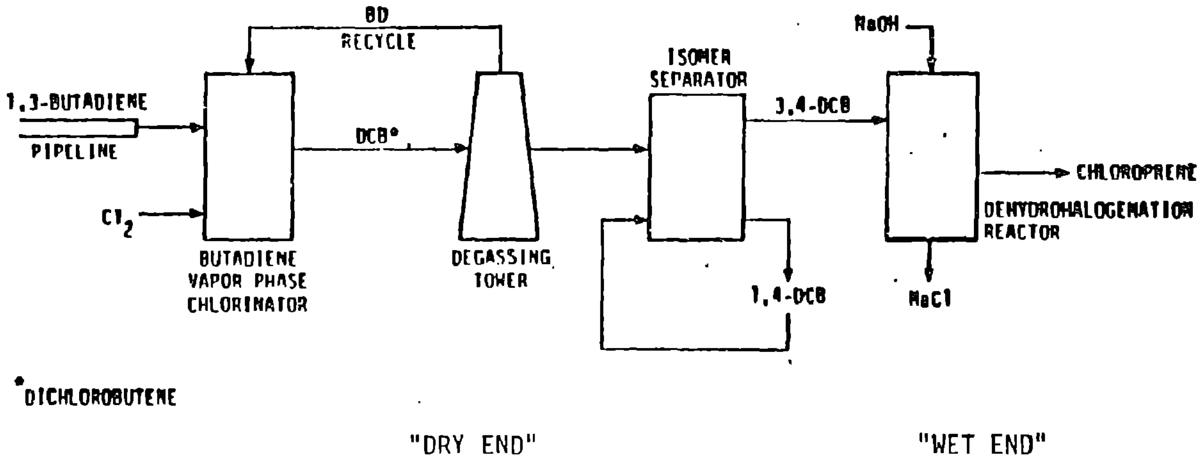

Figure 6 Process flow diagram for production of chloroprene monomer in the neoprene rubber production process at Plant D.

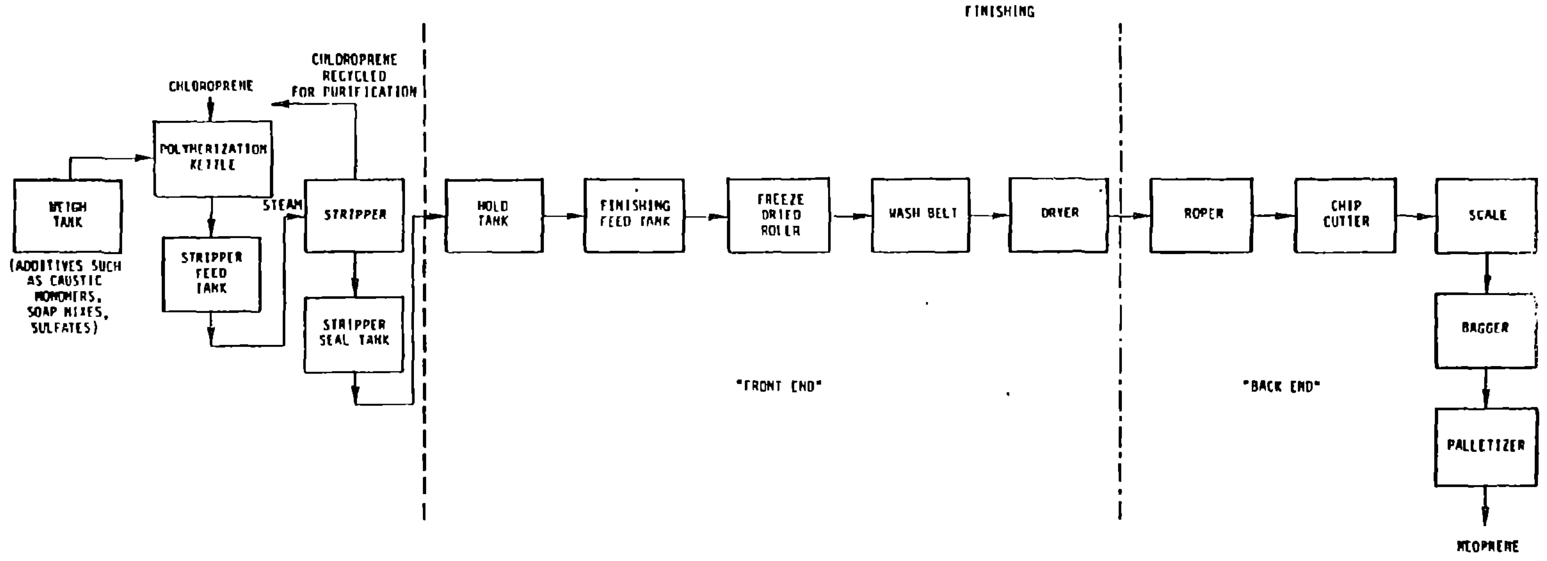

Figure 7 Process flow diagram for polymerization and finishing of neoprene rubber at Plant D.

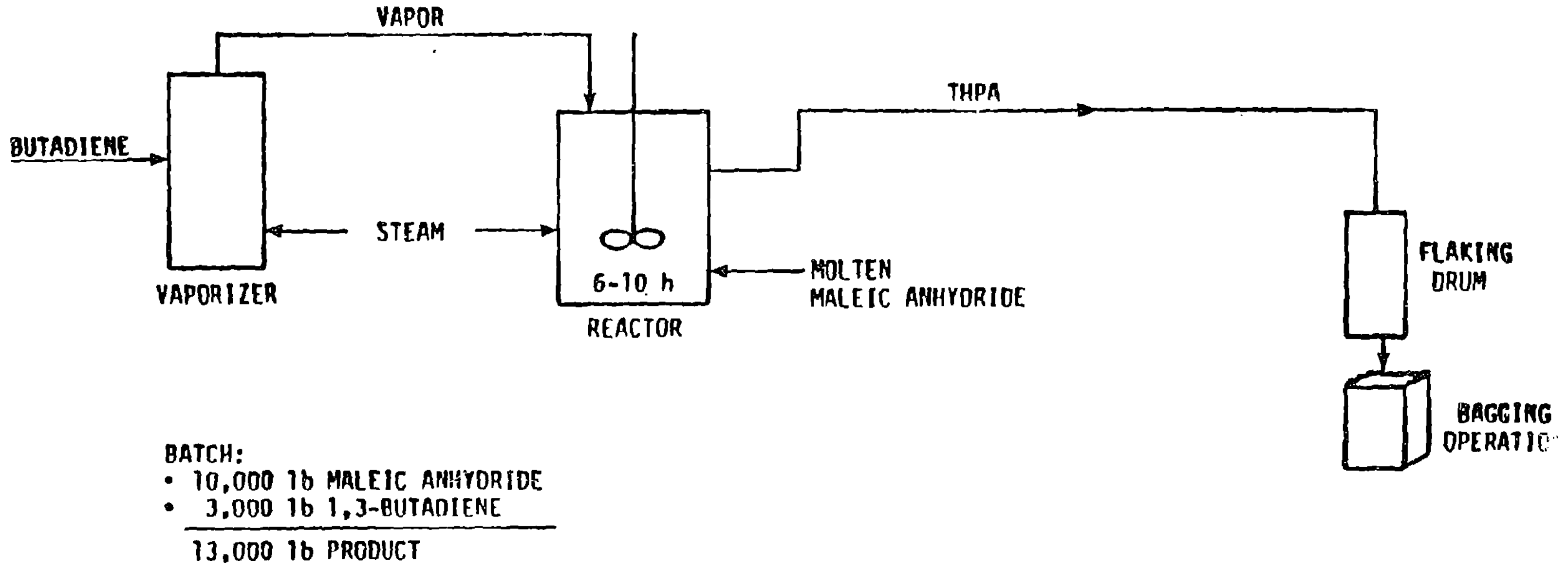

Figure 8 Process flow diagram for the production of tetrahydrophthalic anhydride (THPA) at Plant D.

Figure 9 depicts Plant E's SBR and SB latex production processes. Production of NBR is similar to SBR production except that acrylonitrile is substituted as a raw material instead of styrene. All 1,3-butadiene used for production is received at the plant by pipeline. Approximately 30 million pounds of 1,3-butadiene monomer are received per month.

In SBR production, the 1,3-butadiene monomer is pretreated to remove inhibitors by scrubbing with a caustic wash, followed by decantation. The uninhibited pure 1,3-butadiene is then blended with recovered 1,3-butadiene of lower purity from the vacuum flash tanks. Pure styrene (or acrylonitrile for NBR) is blended with recovered styrene (or acrylonitrile) of lower purity from the steam stripper.

A soap solution, activator, catalyst, and modifier are mixed with the uninhibited monomers prior to polymerization in the reactor. The soap solution acts as an emulsifier, and the activator provides free radical generation in the water phase. The catalyst facilitates the generation of free radicals at lower temperatures. The modifier controls the chain length and molecular weight distribution of the SBR and NBR.

The continuous polymerization process proceeds in a series of reactors providing flexibility in producing different grades of crumb rubber.

Reactors can be bypassed at any time if desired. The polymerization temperature in each reactor is regulated by internal cooling coils. The reaction product is a milky white emulsion (latex). In post-treatment, polymerization is stopped as the latex exits the reactors by the addition of a shortstop such as sodium dimethyldithiocarbanate. The "stopped" latex is held in blowdown tanks that serve as flow regulating holding tanks. The latex in the blowdown tanks is not completely polymerized and contains some unreacted monomers. It is fed continuously into two flash tanks where 1,3-butadiene is vaporized by reducing the pressure. The vapors are vented, compressed, and condensed for recycle. Any rejected 1,3-butadiene is returned by pipeline to the supplier. Styrene is then recovered from the latex by low-pressure steam stripping in a perforated plate column. The monomer-stripped latex is sent to a blend tank where it is stabilized by the addition of extender oil (optional) and antioxidant.

To complete the production of SBR, the stabilized latex is coagulated to remove water by the addition of a dilute acid and brine (coagulation liquor) in an agitated coagulation tank. The brine causes a "creaming" of the latex; this partial flocculation of the rubber particles causes the consistency of the latex to change from a mobile liquid to a heavy cream. The pH of the latex is adjusted by the addition of dilute sulfuric acid. The acid causes the soap molecules to convert to organic fatty acids and the rubber particles to agglomerate. The particles are then separated from the coagulation liquor on a shaker screen. The liquor is recycled along with fresh acid, and brine make-up is added as needed. The screened rubber particles are slurried with water and sent to the washing, drying, and baling portions of the process. The rubber product is boxed and stored in the plant warehouse.

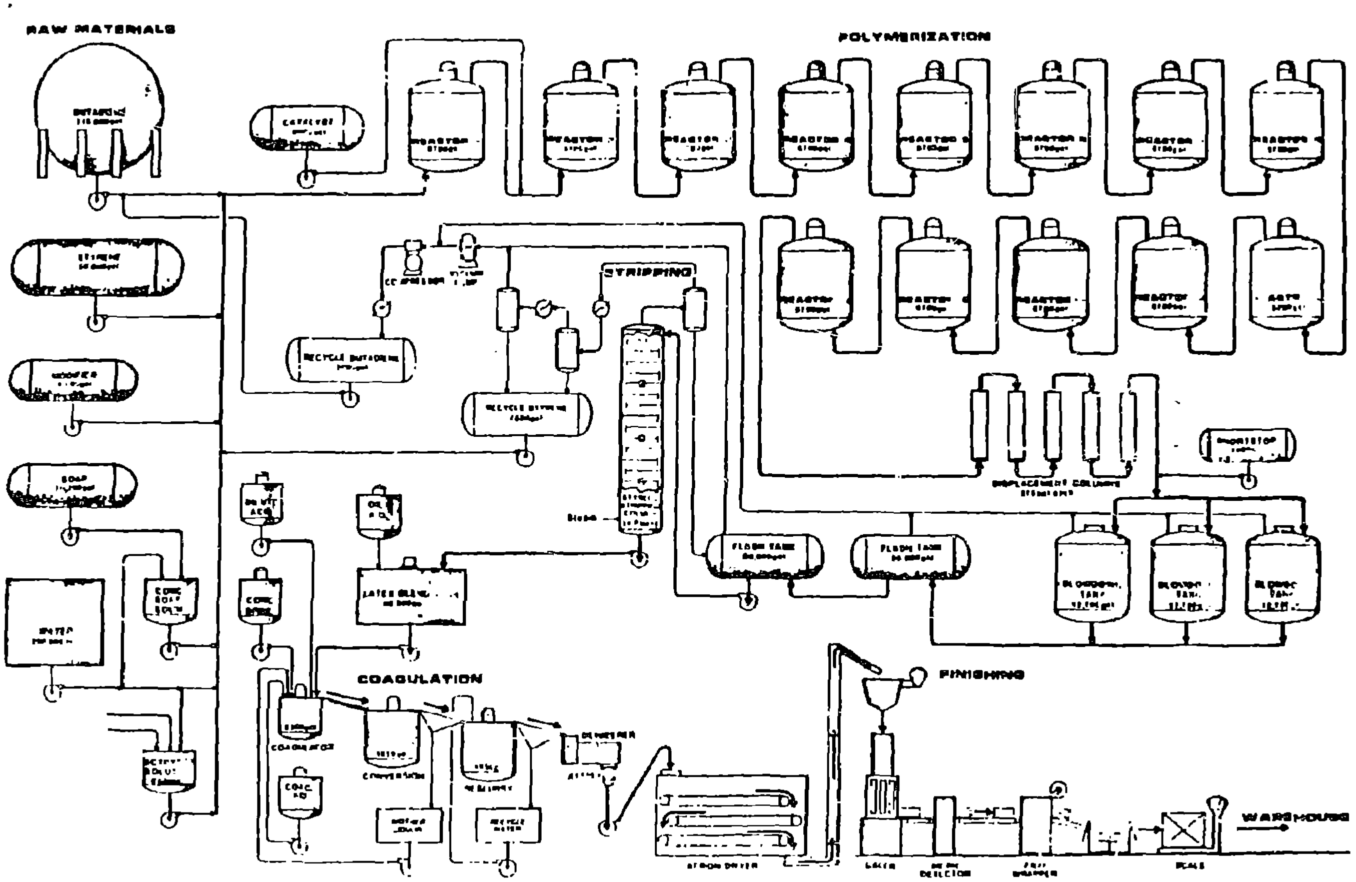

Figure 9 Process flow diagram for production of SBR and SB latex at Plant E.

WORKFORCE CHARACTERIZATION

A generic job classification scheme has been developed so that individual plant job descriptions could be grouped into similar exposure categories. The following is a detailed description of the generic job classifications. The discussion of these job classifications is essential to understanding the NIOSH survey results presented in Tables 13-25. This was necessary because of the wide variety of job classifications among the different plants. The generic job classifications were developed by grouping the jobs according to the areas within the plant.

Process Technician-Barge Unloading Area

These process technicians are responsible for operations involving unloading of butadiene barges. Duties include connecting hoses through which the butadiene is transferred, monitoring the level in the vessel being unloaded, and taking quality control (QC) samples of incoming 1,3-butadiene. Under normal conditions, the barge unloading process takes approximately 24 hours to complete.

Process Technician-Tank Farm

Tank farm process technicians are responsible for receiving, storing, and distributing butadiene and other raw materials. Duties include: monitoring the gauges, temperatures in the process and the tank farm area; monitoring the flow of materials from tank cars or pipelines to the tank farm and to the production areas; and occasionally obtaining QC samples from the storage tanks. Activities which result in high potential for exposure include monitoring the flow of 1,3-butadiene from tank cars to the tank farm and obtaining quality control samples.

Process Technician-Purification or Recovery

These process technicians are responsible for the day-to-day operation of the purification or recovery (stripping) stage of the process area. Duties include: control and monitoring of the purification recovery process; collection of quality control samples from this process stage; decontamination of purification recovery equipment prior to maintenance; and monitoring pipes, lines and purification recovery vessels. Activities which result in high exposures to butadiene include QC sampling and decontamination of equipment.

Process Technician-Polymerization or Reaction

These process technicians are responsible for the day-to-day operation of the polymerization reaction stage of the process area. Their duties and activities are analogous to those of the process technician-purification recovery as they apply to the polymerization or reaction area. Exposures in this group appear to be somewhat lower than those for the process technician-polymerization reaction since they spend spend a higher percentage of their time in an enclosed, ventilated control room.

Process Technician-Solutions and Coagulation

These process technicians are responsible for control and monitoring of the mixing and transfer of solutions in the coagulation stage of the process area. Duties include: mixing, storing, and disbursing solutions to the coagulation operations; monitoring the operation of coagulation pumps and flow equipment; cleaning the coagulators and associated equipment; and obtaining quality control samples from the coagulation streams. Exposures in this group are generally low because most of the unreacted butadiene has been removed from the product in the earlier purification and recovery reaction. Activities which result in butadiene exposures are QC sampling and cleaning of coagulation equipment.

Process Technician-Crumbing and Drying

These process technicians are responsible for control and monitoring of the crumbing and drying stage of the process area. Duties include: maintaining all crumbing and drying process equipment; operating the dryers; monitoring the dryers for speed, crumb size, temperature, and buildups; and obtaining QC samples from the final product. Exposures in this group are generally low because most of the unreacted butadiene is removed from the product in the purification and recovery reaction.

Process Technician-Packaging

These process technicians are responsible for monitoring and operating the baling and packaging of the final product. Duties include: wrapping blocks of product in plastic; assembling blocks on pallets; packing bales in boxes or bags; and collecting QC samples of the product. Because the product is at room temperature when it is handled by these process technicians, exposures in this group are minimal. The primary determinant of exposure is frequently the proximity of the baling and packaging equipment to the dryer or reaction process areas.

Process Technician-Warehouse

These process technicians are responsible for transporting product packages to the warehouse by fork lift for storage. Exposures are low in this group because the product is at room temperature and is packaged.

Process Technician-Control Room

These process technicians are responsible for the overall operation and productivity of the polymerization facility. Duties include: implementing written production orders; overseeing activities in the polymerization (reactor), purification (recovery), and finishing areas (solutions and coagulation, crumbing and drying, and packaging); and conducting periodic supervision of production and maintenance activities. Because the majority of their time is spent either inside the enclosed and ventilated control room in the reactor and recovery areas or outside of these areas altogether, exposures in this occupational group are generally low. Those activities which increase the technicians exposure include troubleshooting, conducting routine inspections, and supervising maintenance activities.

Laboratory Technician-Laboratory

The laboratory technician is responsible for collecting and/or analyzing quality control samples of raw materials, intermediate products and solutions, and finished product. The level of exposure is highly dependent on the manner in which these activities are conducted, and on the ability of the laboratory ventilation equipment to remove releases of butadiene both in the hood and from the general laboratory area.

Maintenance Technician

The maintenance technician is involved in the scheduled and unscheduled maintenance and repair of equipment in all areas of the plant. This group includes machinists, electricians, pipefitters, welders, and others performing a variety of craft-specific activities. In many cases exposure is limited to the ambient concentrations typical of those in the particular process area. In other cases, however, maintenance technicians must work in close proximity to or actually inside the reactor or recovery vessels. While these vessels would have been decontaminated prior to any tank entry, the sustained release of butadiene from polymeric residues lining the interior of the vessel would ensure a continued high level of exposure inside such vessels. Maintenance technicians generally wear an air-purifying respirator while performing maintenance operations. Therefore, while their potential butadiene exposures are high, their actual exposures are dependent on respirator usage and worker practice. The butadiene exposure to members of this group is generally considered to be intermittent.

Utilities Operator

The utilities operator group includes those workers who are not directly involved in process operations but who may have limited potential exposure to butadiene because they are working at the polymer plant facility. Included in this group are environmental control operators, utility pump house operators, and equipment inspectors. Exposures in this group are considered to be low because the workers are not directly involved with butadiene-associated process operations.

Plant A

The company employs 470 persons which include personnel involved in plant operations, ancillary corporate operations, and research and development. Of the 470 employees, 437 have potential exposure to 1,3-butadiene.

One-hundred and forty-three (143) employees spend their entire workshift potentially exposed to 1,3-butadiene 8 hours per day. An additional 294 employees are potentially exposed intermittently to 1,3-butadiene.

The plant operates round-the-clock, 24 hours per day, 365 days per year. Four crews rotate through 3 shifts/day on a 28-day cycle. Maintenance and administrative personnel work day shift only.

Job descriptions for employees potentially exposed to 1,3-butadiene that were sampled by NIOSH are as follows:

Reactor/Recovery Area

Leaderman	Senior operator and lead operator for area. Monitors instruments, pumps, and levels in caustic tank, 1,3-butadiene feed tank, and 1,3-butadiene separator. Monitors equipment at the north end of the recovery unit. Checks safety equipment and safety valves once a week. Monitors absorber/desorber vent flow and 1,3-butadiene continuously.
Tank Farm Operator	Monitors gauges, temperatures, and levels of all equipment and tanks at least twice per shift. Loads and unloads all raw materials, including 1,3-butadiene. Prepares vessels, lines, and pumps for maintenance work. Responsible for maintenance work permits. Oils pumps as necessary. Switches tanks on recycled 1,3-butadiene as necessary.
Reactor No. 1 Operator (Control Room)	Monitors process at control panel; inside control room for 60 percent of the shift. Rotates feed pumps daily, checking to make sure they are ready for service. Inspects relief valves and rupture discs once per week.
Reactor No. 2 Operator	Checks reaction conditions, pump seals, etc. Checks ammonia level in reactors several times per shift. Assures that all agitators are running and shortstop valves are closed. Checks shortstop levels in tanks at least four times per shift. Evaluates blowdowns to recovery once per shift. Blocks off all lines and process pumps prior to maintenance operations. Takes process equipment in and out of service.
Pigment Operator	Prepares emulsifiers and charge makeup solutions. Checks and lubricates pumps in the pigment building once per shift. Monitors tank levels in the pigment building. Spends 98 percent of the shift in a pressurized building.
Recovery No. 2 Operator	Inspects all columns in service for vacuum readings, latex levels, etc. Monitors charts in recovery control room for column flows, flash tank levels, pressure and vacuum instruments, and blowdown levels. Rotates column charge pumps. Checks seal to all pumps, vacuum pumps, and compressors at the start of each shift and as required. Blocks off lines and process pumps prior to maintenance operations. Pressure tests columns coming back into service.

Reactor/Recovery Operator	Obtains solid QC samples and residual styrene QC samples and transports them to the appropriate laboratory. Obtains QC samples on both streams for raw viscosity and transports them to the rubber laboratory (once per hour). Switches vacuum pumps and compressors. Checks temperature of 1,3-butadiene condensers twice per shift.

Finishing Process Area

Leaderman (Coagulation Operator)	Lead operator in latex coagulation area. Calibrates pH and coagulation tanks. Checks acid for specific gravity. Checks temperature in coagulation tank. Obtains latex QC samples from coagulation streams.
Dryer Operator	Operates two fluid bed units and two tray/apron driers. Monitors the dryer for speed, crumb size, temperature, and buildups. Checks pH and temperature. Maintains oil levels in the process equipment. Obtains QC samples on all latex tanks.
Baler Operator	Compresses polymer crumb into 75- and 90-pound bales; applies coating and film wrap. Checks metal detectors. Checks oil levels on hydroquips and film wrappers. Obtains QC samples from all units once per hour.
Hogman	Operates rerun rubber on the "hog". Operates the hot rod. Assists cleanup operators in cleaning the pit and the dryers.
Packager (Utility)	Packages and palletizes rubber. Inspects packages for vacuum seal and abnormalities. Removes plug-ups. Occasionally carries QC samples of product to the laboratory. Performs housekeeping duties around the soapstone tank.
Fork Lift Operator	Transports product packages to warehouse. Transports rerun rubber to the "hog". Transfers soapstone to makeup tanks and loads it.
Clean-up Operators (Utility)	Cleans the spin dryers, the area around the hammermill, and the soapstone bin. Performs housekeeping duties. Digs out the baler pit.
Vacation Relief Operator	Trained in all jobs.

Utilities

Power House Operator	Operates power house and associated equipment. Responsible for equipment such as demineralizer units, pumps, valves, neutralizers, etc. Performs housekeeping duties inside and outside of the power house building. Responsible for the turbogenerator and instruments associated with the boiler and dilute acid-making system in the power house.
Utility Pump House Operator	Operates the large ammonia compressors, all plant air compressors, cooling tower pumps and fans, and the domestic sewer unit.
Environmental Control Unit Operator	Operates all equipment associated with the dissolved air flotation unit, equalization basin, aeration basin, clarifiers, and other miscellaneous facilities associated with waste water treatment operations. Assists with unloading cationic chemicals and other chemicals. Operates incinerator for non-hazardous liquid and solid waste.
Fireman	Checks process equipment for leaks and repair permits.

Laboratories

Hydrocarbon Laboratory Technician	Obtains cylinder samples. Also obtains vapor samples from the top of 1,3-butadiene spheres once a week. Conducts gas chromatograph analyses on 1,3-butadiene QC samples.
Control Laboratory Technician	Conducts laboratory analyses on unstripped latex QC samples.
Rubber Laboratory Technician	Conducts laboratory analyses on stripped latex and rubber QC samples.
Maintenance	This includes various craftsmen such as pipefitters, boilermakers, machinists, electricians, and utility men.

Plant B

Plant B employs 2,100 people of which 305 (15 percent) are dedicated to ADN production. The majority of the employees, 210 of 305, work 8-hour day shifts which include some day shift mechanics. The production employees (95) work 12-hour rotating shifts. The nitrile area of the ADN process employs a total of 124 employees: 36 production (12-hour shift) workers and 88 (8-hour) day workers. (This is an area which Plant B identified as having potential for 1,3-butadiene exposure.) Only four employees per day (two process operators and two mechanics, one of each per shift) work in the Step I pentenenitrile synthesis area, where 1,3-butadiene is brought in as a raw material and is consumed in the synthesis reaction. ADN production-related job descriptions for potentially exposed employees are as follows:

Tank Farm Operator	Responsible for monitoring the storage tanks. Obtains QC samples form the storage tanks.
Outside Operator	Responsible for monitoring the equipment at the tank farm and at the multi-purpose storage tanks. Transfers QC samples to the laboratory. Drives truck and runs errands in the ADN production.
Synthesis Operator A (Step I Operator)	Responsible for monitoring the 1,3-butadiene equipment and the synthesis equipment for pentenenitrile synthesis. Obtains QC samples from the reactors. Decontaminates equipment prior to maintenance operations.
Synthesis Operator B (Step II Operator)	Responsible for monitoring the equipment for dinitrile synthesis. Checks for leaks on pumps. Obtains QC samples. Decontaminates equipment prior to maintenance operations.
ADN Recovery Operator	Responsible for recovery equipment. Obtains QC samples from this equipment.
ADN Refining Operator	Works in ADN product refining area. Obtains QC samples from the refining system and from the product storage tanks. There are a total of two operators per shift in the east and west sections of the refining area.
HCN Boiler Operator (Power Operator)	Responsible for monitoring the flame arrestor, refrigeration unit, and condensate receivers in the HCN area. Regenerates 1,3-butadiene molecular sieves. Obtains QC samples of the feed water and the blowdown from the boiler.
Control Room Operator	Responsible for monitoring the control room equipment.
Tankerman	Responsible for operations involving unloading of 1,3-butadiene barges. Conducts barge sampling and stripping. Seventeen of the twenty-three qualified operators are licensed "tankermen," having passed the necessary examinations that qualifies them for handling 1,3-butadiene barges.
Laboratory Technician	Performs gas chromatographic and wet chemical analyses of the 1,3-butadiene QC samples.

Maintenance Technician	Responsible for maintenance and repair of process equipment. Connects and disconnects barges for 1,3-butadiene unloading.

The workforce is 88 percent male. The turnover rate is estimated to be less than 3 percent, indicating a stable workforce. The mean age of the employees is 38.7 years.

Plant C

The company employs a total of approximately 300 personnel; of these, 101 are potentially intermittently exposed in the 1,3-butadiene polymer production process.

Production of SBR and PBR is carried out 24 hour/day, 365 days/year. Production of VPL is carried out in 24 hours/day campaigns, as necessary to meet sale demand. Four work crews rotate on a 28-day cycle, covering 3 (8-hour) shifts per day. Maintenance personnel are scheduled only on the day shift, except as required on the other shifts.

Job descriptions for employees potentially exposed to 1,3-butadiene are as follows:

A Operator-200 Area	Controls the operation of the purification unit and tank farm.
B Operator-200 Area	Assists A Operator in tank farm area.
A Operator-Reactor Area	Maintains control of reactor area.
B Operator-Reactor Area	Assists A Operator in the reactor area; operates pumps and valves.
B Operator-Process Area	Operates the dewatering equipment and dryer in process area.
B Operator-Crumbing Area	Monitors crumbing of rubber and flashing of hydrocarbons.
Baler Operator	Operates on the dry end of the dryer. Operates baling machine.
Hogman	Processes reclaimed SBR.
Sumpman	Cleans the dewatering area, plugged equipment, and sumps.
Crate Driver	Operates gas fork-lift truck. Delivers crates to the production area.

Crate Maker	Builds crates. Works south of the plant.
Rubber Loader	Places finished bales into crates. Works in the dryer building.
Film Wrap Operator	Operates the film wrap machine. Works in the same location as the rubber loader in the dryer building.
Production Puller	Transfers finished product to warehouse storage.
Chemical Laboratory Technician	Maintains quality control and testing of solvents.
Field Laboratory Technician	Obtains quality control samples from reactor.
Water Laboratory Technician	Maintains quality control and testing of outgoing water.
Physical Laboratory Technician	Completes physical tests of the field lab samples and of the finished product.
Pipefitter	Responsible for blinding pipes and removal of pressure relief valves in the tank farm/reactor area. Repairs pipe.
Boilermaker	Changes strainer pots in crumbing area.

Plant D

Of the 289 employees at Plant D, 186 are production/wage personnel and 103 are salaried. Table 4 shows the distribution of the wage employees by area; maintenance employees are responsible for the entire plant.

Table 4. Workforce Distribution at Plant D

Area.Location	Number of Employees
Neoprene plant (monomer, polymerization, and finishing areas)	83
Maleic anhydride plant	11
Quality Control Laboratory	12
Storehouse	4
Maintenance	
Craftsmen	55
Laborers	14
Trainees	7
Total	186

In the production of neoprene, employees in the dry end of the chloroprene monomer process area have a greater potential for exposure to 1,3-butadiene than employees in the wet end of the monomer area, and the polymerization and finishing areas, since 1,3-butadiene has been stripped from chloroprene in the latter process stages. Nineteen employees (16 operators, 1 day helper, and 2 supervisors) work directly with DCB during production of chloroprene.

In the production of THPA, employees are potentially exposed to 1,3-butadiene as a raw material. A total of seven employees (three operators and four warehousemen) work in the maleic anhydride plant where THPA is produced.

The plant operates 24 hours/day, 365 days/year. Four work crews rotate on a 28 day cycle, covering three 8-hour shifts/day. Maintenance personnel work mainly on the day shift.

Job descriptions for employees potentially exposed to 1,3-butadiene are as follows:

Neoprene

Tank Farm Operator	Unloads raw materials (e.g., chlorine, caustic), and controls the operation of the tank farm. Loads truck shipments of waste DCB byproduct for recovery.
Head Operator-Monomer Area	Supervises the chloroprene monomer production unit. Monitors the board in the control room.
Dry End Man-Monomer Area	Operates chlorination, purification, and DCB isomerization units. Performs decontamination of process equipment. Conducts QC sampling for 1,3-butadiene, DCB, and chlorine.
Wet End Man-Monomer Area	Operates chloroprene side of the monomer production process. Performs decontamination of process equipment. Alternates QC sampling of 1,3-butadiene with dry end man every other day.
Head Operator-Polymerization Area	Supervises the polymerization process.
Assistant Operator-Polymerization Area	Mixes chemicals for coagulation. Monitors level in tanks. Operates polymerization and coagulation units.
Helper-Polymerization Area	Assists the polymerization area assistant operator.
Head Operator-Finishing Area	Supervises the neoprene finishing process.

Assistant Operator-Finishing Area	Operates the neoprene finishing process.
Front End Helper-Finishing Area	Assists the finishing area assistant operator on the front end of the neoprene finishing process through the drying step.
Back End Helper-Finishing Area	Assists the finishing area assistant operator on the end of the neoprene finishing process from roping through palletizing.
Head Shift Tester-QC Laboratory	Performs gas chromatographic analyses of DCB and 1,3-butadiene samples. Responsible for voiding and cleaning of sample bombs after analyses are completed. Performs physical tests on neoprene samples.
Special Lab Tester-QC Laboratory	Performs DCB distillation tests. Operates pilot unit for polymerization and finishing processes located outside QC laboratory.
Lab Tester-QC Laboratory	Performs wet chemistry analysis on DCB and 1,3-butadiene samples.
Pipefitter-Polymerization Area	Maintenance of pipe on strippers and other units in polymerization area.
Utility Man-Polymerization Area	Conducts janitorial duties in polymerization area.

THPA

Assistant Operator	Charges reactor with raw materials. Monitors process conditions. Flakes product. Performs decontamination of process equipment.
Warehouseman	Weighs and packages product material. Stores inventory in the warehouse. Loads truck shipments for delivery.

Plant E

There are a total of 658 employees at Plant E. The plant operates 24 hours a day, 7 days a week, 52 weeks a year. Four shifts work on a 28-day rotation schedule. Plant E estimates that a total of 466 employees are involved in the handling of the 1,3-butadiene monomer or polymers. A total of 53 personnel are employed in the tank farm, reactor, and recovery areas, where the concentrations of 1,3-butadiene are expected to be potentially higher than in other areas of the plant. For the purpose of clarification, the finishing area process operators in the NIOSH data base are the solutions operator, coagulation operator, dryer operator, baling operator, sacker, and warehouseman.

Job descriptions in the areas which are potentially exposed to 1,3-butadiene are as follows:

Tank Farm Operators	Duties consist of receiving, storing, and distributing monomers and other raw materials. Responsible for monitoring flow of materials from tank cars or pipelines to tank farm and to production areas.
Material (Pigment) Preparation Operators	Duties consist of preparing solutions and dispersions of chemicals for use in the synthesis and processing of synthetic rubber latex.
Reactor Operator	Duties consist of polymerizing raw materials to produce synthetic rubber latex by charging and operating a bank of higher pressure reaction vessels. Cleans and prepares reactors.
Monomer Recovery and Purification Operator	Duties consist of recovery of unreacted monomers from synthetic rubber latex by circulating latex through a continuous system of vacuum flash tanks and steam stripping columns. Withdraws 1,3-butadiene vapors using a two stage flashing system.
Solutions Operator	Duties consist of receiving latex and oil, making up blends and antioxidant, and storing and disbursing ingredients to the coagulation operations.
Coagulation Operator	Duties consist of operating pump and flow control equipment to assure flow of latex to rubber crumb area for drying. Cleans the coagulators, conversion tanks, reslurry tanks, feed boxes, and connecting troughs.
Dryer Operator	Duties consist of operating the dryers that dry the final rubber product.
Baling Operator	Duties consist of conveying, weighing, baling, coating, and packaging of finished rubber. Responsible for quality control of the finished product.
Sacker	Duties consist of placing bale or crumb in bag, sewing bag shut, and packing in shipping container. Assists baling operator in disposal of rejected rubber. Also responsible for clean-up of the finishing area.
Clean-up Operator	Duties consist of cleaning vessels, dryers, process equipment, floors, and trenches.

Warehouseman	Duties consist of transporting rubber by fork truck and storage of rubber and other supplies.
Laboratory Technician	Duties consist of sampling, testing, and reporting results of QC analyses performed on latex, crumb rubber, and baled rubber.
Process Chemist	Duties consist of sampling, testing, and reporting results of tests performed on latex, solutions, raw materials, and finished products. Performs wet chemistry analysis on samples. Also prepares and standardizes solutions.
Instrument Lab Chemist	Duties consist of obtaining, testing, and reporting results of samples pertaining to the antioxidant plant, and various rubber plant samples which require special instruments for analysis. Collects fresh and recycled 1,3-butadiene QC samples.
Maintenance Technician	Duties consist of maintenance on process equipment. Includes craftsmen such as electricians, pipefitters, and mechanics. Potential exists for intermittent exposure to 1,3-butadiene.

CONTROLS

Consumption of 1,3-butadiene at polymer plants occurs in enclosed process systems. The different processing operations and high consumption rates of the monomer at these facilities necessitates the use of a wide variety of process equipment. These operations incorporate a number of controls designed to prevent the release of chemical intermediates and products into the environment. Many of these controls are a major part of the process equipment, whereas others have been added for a specific purpose. Some controls are designed to reduce worker exposures, which can arise from inhalation or skin contact, whereas others are intended to abate environmental releases. Frequently, the environmental controls can function indirectly to reduce the level of toxic contaminants in the workplace air.

The survey team examined each of the five polymer production facilities during the in-depth monitoring surveys to identify those controls that directly or indirectly reduce workplace exposures. This section presents a description of the existing controls in 1,3-butadiene polymer plants by process operation or work task they are designed to control. Both engineering controls and administrative controls are discussed. The controls identified at each plant during the in-depth surveys are presented following the general discussion on controls.

Warehouseman	Duties consist of transporting rubber by fork truck and storage of rubber and other supplies.
Laboratory Technician	Duties consist of sampling, testing, and reporting results of QC analyses performed on latex, crumb rubber, and baled rubber.
Process Chemist	Duties consist of sampling, testing, and reporting results of tests performed on latex, solutions, raw materials, and finished products. Performs wet chemistry analysis on samples. Also prepares and standardizes solutions.
Instrument Lab Chemist	Duties consist of obtaining, testing, and reporting results of samples pertaining to the antioxidant plant, and various rubber plant samples which require special instruments for analysis. Collects fresh and recycled 1,3-butadiene QC samples.
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Engineering Controls

Engineering controls are implemented in three operational categories:

A. Process Flow--Leak prevention from pumps at 1,3-butadiene polymer facilities is accomplished through the use of various types of seals which isolate the interior of the pump from the atmosphere.

Mechanical seals offer better protection against leaks than packed seals. These seals are further categorized as either single or dual mechanical seals. Figure 10 shows a typical single mechanical seal. In a single mechanical seal application, the rotating seal ring and stationary element faces of the motor shaft are lapped to a very high degree of flatness to maintain contact throughout their entire mutual surface area. The faces are held together by a combination of pressure supplied by a spring and pump pressure transmitted through the fluid which is being pumped. The close contact between the two surfaces is designed to prevent leakage. If these faces wear out or become misaligned, however, a single mechanical seal will release the material being transferred directly into the work environment.[28]

Figure 11 and 12 present two different configurations for a dual mechanical seal: back-to-back and tandem. In both configurations, a liquid, usually oil, is circulated through the cavity between the two mechanical seals. The circulating liquid is normally maintained at a higher pressure than the process fluid. Any leakage across the seal face causes the seal liquid to be released first, indicating seal failure, before releasing the material being transferred, thus providing additional protection over a single mechanical seal.[28]

B. Quality Control (QC) Samples--A QC program typically requires workers to perform three major tasks: 1) collection of 1,3-butadiene samples using sampling cylinders or "bombs", 2) laboratory analysis of the samples, and 3) purging/cleaning of the sampling cylinders. Each task had individual controls associated with it.

1) Sample collection--In general, there are two types of sampling methods--the use of on-line gas chromatographs and manual sampling employing either an "open-loop" or "closed-loop" system. The use of on-line gas chromatographs may decrease the need for some manual sampling.

Manual collection of samples consists of attaching the bomb to fittings on the process equipment, opening the process stream in order to allow the sample to flow through the bomb, closing off the sampling stream, and disconnecting the bomb. Open-loop or closed-loop manual sampling may be done.

Open-loop atmospheric sampling systems represent the older technology and present greater potential for exposure. In these systems, the bomb is attached to a process release valve, opened at both ends, and a sample is taken following release of 1,3-butadiene through the bomb directly into the workplace. This stream of 1,3-butadiene detracts from the air quality in the work environment, and may result in exposure to workers through both inhalation and direct dermal contact.

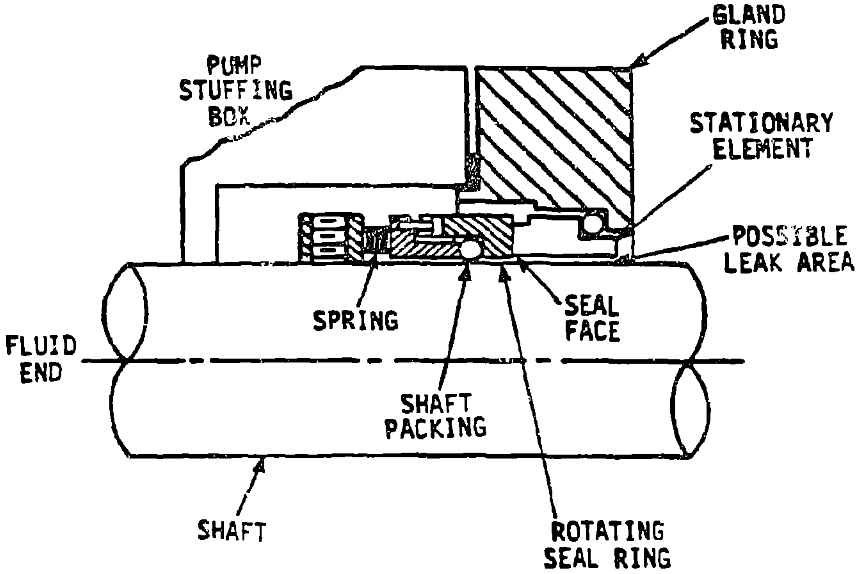

Figure 10 Diagram of a single mechanical seal.

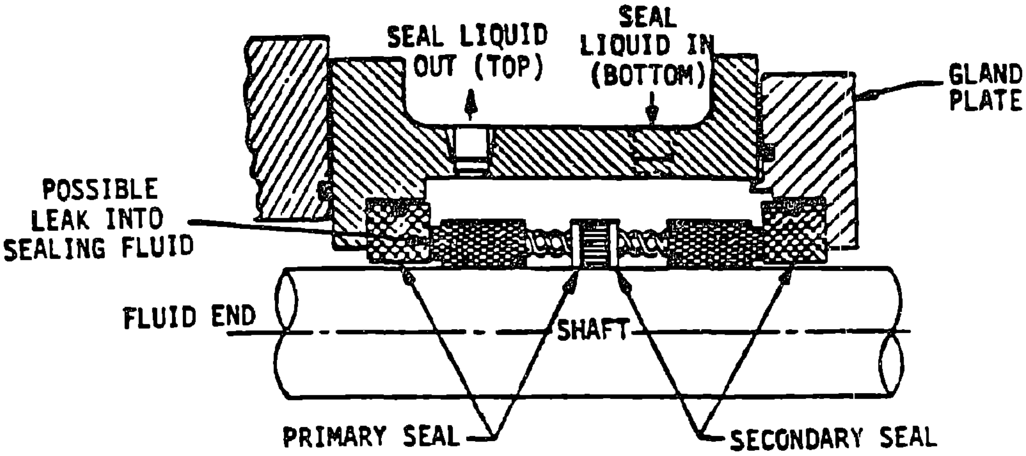

Figure 11 Diagram of a dual mechanical seal (back-to-back arrangement).

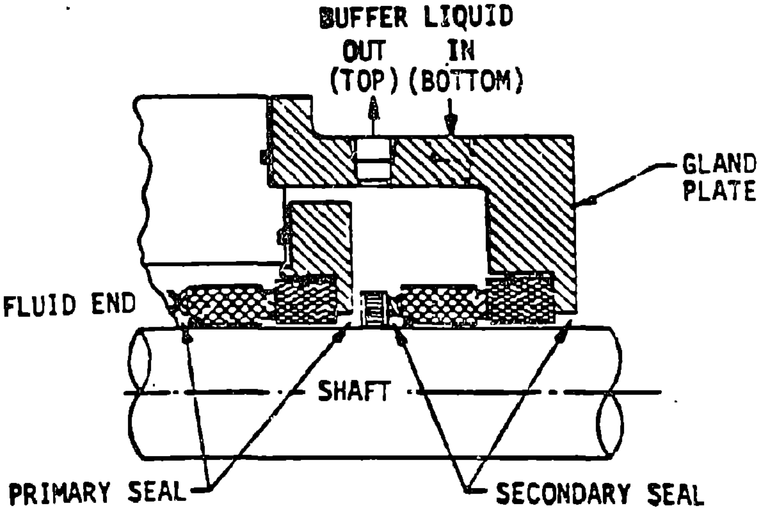

Figure 12 Diagram of a dual mechanical seal (tandem arrangement).

The potential for worker exposure during sampling is greatly minimized by the use of closed-loop sampling techniques. Figure 13 depicts a closed-loop sampling system. These systems represent a recent solution towards minimizing the release of process fluid to the work environment during bomb sampling. The closed-loop system allows the sampled fluid to circulate from the process through the bomb, and back to the process. Sampling occurs by "grabbing" a sample of the process stream through the bomb. Sampling lines connecting the process to the bomb are a permanent part of the process equipment. Properly designed closed-loop systems also have provisions to purge or evacuate the sample lines of 1,3-butadiene before removing the bomb. Improperly purged sampling lines are a source of 1,3-butadiene during the disconnecting of the bomb because the sampling line is under positive pressure with respect to the work environment.

2) Laboratory analysis--Laboratory analyses of the quality control samples may present a potential for additional exposures through dermal contact or inhalation. The sample bombs are taken to the plant laboratory for analysis by instrumental methods (gas chromatography) and wet chemical procedures. The release of the 1,3-butadiene sample for analysis can consist of either direct connection of the sample bomb to analytical equipment (e.g., gas chromatograph) or release of a small volume of the sample from the bomb into an open container. The connection of the bomb to analytical equipment can result in small releases of 1,3-butadiene into the laboratory workplace. Engineering controls in the laboratory may include dilution ventilation of the laboratory air, the use of laboratory hoods with adequate face velocities, and the employment of sample connections that minimize leakage and dead volume.

3) Sample cylinder purging--The complete voiding or purging of sample cylinders (bombs) is performed following analysis in order to evacuate the bomb and make it available for reuse. Bomb voiding may be accomplished by several methods: 1) manual or uncontrolled voiding of the bombs directly to the atmosphere, 2) controlled voiding under laboratory hoods or enclosed vacuum vents, and 3) controlled voiding of bombs by recycling to the process.

C. Transportation--The transportation of 1,3-butadiene product to and from the polymer production facilities is accomplished using four transfer methods: pipelines, rail tank cars, tank trucks, and marine vessels. Of these methods, only pipeline transfer (which is a totally enclosed system) represents a situation where no exposure to or release of 1,3-butadiene occurs.

Monitoring of the loading/unloading of the rail tank cars, tank trucks, and marine vessels may present a potential for 1,3-butadiene exposure. For rail tank cars, two types of "fill" gauges are used to monitor the loading/unloading process: slip-tube and magnetic.

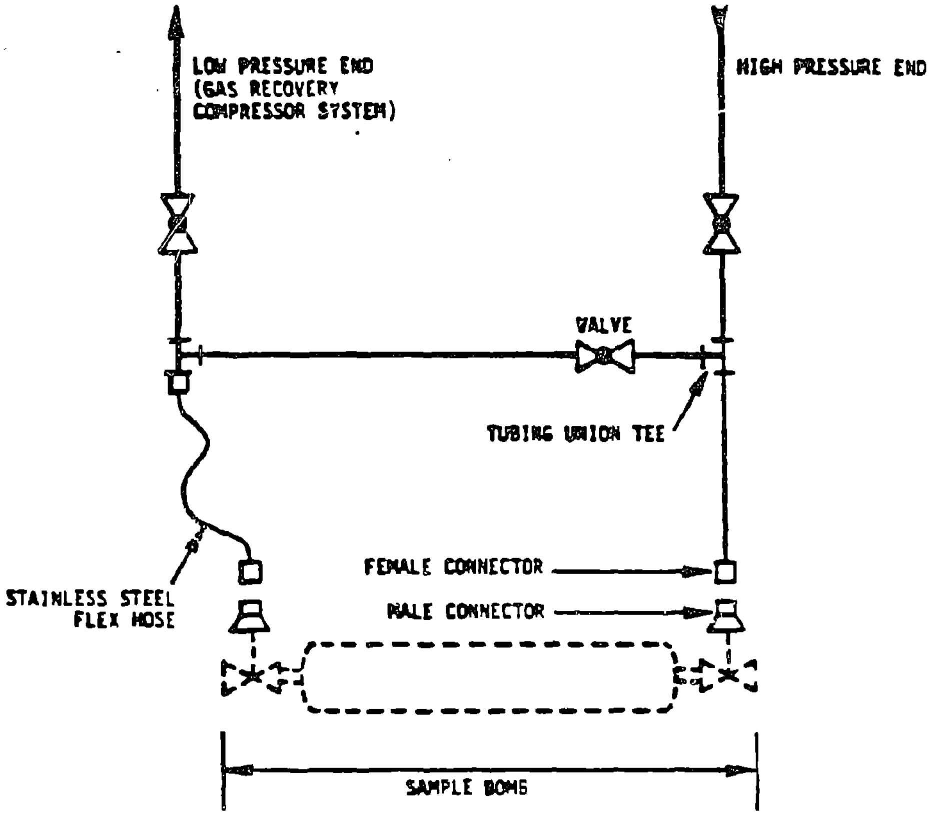

Figure 13 A closed-loop sampling system.

1) The slip-tube gauge achieves this task by releasing a small plume of 1,3-butadiene vapor to the ambient air. The vapor acts as a visual signal to the loading area process technician that the 1,3-butadiene in the tank car has reached a predetermined level.

2) The magnetic gauge, which is a completely sealed metering system operating without the release of vapor into the air, can be considered an improvement over the slip-tube design. A magnetic ring or "doughnut" located inside the tank car floats on the surface of the 1,3-butadiene. As the tank car fills, the ring rises over an enclosed shaft. Inside the shaft is a metered steel rod that projects out over the top of the car. The extent of this projection is monitored by the loading area process technician and provides an accurate measure of the level of 1,3-butadiene in the tank car.

   The monitoring of the loading/unloading operation for tank trucks differs from that of rail tank cars in that the gauging system on the trucks is an open-ended rotameter which releases 1,3-butadiene into the atmosphere, thereby creating an increased potential for 1,3-butadiene exposure.

   Marine vessels typically utilize slip-tube gauges similar to those used by rail tank cars for monitoring the loading/unloading process.

Administrative Controls

Administrative controls are changes in work practices or procedures which act to decrease the potential for employee exposure to a harmful agent.

As an administrative control, some plants require that certain decontamination procedures be followed during the repair, maintenance, or cleaning of process equipment. These precautions are designed to assure that maintenance workers are not overexposed to 1,3-butadiene during the performance of their tasks. The decontamination procedures produce two effects, the latter of which can be classified as an administrative control:

1) The most qualified personnel (process area technicians) shut down and clean the equipment.

2) Exposures to maintenance technicians are limited to the time it takes to repair the equipment, not to the full decontamination/repair task.

The specific engineering and administrative controls employed at each of the five plants surveyed are described below.

Plant A

Engineering Controls

A. Process Flow

The older 1,3-butadiene process pumps are equipped with single mechanical seals; this includes three blend pumps, two 1,3-butadiene charge pumps to each of the two reactor chains, and the pump on a recycle tank in the recovery area. The company replaces single mechanical seals with dual mechanical seals when an opportunity arises. All new process pumps handling 1,3-butadiene are equipped with dual mechanical seals. Nitrogen-pressurized (140 psig) dual mechanical seal systems with oil as the seal fluid have been installed on two pumps transferring 1,3-butadiene from the spheres to the tanks in the tank farm area. This represents an improvement over the water seal system in decreasing the occurrence of the seal liquid freezing in winter. In the rubber tank farm, positive displacement-type steam-driven pumps have been replaced by electrical pumps equipped with double seals.

Reactor agitators are equipped with dual mechanical seals with oil at 145 psig pressure between the seals. Compressors are of the reciprocating-type and are equipped with packed seals.

Tank farm pressure vessels for storage of 1,3-butadiene, including 3 non-working bulk storage tanks and 3 process storage tanks, vent discharges from safety valves directly to the atmosphere. The plant has experienced only one release of this nature in the last 30 years of its operating history. All other process equipment vent to scrubbers, absorbers, or to the flare system to prevent emissions of 1,3-butadiene. The absorber/desorber unit located in the recovery area is vented to the boilers where 1,3-butadiene is burned.

B. Quality Control (QC) Samples

The QC program at Plant A requires workers to perform three major tasks: 1) collection of the 1,3-butadiene and latex samples, 2) laboratory analysis of the samples, and 3) purging/cleaning of the sample cylinders ("bombs").

QC samples are collected from each rail tank car of incoming stock of 1,3-butadiene, on the blended 1,3-butadiene monomer feed as it enters the reactor chain, and at several points in the production process. The plant has converted all open-loop sampling systems to closed-loop purged systems with quick-disconnect bomb fittings.

Vapor samples are collected once a week from the 1,3-butadiene spheres. The vapor samples are obtained using cylinders referred to as "volleyball bladders" that are attached to the top of the 1,3-butadiene spheres. The amount of oxygen in the vapor is monitored in an effort to minimize peroxide formation within the spheres.

A new syringe sampling system for obtaining some of the liquid QC samples was initiated in 1985. Fourteen of the projected twenty-five such systems had been installed and were operational at the time of the survey. Samples are collected by using small plastic hypodermic syringes to extract 2 cubic centimeter (cc) samples through a small fitting at the sample location. This sampling system is currently used for checking for solids in the latex (that can be related to conversion), for checking the level of water and acrylonitrile in the acrylonitrile system, and for limited sampling of incoming stock. The potential for release of 1,3-butadiene into the environment and for worker exposure while obtaining QC samples is greatly reduced by use of this sampling technique.

At the latex sampling locations, positive displacement-type "Strahman" valves are used which eliminate the purge volume requirements of some other valve and line configurations.

In the laboratory, two types of analyses are run on 1,3-butadiene QC bomb samples. For one analysis, a cylinder of 1,3-butadiene is opened and the sample is allowed to weather off under one of the laboratory hoods. A gas chromatograph analysis is performed on the nonvolatile residue to test for impurities. The second analysis involves attaching a sample cylinder directly to the gas chromatograph via zero dead-volume fittings. The entire system is connected to a vacuum exhaust system. There are two laboratory hoods located in the laboratory. The hood which is used during collection of the nonvolatiles for impurity analysis measures 4 ft 2 in x 3 ft 2 in and was found to have a mean face velocity of 100 linear feet per minute (lfpm) (range of 75 to 140 lfpm) with the door all the way up. The second hood is smaller (3 ft 2 in x 2 ft 6 in) and had a mean face velocity of 90 lfpm (range of 50 to 150 lfpm) with the door all the way up. This hood is used for cylinder storage. Both hoods had mean face velocities of 150 to 200 lfpm when the doors were in the normal operating position (3/4 of the way down).

In the control laboratory, samples of unstripped latex are coagulated in a sink under a 2 ft 10 in x 1 ft 9 in laboratory hood having a mean face velocity of 750 lfpm. A dryer hood measuring 4 ft 2 in x 2 ft 6 in with a local exhaust ventilation duct 1 ft 6 in in diameter and having a face velocity of 500 lfpm is also located in the control laboratory. The 2 cc syringe sample solids are dried in a cooled room under a hood measuring 3 ft 9 in x 3 ft and having a face velocity of 420 lfpm at a local exhaust ventilation duct 6 inches in diameter.

In the rubber laboratory, muffle furnaces connected to a vacuum exhaust system are used to burn the talced rubber samples to determine the percent ash and carbon black in the product. Mooney viscosity tests are conducted on coagulated latex samples after they have been dried and milled under a 10 in. diameter hood (face velocity = 1050 lfpm).

All sample bombs are voided by connecting them back to the process. The syringes used in the syringe sampling system are disposed of in a covered plastic-lined bottle.

C. Transportation

Fresh 1,3-butadiene is delivered principally by pipeline although rail car facilities are available. The final product is shipped to customers by rail car. Vapor space in the rail car head is vented to a flare when unloading 1,3-butadiene. Rail cars are equipped with magnetic gauges to monitor the level of 1,3-butadiene in the tank car.

Administrative Controls

Plant A requires that certain decontamination procedures be followed during the repair, maintenance, or cleaning of process equipment. These procedures are designed to assure that maintenance workers are not overexposed to 1,3-butadiene during the performance of their tasks. One such procedure is to have the production workers decontaminate process equipment before maintenance workers enter the area to open equipment. Decontamination is conducted by water displacement and steam cleaning (optional).

Exposure Surveillance

Airborne concentrations of acrylonitrile, styrene, and 1,3-butadiene at the plant are monitored by fixed-point area monitors associated with an on-line gas chromatograph monitoring system. The system is calibrated with an acrylonitrile, 1,3-butadiene, and styrene mixture and is set to alarm at airborne concentrations of 2 ppm, 10 ppm, and 50 ppm respectively. A printout is generated at each sampling location indicating average, high, and low concentrations and concentration distribution for each of the analytes over the 8-hour shift and for the day. Fourteen sampling locations including the 1,3-butadiene tank farm, the tank farm loading racks, the finishing lines, and the recovery process are currently on-line. This system serves as a technologically-advanced means of monitoring daily exposures and as an early warning system of process equipment malfunction and possible pump or seal failure.

Equipment Maintenance Program

As part of the equipment maintenance program, pumps, columns, and lines are cleaned when required. Each vessel has a frequency of inspection schedule ranging from every three months to every five years. Inspections are divided into internal and external parts, with a frequency assigned to each (see Table 5).

Inspections flanges in the reactor area header lines are removed and inspected semiannually for possible restriction formations. Relief valve inspections range from quarterly to every two years in frequency. In the polymerization area, relief valves that are equipped with a safety disc are inspected weekly to determine if the safety disc has been ruptured. Relief valves on the 1,3-butadiene spheres are not equipped with a safety disc and upon opening discharge to the atmosphere rather than to the flare stack. An explosion meter is used to test the relief valve seat for possible leakage of 1,3-butadiene to the atmosphere.

TABLE 5. VESSEL INSPECTION SCHEDULE AT PLANT A

Area: Vessel	Frequency Interior	Frequency Exterior
1,3-butadiene Tank Farm:		
1,3-Butadiene storage spheres, Recycled 1,3-butadiene storage tank	3 years	1 Year
Rubber Tank Farm:		
1,3-Butadiene storage tank	1 Year	3 years
Latex storage tank	3 years	5 years
Reactor Area:		
Reactors and accumulators, Blowdown tanks	1 Year	4 years
Duraseal tanks	3 years	5 years
Recovery Area:		
Stripping columns, Vacuum and pressure flash tanks, Vacuum pump knockout drums, Compressor knockout drums	2 years	4 years
1,3-Butadiene condensers	2 years	3 years
Pigment Vessels:		
Pigment solution batch makeup and feed tanks	3 years	5 years
Finishing Line:		
Coagulation tank, Soap conversion tank	1/4 Year	1/4 Year
Latex blend tank	1 Year	1 Year
Environmental Control Unit:		
Makeup tank, Aeration Basin	1 Year	Not Applicable

Additional precautionary procedures are taken to prevent atmospheric contamination during production of NBR. Prior to unloading acrylonitrile tank cars, the unloading pumps and associated transfer lines are pressure-tested to 50 psi. Transfer lines to the reactor charge are pressure-tested to 50 psi before charging begins (normal operating pressure is 20 psi). Recovery unit vessels are checked by filling the vessels, connecting lines, and pumps with water after being cleaned and headed up. All lines to and from the tank farm storage tanks and the recovery unit are pressure-tested for possible leaks with high-pressure water at approximately 90 psi (normal operating pressure is 25 psi). Acrylonitrile storage tanks are opened annually for inspection and cleaning. Before these tanks are returned to service, they are filled with water and pressure-tested at 90 psi (normal operating pressure is 5 to 7 psi).

Plant B

Engineering Controls

Several engineering controls are in place at Plant B facility that directly control the release of 1,3-butadiene to the work environment.

A. Process Flow

Pumps in service at the barge dock and 1,3-butadiene storage sphere have single mechanical seals. Ten pumps handling 1,3-butadiene in the ADN production building are equipped with dual mechanical seals flushed with high boiling dinitriles. Centrifugal pumps on the process line and transfer pumps in the tank farm are overhauled every six months.

At the ADN plant, there are numerous valves that are in use at the ends of open pipes. These valves are normally used during the cleanup of the pipelines and equipment in the plant. The normal procedure is to use blind flanges on these lines as caps. In addition to the normal steps taken to prevent leaks from valves, the plant has recently replaced 14 plug valves at the 1,3-butadiene molecular sieves with disk valves incorporating special seats, packing and gaskets in order to reduce both the potential for personnel exposure and flammable vapor cloud formation.

All major pieces of equipment and pipelines have relief valves, many of which were installed to meet pressure codes. In addition, the 1,3-butadiene storage sphere is also equipped with a rupture disk. Potential releases of 1,3-butadiene from relief valves on process equipment are collected and routed to a flare.

B. Quality Control (QC) Samples

The QC program at Plant B requires workers to perform three major tasks: 1) collection of the 1,3-butadiene samples, 2) laboratory analysis of the samples, and 3) purging/cleaning of the sample cylinders.

No routine QC sampling of the 1,3-butadiene streams is performed in the ADN process; gas bags, however, are used whenever any sampling is required. There is thus minimal potential for exposure from QC sampling of the process. QC sampling, however, is performed on all incoming 1,3-butadiene prior to unloading of the barges. Shipping technicians collect QC samples with 500 cc stainless steel sample cylinders. The sample cylinder is attached to an open-loop system by fittings and hoses to the high-pressure side of the sampling connection; valves are then opened to fill the cylinder. Cylinder sampling has the greatest potential for exposure to 1,3-butadiene. The use of closed-loop sampling systems as an engineering control measure was not observed at this plant.

Samples are analyzed in the laboratory by gas chromatography and wet chemistry tests both performed under a Class I laboratory hood. The mean face velocity measured during the survey in the laboratory hood (dimensions: 2 ft 6 in x 1 ft 10 in) was 158 lfpm, with a range of 110 to 180 lfpm. Sample cylinders are emptied inside the laboratory hood, following completion of the analyses. The general ventilation in the laboratory is designed for "once-through" air.

C. Transportation

The level of 1,3-butadiene in barges is monitored by two types of gauges: slip-tube gauges are the original equipment on each barge. Six magnetic gauges, however, were installed in 1983 to minimize personnel exposures during level checks of the barges. The magnetic gauges monitor the level of liquid from the full level down to a 13-inch depth. The slip-tube gauges measure the level below the 12-inch depth. There is a vapor recovery system at the barge unloading area. In this area, the plant has also installed a vent stack that is used during the connection and disconnection of barges, to disperse 1,3-butadiene vapors and to prevent areas of high concentrations of 1,3-butadiene from forming at the ground levels.

Administrative Control

Plant B requires that certain decontamination procedures be followed during the repair, maintenance, or cleaning of process equipment. These procedures are designed to assure that maintenance workers are not overexposed to 1,3-butadiene during the performance of their tasks. Decontamination procedures include the draining of all process fluids into an enclosed and sealed sump system. The equipment is then steamed at 175 psig to remove residual organics, and purged with nitrogen. The resulting vapors are burned in a flare. After the equipment is opened, an explosimeter is used to ensure total decontamination of flammables. Explosibility must be at zero percent before maintenance can begin.

Plant C

Engineering Controls

A. Process Flow

All of the process pumps handling 1,3-butadiene are equipped with single mechanical seals.

B. Quality Control (QC) Samples

The QC program at Plant C requires workers to perform three major tasks: 1) the collection of the 1,3-butadiene samples, 2) laboratory analysis of the samples, and 3) purge/cleaning of the sample cylinders.

QC samples are collected of the incoming stock and at several points in the production process. Sample cylinders are used to collect process samples. The sample cylinder is attached in an open-loop system by fittings and hoses to the high pressure side of a point in the process; valves are then opened to fill the cylinder. The trapped material is analyzed by gas chromatography in the laboratory. Three quality control analyses are done regularly:

1. Purity of 1,3-butadiene (stored at the tank farm);
2. Percent conversion of monomer (after reaction); and
3. Percent 1,3-butadiene in paraffinic hydrocarbon solvent (in the purification area).

The sample cylinders are cleaned and purged at a central area in the process unit. The sample cylinders are connected to vacuum and the 1,3-butadiene is recycled into the process. The sample cylinders are steam cleaned and color coded so that only 1,3-butadiene is collected in the same sample cylinder.

C. Transportation

Slip-tube gauges are used to monitor the level of 1,3-butadiene on barges and in rail tank cars.

Administrative Controls

Plant C requires that certain decontamination procedures be followed during the repair, maintenance, or cleaning of process equipment. These procedures are designed to assure that maintenance workers are not overexposed to 1,3-butadiene during the performance of their tasks. One such procedure is to have the production workers decommission and nitrogen-purge process equipment before maintenance workers enter the area to open equipment. Often, water flushing or steam purging is performed before opening equipment.

Plant D.

Engineering Controls

A. Process Flow

Neoprene Production

All of the process pumps handling light end streams in the dry end of the chloroprene monomer production process are equipped with single mechanical seals. During the last year, Plant D has redesigned the single mechanical seals on the 1,3-butadiene pumps. This new design, which consists of replacing the stainless steel on one of the seal surfaces with Hastelloy®, has improved the performance of the seals. In the chloroprene monomer process, dual mechanical seals in a tandem arrangement are used for the heavy bottom streams which usually contain gritty coke.

Axial blowers supply fresh and recycled 1,3-butadiene to the chlorinators. In-line valves are compression-type diaphragm valves which withstand coke buildup. Fresh 1,3-butadiene is delivered by pipeline which provides better containment of raw material and requires less maintenance.

THPA Production

In the THPA area, there are no 1,3-butadiene transfer pumps; liquid 1,3-butadiene is pressure fed to the reactor.

B. Quality Control (QC) Samples

Neoprene Production

The QC program at Plant D requires workers to perform three major tasks: 1) the collection of the 1,3-butadiene samples, 2) laboratory analysis of the samples, and 3) purge/cleaning of the sample cylinders.

1,3-Butadiene QC samples are collected using sample cylinders ("bombs") in a "closed-loop" mode. The closed-loop sampling system for 1,3-butadiene feed sampling has been retrofitted from an open-loop system over the past 12 months. One QC sample of 1,3-butadiene per day is collected in the chloroprene monomer area.

In the laboratory the bomb samples are enclosed in an exhaust cabinet when coupled to the gas chromatograph for analysis. Wet chemistry tests are conducted under a laboratory hood. The mean face velocity measured during the survey in the laboratory hood (dimensions: 5 ft 3 in x 2 ft 6 in) was 110 lfpm, with a range of 60 to 160 lfpm. Following sample analysis, the bombs are voided outside the laboratory building using steam purge, cleaned with nitrogen, and dried.

THPA Production

No QC sampling for 1,3-butadiene is conducted on the THPA line when production occurs

C. Transportation

1,3-butadiene is conveyed to Plant D by pipeline. These pipelines provide maximum control and containment of 1,3-butadiene during transfer and eliminate the possibility of release of 1,3-butadiene into the workplace.

Administrative Controls

Plant D requires that certain decontamination procedures be followed during the repair, maintenance, or cleaning of process equipment. These procedures are designed to assure that maintenance workers are not overexposed to

1,3-butadiene during the performance of their tasks. In the neoprene area, whenever pumps are overhauled they are blinded and depressurized before opening.

For decontamination of reboilers, the DCB's are pumped out, the reboiler is washed with soap and then blinded. Nitrogen purge does not occur during decontamination. Water washing of the chlorination reactors is performed before opening the reactors. Checks are conducted for oxygen and DCB's before entering the reactors for cleaning.

On the THPA line, the one pump that is employed to transfer maleic anhydride is decontaminated each week by steam cleaning and nitrogen purge. The 1,3-butadiene vaporizer is inspected after each 5-day run and cleaned once a year.

Plant E

Engineering Controls

A. Process Flow

All of the process pumps that handle 1,3-butadiene in the tank farm and process areas are equipped with single mechanical seals. The plant is contemplating retrofitting to dual mechanical seals on the 1,3-butadiene pumps. The compressor handling acrylonitrile is under negative pressure and uses activated carbon filters.

B. Quality Control (QC) Samples

The QC program at Plant E requires workers to perform three major tasks: 1) the collection of the 1,3-butadiene samples, 2) laboratory analysis of the samples, and 3) purge/cleaning of the sample cylinders. Samples are collected by laboratory technicians/chemists using sample cylinders ("bombs") in a open-loop mode. Cylinder sampling has the greatest potential for exposure to 1,3-butadiene. The use of closed-loop sampling systems as an engineering control measure was not observed at the plant.

The survey team performed an evaluation of the face velocities for hoods in the laboratories. The gas chromatographic analyses are performed in the open laboratory. The mean face velocity measured during the survey in the laboratory hood (dimensions: 5 ft x 2 ft 5 in) used for storing the sample cylinders was 30 lfpm with a range of 5 to 45 lfpm when the doors were fully open. When the doors were only half open, the mean face velocity increased to 78 lfpm, with a range of 30 to 110 lfpm. The mean face velocities measured in an adjacent laboratory hood (dimensions: 9 ft 6 in x 2 ft 8 in) used for wet chemistry tests were 107 lfpm (with a range of 30 to 180 lfpm) when the sliding door was moved to the right, and 73 lfpm (with a range of 40 to 120 lfpm) when the sliding door was moved to the left. The QC analysis for inhibitor

1,3-butadiene during the performance of their tasks. In the neoprene area, whenever pumps are overhauled they are blinded and depressurized before opening.

For decontamination of reboilers, the DCB's are pumped out, the reboiler is washed with soap and then blinded. Nitrogen purge does not occur during decontamination. Water washing of the chlorination reactors is performed before opening the reactors. Checks are conducted for oxygen and DCB's before entering the reactors for cleaning.

On the THPA line, the one pump that is employed to transfer maleic anhydride is decontaminated each week by steam cleaning and nitrogen purge. The 1,3-butadiene vaporizer is inspected after each 5-day run and cleaned once a year.

Plant E

Engineering Controls

A. Process Flow

All of the process pumps that handle 1,3-butadiene in the tank farm and process areas are equipped with single mechanical seals. The plant is contemplating retrofitting to dual mechanical seals on the 1,3-butadiene pumps. The compressor handling acrylonitrile is under negative pressure and uses activated carbon filters.

B. Quality Control (QC) Samples

The QC program at Plant E requires workers to perform three major tasks: 1) the collection of the 1,3-butadiene samples, 2) laboratory analysis of the samples, and 3) purge/cleaning of the sample cylinders. Samples are collected by laboratory technicians/chemists using sample cylinders ("bombs") in a open-loop mode. Cylinder sampling has the greatest potential for exposure to 1,3-butadiene. The use of closed-loop sampling systems as an engineering control measure was not observed at the plant.

The survey team performed an evaluation of the face velocities for hoods in the laboratories. The gas chromatographic analyses are performed in the open laboratory. The mean face velocity measured during the survey in the laboratory hood (dimensions: 5 ft x 2 ft 5 in) used for storing the sample cylinders was 30 lfpm with a range of 5 to 45 lfpm when the doors were fully open. When the doors were only half open, the mean face velocity increased to 78 lfpm, with a range of 30 to 110 lfpm. The mean face velocities measured in an adjacent laboratory hood (dimensions: 9 ft 6 in x 2 ft 8 in) used for wet chemistry tests were 107 lfpm (with a range of 30 to 180 lfpm) when the sliding door was moved to the right, and 73 lfpm (with a range of 40 to 120 lfpm) when the sliding door was moved to the left. The QC analysis for inhibitor content is performed on a hot plate outside the laboratory. Latex samples are analyzed at two locations in the latex laboratory approximately 20 feet apart. At one location, ovens are used for QC analysis with an overhead ventilation duct (dimensions: 8 ft 6 in x 1 ft 4 in) having a mean face velocity of 40 lfpm. Some other analyses for SB latex are performed in a laboratory hood (dimensions: 5 ft 11 in x 1 ft 10 in) with a side ventilation duct (dimensions: 9 in x 7 1/2 in) having a mean face velocity of 50 lfpm. The engineering laboratory used for conducting QC tests on rubber samples had a mill with an overhead local exhaust ventilation duct measuring 7 1/2 inches in diameter and having a mean face velocity of 55 lfpm.

The sample cylinders are cleaned by connecting to a manifold and purging the residual 1,3-butadiene; no special controls are employed for this operation.

C. Transportation

The 1,3-butadiene monomer is delivered to the plant by pipeline; therefore, gauges or other means of measuring the delivered product are not needed.

Administrative Controls

Maintenance to process equipment is not performed on any specific schedule. Decontamination of process equipment prior to maintenance consists of bleeding it to the atmosphere and flushing with water. Steam cleaning or purging with nitrogen is not practiced.

PAST WORKER EXPOSURES

This section presents the results of the historical monitoring data for 1,3-butadiene collected by the respective companies at Plants A, B, C, D, and E. It was not known how the limit of detection was handled in the company data.

Plant A

Since 1980, Plant A has had an ongoing program to monitor personal exposures and area concentrations of 1,3-butadiene. Table 6 summarizes personal monitoring data collected by the plant during 1980-85 for the major job categories. Sampling results reported as less than the detection limit were assigned the lower detection limit, usually 0.1 ppm. Trace results as well as "none detected" results were assigned a value of 0 ppm for computing mean 8-hour TWAs. The weighted mean of the TWA exposures for all job categories was 2.4 ppm (n = 145).

While no area data were obtained for the plant, the company reported that area monitoring results collected in 1976, 1980, 1981, and 1985 ranged from below the limit of detection to 52.5 ppm (measured beside a column in the recovery area when the plant was conducting a short-term equipment test program). The mean of the area sample concentrations was 2.4 ppm (n = 114). Due to the levels of 1,3-butadiene typically reported by the plant, the chromatographic column was not optimized to obtain complete resolution of all C_4 compounds. Additionally, the analyses were performed in a laboratory area where 1,3-butadiene was routinely present and being handled for other purposes. In brief, the sampling and analytical method included 15-minute spot sample collection on activated charcoal, desorption in carbon disulfide or methylene chloride, and analysis by flame ionization detection gas chromatography. This method is similar to NIOSH Method P&CAM 127.[16]

TABLE 6. SUMMARY OF PLANT A PERSONAL MONITORING FOR 1,3-BUTADIENE 1980-1985

Job category	Number of samples	8-hour TWA,[a] ppm arithmetic mean
Reactor/Recovery Area		
Leaderman	4	0.3
Tank Farm Operator	19	3.9
Reactor Operator	12	0.7
Recovery Operator	29	2.9
Pigment Operator	3	0.4
Utility A Operator	5	0.3
Finishing Process Area		
Leaderman	2	0.1
Finishing Operator	13	2.2
Maintenance Personnel	43	2.6
Hydrocarbon Laboratory Staff	9	6.8
Rubber Laboratory Staff	6	0.3

[a] Time-weighted average

Plant B

Plant B has conducted personal monitoring for 1,3-butadiene since 1978. However, in 1976, Draeger detector tubes were used for area monitoring for 1,3-butadiene. Table 7 summarizes the data for employees exposed to 1,3-butadiene in the barge loading and unloading area, the ADN process area, and the analytical laboratory. The weighted mean of the 8-hour time-weighted average (TWA) mean exposures for all job categories is 4.1 ppm (n = 157). The TWA exposures for 1983-1985 are significantly lower than those for previous years; mean TWAs for all job categories during these years are at or below 1 ppm. The plant has used three different sampling methods since 1976.

1976 = Draeger Detector Tubes
1978 = DuPont P-200 Pump and Charcoal Tube
1980-1985 = Pro-Tek® Organic Vapor Air Monitoring Badge

TABLE 7. SUMMARY OF PLANT B'S PERSONAL MONITORING FOR 1,3-BUTADIENE, 1976-1985.^{a}

Job category/ year	No. of samples (n)	Range, TWA^b	Arithmetic mean, (n)
BARGE LOADING AND UNLOADING AREA			
Shipping Technician, Sample Barge			
1978	7	<0.01 - 31	5.1 (7)
1980	1	62.7	62.7 (1)
1981	13	<0.01 - 31.6	7.7 (13)
1982	22	<0.01 - 34.2 (162)^c	5.0 (21)
1983	11	<0.01 - 1.2	0.3 (11)
1984	14	<0.01 - 8.6	1.0 (14)
Shipping Technician, Unloading Barge			
1978	12	<0.01 - >25^d	3.9 (12)
1981	5	<0.01 - <0.01	<0.01 (5)
1982	1	12.2	12.2 (1)
1984	2	<0.1 - <0.1	<0.1 (2)
Shipping Technician, Clearing for Barge Connect			
1981	5	<0.1 - <0.1	<0.1 (5)
Shipping Technician, Stripping Barge			
1981	7	<0.1 - 16 (147;865)^c	10.7 (5)
1982	3	<0.1 - 3.4 (145)^b	1.7 (2)
1983	2	<0.1 - <0.1	<0.1 (2)
1984	6	<0.1 - 0.2	0.15 (6)
Shipping Technician, Clearing for Disconnect			
1981	3	2.8 - 35	24.2 (3)
1982	1	<0.1	<0.1 (1)
1984	1	<0.1	<0.1 (1)
Mechanic, Connecting and Disconnecting Barge			
1978	10	<0.1 - 2.3	0.6 (10)
1980	4	2.7 - 71 (543)^c	39.9 (3)
1984	8	<0.1 - 0.7	0.1 (8)
1985	4	0.1 - 2.7	0.9 (4)
ADIPONITRILE PROCESS AREA			
Synthesis Operator A			
1984	6	<0.01 - 0.04	0.02 (6)
Refining Operator			
1984	2	<0.01 - <0.01	<0.01 (2)

Table 7 Cont.

Job category/ year	No. of samples (n)	Range, TWA[b]	Arithmetic mean, (n)
		ANALYTICAL LABORATORY	
Lab Technician			
1983	1	<0.1	<0.1 (1)
1984	11	<0.1 - 1.4	0.5 (11)
			4.1 (157)

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[a] Data as reported by the company
[b] Time-weighted average (8-hr).
[c] Suspect values (outlier).
[d] Breakthrough observed into rear section of charcoal tube.

All samples were analyzed by a gas chromatographic method similar to NIOSH Method S-91.[10] N-pentane was used as a calibration standard.

Under normal conditions, one 1,3-butadiene barge arrives every 7 to 10 days. The barge unloading process usually takes two shifts (24 hours) to complete. Under normal conditions, two shipping technicians are responsible for the unloading, sampling, and purging operations while two mechanics connect and disconnect the liquid/vapor lines from the unloading station to the pump.

Operators are potentially exposed to 1,3-butadiene while sampling 1,3-butadiene during the barge unloading operation. Barge stripping operations involve using an atmospheric slip-tube to measure the last 12 to 13 inches remaining in the barge. Operators are instructed to stand upwind of the vent when either operating the stripping slip-tube or purging the sample cylinder.

Plant C

Personal exposure monitoring for 1,3-butadiene was conducted by Plant C in 1985 using the 3M 3500 organic vapor monitor (passive dosimeter). The sampling and analytical method was not specific to 1,3-butadiene; in the evaluation of the results, however, it has been assumed by the plant that all compounds identified as containing a four carbon chain (C_4) are 1,3-butadiene since the purity of the butadiene, as received, is greater than 99.5 percent. Table 8 presents a summary of the company's personal air monitoring conducted in 1985. All time-weighted average (TWA) exposures (not 8-hour) are below 1 ppm. The mean for the 56 samples is 0.14 ppm. The passive dosimeters were reportedly analyzed according to NIOSH Method P&CAM 127[10] via gas chromatography.

TABLE 8. SUMMARY OF PLANT C'S PERSONAL MONITORING DATA FOR C_4 COMPOUNDS, 1985[a]

		TWA exposures[b]	
Job category	No. of samples	Range ppm	Arithmetic mean, ppm
A operator, process area	3	ND[b] - 0.54	0.21
B operator, process area	12	ND - 0.67	0.19
Finishing operator	6	ND - 0.80	0.17
Laboratory technician	4	ND	ND
Supervisor, all areas	4	ND - 0.08	0.05
Tank and vessel cleaner	7	ND - 0.07	0.03
Tank farm pipefitter	5	ND - 0.12	0.07
Yard keeper	3	ND - 1.0	0.50
Mechanic	3	ND - 0.11	0.06
Boilermaker	3	ND - 0.11	0.04
Sumpman	3	0.05 - 0.35	0.17
Belt cleaner	1	0.01	0.01
Painter	1	0.07	0.07
Janitor	1	0.87	0.87
Total	56	ND - 1.0	0.14

[a] Data as reported by company.

[b] Time-weighted average; sampling time varied from 4 to 6 hours.

[c] Not detectable; assumed by the plant to be 0 ppm for computing means.

Plant D

Plant D has conducted air monitoring for 1,3-butadiene in 1984 to characterize personal exposures and area concentrations. Personal monitoring results, as reported by the plant, are summarized in Table 9 and show that exposures to 1,3-butadiene are low in the neoprene area; no individual result exceeded 1 ppm. For 12 personal air samples in the neoprene plant, the weighted mean time-weighted average (TWA) is 0.47 ppm. Personal monitoring results from THPA production indicate higher exposures for this process. The weighted mean of six personal samples for THPA employees is 4.23 ppm. A head operator in the THPA area recorded the highest personal monitoring results of 9.72 ppm.

Area air monitoring data for 1,3-butadiene, as reported by the company, are limited. Of 10 samples collected at various locations in the neoprene plant, four results (0.55, 0.96, 1.07, and 1.17 ppm) were quantifiable. The remaining six sample results were less than 0.02 ppm. In the THPA area, two samples placed above the operator station recorded 0.82 and 2.26 ppm.

Air concentrations were monitored with 3M passive dosimeters. The badges were disassembled, desorbed in carbon disulfide, and analyzed by gas chromatography, a method similar to NIOSH Method S-91.[16]

TABLE 9. SUMMARY OF PLANT D'S PERSONAL MONITORING DATA FOR 1,3-BUTADIENE, 1984

Job classification	No. of samples	Mean 1,3-butadiene TWA[a] concentrations, ppm
Neoprene plant		
Head operator	1	0.19
Assistant operator	9	0.61
Day helper	1	0.01
Maintenance	1	0.01
Total	12	0.47
THPA plant		
Head operator	1	9.72
Maintenance	4	2.27
Day helper	1	6.57
Total	6	4.23

[a] Time-weighted average

The past practice of collecting quality control samples by an open-loop sampling system created an increased potential for exposure to 1,3-butadiene.

The current practice of closed-loop sampling should greatly reduce the potential for 1,3-butadiene exposure.

Plant E

The company's industrial hygiene staff has conducted personal and area monitoring for 1,3-butadiene exposure since 1977. Table 10 and Table 11 present the results of personal monitoring for the periods of 1977-80 and 1982-85, respectively. The data for these two periods are presented separately because the plant switched to the use of 3M Organic Vapor Monitors for industrial hygiene sampling in 1981. Prior to that time, activated charcoal tubes were used. The analytical method involves desorption with carbon disulfide and analysis by gas chromatography with a flame ionization detector (NIOSH Method S-91[10]). The majority (92 percent) of the plant's personal samples were collected during 1982-1985. The mean 8-hour TWA of 31 personal samples collected during 1977-1980 was 4.00 ppm, while that for 366 personal samples during 1982-1985 was 5.87 ppm. Table 12 presents Plant E's results for area monitoring conducted during 1982-85. The mean of 67 area samples collected in different process areas during 1982-1985 was 4.40 ppm. Mean exposures to tank farm operators were above 10 ppm with both types of sampling methods. The highest individual exposure of 139 ppm was also observed for a tank farm operator. Mean 8-hour TWA exposures greater than 10 ppm were also observed for the reactor operator during the 1977-1980 period and for the recovery operators and laborers during the 1982-1985 period. Finishing operators had mean TWA's less than 1 ppm for both monitoring time

TABLE 10. SUMMARY OF PLANT E'S PERSONAL MONITORING DATA FOR 1,3-BUTADIENE, 1977-80[a]

Job category	No. of samples	8-hour TWA[b] Range ppm	 Arithmetic mean, ppm
Foreman/Supervisor	1	<0.17	<0.17
Tank Farm Operator	3	13.65-20.04	16.88
Reactor Operator	3	2.86-24.10	10.05
Recovery Operator	5	<0.13-15.86	3.67
Clean-up Crew	1	0.52	0.52
Finishing Operator (including Baler Helper)	8	0.04-0.86	0.22
Laboratory Technician	6	0.15-15.86	3.00
Mechanic	2	<0.10-1.90	1.00
Laborer	2	<0.10-2.20	1.15
Total	31	0.04-24.10	4.00

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[a] Analytical method used activated charcoal tubes and GC/FID (NIOSH Method S-91).

[b] Time-weighted average

TABLE 11. SUMMARY OF PLANT E'S PERSONAL MONITORING DATA FOR 1,3-BUTADIENE, 1982-85[a]

Job category	No. of samples	8-hour TWA[b] Range ppm	 Arithmetic mean, ppm
Foreman/Supervisor	20	0.45-22.00	5.03
Development Engineer	43	0.20-24.79	4.15
Tank Farm Operator	20	0.06-139.00	28.04
Reactor Operator	47	0.15-9.74	2.49
Recovery Operator	46	0.57-87.0	14.09
Pigment Preparation Operator	4	0.02-1.06	0.43
Clean-up Crew	9	<0.04-13.32	3.82
Finishing Operator (including Baler Helper)	61	<0.01-1.90	0.32
Laboratory Technician (including Chemist)	53	0.26-12.84	4.82
Mechanic	37	<0.03-9.50	1.45
Laborer	11	0.37-88.24	14.94
Waste Treatment Operator	8	<0.03-6.07	0.95
Fireman	7	0.40-2.26	1.24
Total	366	<0.01-139.00	5.87

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[a] Analytical method used activated charcoal tubes and GC/FID (NIOSH Method S-91).

[b] Time-weighted average

TABLE 12. SUMMARY OF PLANT E'S AREA MONITORING DATA FOR 1,3-BUTADIENE, 1982-85[a]

Location	No. of Samples	Concentration Range, ppm	Concentration Arithmetic Mean ppm
Tank Farm Area	8	0.07 - 41.60	5.71
Reactor Area	23	0.12 - 23.40	4.45
Recovery Area	8	0.09 - 121.00	21.93
Laboratory, Pigment Preparation Area	3	0.37 - 1.01	0.66
Finishing Area	22	0.03 - 1.55	0.42
Waste Treatment Area	3	0.05 - 0.18	0.12
Total	67	0.03 - 121.00	4.40

[a] Analytical method used 3M Organic Vapor Monitors and GC/FID (NIOSH Method S-91)

frames, indicating that the potential for exposure to 1,3-butadiene primarily exists before the stripped latex stage. Mean area concentrations greater than the 10 ppm of 1,3-butadiene were observed in the recovery area of the plant.

MEDICAL, SAFETY AND INDUSTRIAL HYGIENE PROGRAMS

Plant A

Medical Program--
The company employs one part-time physician and one full-time registered nurse. In addition, one part-time medical technician is employed to conduct x-rays, pulmonary function tests, and phlebotomy. Ten employees on the day shift are qualified to administer first-aid; all rotating shifts carry a minimum of 5 persons qualified in first-aid techniques. The company requires all employees to take pre-employment physicals, and offers annual physicals to all employees. Physicals include 14 in. x 10 in. chest x-rays, audiometric hearing tests, Snelin vision tests, pulmonary function tests, blood tests, and urine tests for albumin and sugar content. The medical history of the employee is reviewed during the annual physicals.

The plant is located less than 5 miles from the nearest emergency hospital facility and 10 miles from alternate facilities.

Safety Program--
The safety staff includes a safety manager, fire marshall, and three fire and safety inspectors. Inspectors issue vessel entry permits and inspect and maintain safety equipment. The safety manager conducts monthly safety meetings for all employees.

As part of the safety program, all process areas are equipped with safety showers and eye-wash stations for emergency use.

Industrial Hygiene Program--
The plant has established an industrial hygiene committee. This committee, composed of the safety manager, supervisors from the hydrocarbon and environmental laboratories, and an environmental engineer, meets quarterly to discuss industrial hygiene concerns. Industrial hygiene consulting services are also provided as needed by a certified industrial hygienist through a contract arrangement.

Air monitoring is conducted routinely for 1,3-butadiene, styrene, acrylonitrile, and asbestos. Noise monitoring is conducted annually, or when the need arises.

Plant B

Medical Program--
The medical program serves all plant employees. There are two full-time physicians and one full-time physician's assistant. The medical team also has six registered nurses. Personnel trained in first aid (on each shift) includ one nurse and eight laboratory analysts who also serve as ambulance drivers. All employees receive periodic physicals as well as pre-employment exams. Medical tests include the following: chest x-rays, hearing tests, vision tests, lung function tests, blood tests, and urine tests. Electrocardiograms (EKGs) are begun at age 30. The plant is located approximately three miles from the nearest hospital.

Safety Program--
The Safety Superintendent is responsible for the safety and health programs at the plant. The Safety and Occupational Health Division, comprised of 10 employees, is responsible for an organized safety program at the plant. Management has established a Central Safety and Health Committee with standing sub-committees. Each production area has an Area Safety Committee and an Area Occupational Health Coordinator. Monthly meetings are held with all personnel.

Industrial Hygiene Program--
The industrial hygiene program is carried out by five full-time employees: Occupational Health Coordinator, Certified Industrial Hygienist, Area Specialist, Laboratory Technician, and a Stenographer. Several part-time

personnel are responsible for carrying out special sampling surveys such as those for noise, ventilation, and radiation. Each area of the plant has an Area Occupational Health Coordinator.

Since 1978, the plant has conducted personal monitoring for 1,3-butadiene. In addition to 1,3-butadiene monitoring, air sampling is conducted at varying frequencies for the following substances: cyclohexane, dinitriles, pentenenitriles, diatomaceous earth, nickel, ammonia, asbestos, hydrogen chloride, hydrogen cyanide, benzene, and creosol.

Air monitoring techniques involve the use of several sample media: charcoal tubes, silica gel tubes, DuPont Pro-Tek® organic vapor air monitors, or long duration and spot-check detector tubes (area and personal monitoring).

Plant C

Medical Program--
The plant employs one part-time physician who is at the plant one day per week and one full-time nurse. The company conducts pre-employment and annual physicals for all employees. The annual physical is a general exam by the plant physician and includes an eye exam, hearing test, and blood pressure test. Other tests are conducted in addition to the physicals for certain job categories: painters, insulators, and other who use respirators receive pulmonary function tests and chest x-rays; those personnel exposed to solvents have annual urine and blood tests. All personnel receive a blood and urine test every two years as part of their physical.

Safety Program--
The personnel manager maintains an organized safety program. A central safety committee, composed of top management and general foremen, meets monthly. This committee also meets with the union committee once a month at which time safety issues are discussed.

The personnel manager supervises the safety engineer as well as 10 plant employees responsible for plant protection (security) and fire safety. Plant safety personnel also issue permits for hazardous operations such as vessel entry, valve blinding, stack line repair, etc. Quarterly safety audits are conducted by the safety manager and plant safety personnel.

Industrial Hygiene Program--
The plant conducts a semi-annual assessment of paraffinic hydrocarbon solvent, benzene, styrene, 1,3-butadiene, acetone, toluene, asbestos, and noise exposures. The 3M passive dosimeter is used for personal samples (except asbestos). Ventilation measurements of the laboratory hoods are taken with a velometer. Noise measurements are conducted with a sound level meter and noise dosimeters. Industrial hygiene samples are taken by the safety engineer.

The company reportedly uses a contract laboratory for analysis of 1,3-butadiene samples by NIOSH P&CAM 127. No exposures in excess of 1 ppm have been reported to the company for 1,3-butadiene.

Plant D

Medical Program--

Medical personnel include one part-time physician. One licensed nurse is available on day shift, and one backup nurse works in another capacity at the plant. Each shift has one shift foreman and two wage employees trained in first-aid. All employees, including office help, receive pre-employment physicals and annual physical exams which include chest x-rays, hearing tests, vision tests, lung function tests, blood tests, and urine tests. Hospital facilities are located approximately 3 miles from the plant.

Safety Program--

The Safety Department is composed of a Safety Coordinator and one safety employee. Area supervisors administer a safety permit program which assures that equipment complies with safety standards before being placed into production. Monthly safety meetings are held with the management and production employees, including one joint meeting of management and labor. The Safety Policy Committee is composed of the Vice President, Operations Manager, Maintenance Manager, General Manager Corporate Services, Manager of Quality Assurance, Manager of Research and Development, and Safety Coordinator. Wage personnel meet within each department on a monthly basis. Management and labor representatives discuss safety concerns together when the Joint Health and Safety Committee convenes monthly.

As an additional safety measure, entry permits are required for entry into vessels, towers, or equipment for performance of maintenance operations. Testing is conducted for oxygen content and residual vapors prior to entering any equipment for maintenance purposes.

Industrial Hygiene Program--

The Superintendent of Industrial Hygiene conducts quarterly personal monitoring of 1,3-butadiene, chloroprene, dichlorobutenes, dimers of chloroprene, maleic anhydride, toluene, xylene, talc, and noise. Ventilation readings of the laboratory hoods are taken on a nonroutine basis.

Plant E

Medical Program--

A physician is at the plant 1 to 3 hours per week in addition to being on call. The plant also has a registered nurse and 49 employees trained in first-aid procedures.

Employees are required to receive pre-employment physical examinations. They can also obtain periodic examinations each year during the month of their birthday. The physical examination includes the following tests:

- chest x-ray
- hearing
- vision (including Glaucoma screening)
- lung function
- blood
- vital signs
- urine
- electrocardiogram

The medical history of the employee is also reviewed during the physical examination. The plant is located within 3 to 5 miles of several hospitals.

Safety Program--
The plant routinely conducts meetings concerning safety procedures. During the ten months preceding the survey, personnel in the following job classifications have attended safety meetings:

Job Classification	Number of Meetings
Hourly Management	9
Executive Safety	38
Polymerization Area	30
Finishing Area	195
Maintenance	150
Technical and Laboratory	30
Warehouse and Shipping	50
Latex Plant	67

Industrial Hygiene Program--
Industrial hygiene sampling at the plant is comprehensive and uses standard industrial hygiene practices for the evaluation of the work environment. Industrial hygiene sampling is done quarterly for all substances including 1,3-butadiene and data are available since 1977 on 1,3-butadiene. There is one industrial hygienist at the plant. The corporate industrial hygiene department assists the plant in the development of a comprehensive sampling program. All samples are analyzed at the corporate analytical laboratory which is accredited by the American Industrial Hygiene Association for industrial hygiene analytical services. The corporate industrial hygiene department also conducts a health and safety audit every two years.

Plant E has a series of films and training materials that deal with health monitoring and hygiene in the workplace. The information is presented to new employees as part of the New Employees Safety Training (NEST) program. The training materials are also discussed during the regular safety meetings. The titles for some of the industrial hygiene-oriented films are: "Hazardous Materials in the Work Place", "For Your Own Good Health", and "Health and Safety, A Dual Responsibility".

PERSONNEL RECORDKEEPING

Personnel records are maintained in standard forms designed for such purposes by each of the five plants surveyed. Details of recordkeeping procedures for each plant are outlined below:

Plant A
The company maintains personnel records on some terminated as well as current employees, but some records have been destroyed. Records are available for most employees, however, dating back to 1943. A work history consisting of

annual review comments, promotional changes, and salary increases is kept in the personnel record. The standard personnel form includes the following information:

1. Name
2. Personal history
3. Education
4. Family status
5. Date of employment and/or transfer
6. Pay scale
7. Job title

Several unions (e.g., operating engineers, pipefitters, painters, machinists) represent employees in the company workforce. These unions maintain separate membership records.

Plant B

Personnel records are maintained on terminated as well as current employees. Upon retirement or termination, however, some items in the personnel folders of the employees are destroyed. Approximately 4000 records are on file, dating back to 1946. The records contain the following types of information:

1. Name
2. Social Security number
3. Date of birth
4. Work history
5. Termination information
6. Benefits package information

Plant C

Plant C maintains personnel records on both current and terminated employees. Original records dating back to 1943 are stored on microfilm. Personnel records describe the job category and work history for each employee. The following information is available on each record:

1. Name
2. Social Security number
3. Date of birth
4. Age
5. Race
6. Job class (updated)
7. Pay scale (updated)

The plant employees are unionized.

Plant D

Personnel records are maintained on all terminated and current plant employees. Approximately 750 records, dating back to 1950, are stored; old records are never destroyed. Records contain a job history and the following types of information on each employee:

1. Name
2. Social Security number
3. Date of hire
4. Age

A life insurance policy is available to employees as an employee benefit. The company does not maintain death certificates. The union also maintains membership records, but does not keep death records.

Plant E

Plant E maintains personnel records on terminated as well as current employees. Records are never destroyed; files date back to 1944. The files contain information on work classifications of employees in addition to the following standard types of information:

1. Home address
2. Telephone number
3. Social Security number
4. Education
5. Previous employment

The union also maintains membership records.

NIOSH INDUSTRIAL HYGIENE SAMPLING RESULTS

The results of the in-depth exposure monitoring for 1,3-butadiene performed by the survey team at Plants A, B, C, D, and E are presented in this section. At each plant, both personal and area monitoring were performed to evaluate exposures to 1,3-butadiene. The sampling and analytical method and sampling strategy are described in earlier sections of this report. The job descriptions were grouped into generic job titles throughout the 5 plants. This was done so that the data could be analysed among all 5 plants. A detailed discussion of the generic job classification can be found in the section entitled Workforce Characterization. The actual job description used by each individual plant can be found in Appendix B. It should be noted that some job descriptions have a small sample size and this might influence the large geometric standard deviation.

Plant A

Personal Sampling--

A total of 118 full shift personal air samples was collected during the in-depth survey of Plant A. Table 13 presents a summary of the personal samples collected at Plant A. It shows the number of samples taken, the arithmetic mean, the median, the range, the geometric mean, and the geometric standard deviation for each job description. The geometric standard deviation

Table 13. Summary of NIOSH's industrial hygiene samples collected at Plant A (ppm)

Job category	Number of Samples	Arithmetic mean	Median	Range		Geometric mean	Geometric standard deviation
				Minimum	Maximum		
Process technician							
tank farm	6	4.37	0.561	0.113	23.7	0.808	6.10
purification or recovery	6	4.36	5.02	1.33	6.95	3.68	2.00
polymerization or reaction	6	0.696	0.060	0.035	2.71	0.165	6.68
solutions and coagulation	9	0.027	0.025	0.019 [a]	0.046	0.026	1.31
crumbing and drying	9	0.043	0.040	0.014 [a]	0.071	0.039	1.65
packaging	30	0.039	0.028	0.012 [a]	0.154	0.031	1.92
warehouse	2	0.017	0.017	0.014 [a]	0.020	0.017	1.31
Laboratory technician	10	2.91	1.21	0.015 [a]	8.33	0.721	9.91
Maintenance technician	34	0.857	0.100	0.015 [a]	11.0	0.154	5.10
Utilities operator	6	0.118	0.075	< 0.006 [b]	0.304	0.054	5.43
Laboratory technician (short-term sample)	2	20.0	20.0	1.70	38.2	8.07	9.02
Perimeter (area samples)	12	0.014	0.222	< 0.006[a]	0.025	0.010	2.53

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[a] Laboratory analysis of analyte was below limit of quantitation (1.1 ug/sample).

[b] Laboratory analysis of analyte was below limit of detection (0.3 ug/sample).

is used as an indicator of the variability of the data. The raw data on personal samples (including date, sample identification (I.D.), air volume, duration, and concentration) are presented by job description in Appendix B, Table B-1.

The industrial hygiene survey of SBR production at Plant A demonstrated that the workers' full-shift exposures to 1,3-butadiene [with the exception of a tank farm technician's exposure of 23.7 ppm and a maintenance technician's (machinist) exposure of 11.0 ppm] were below both the present OSHA PEL of 1000 ppm[14] and the ACGIH TLV of 10 ppm[15].

Arithmetic and geometric mean full-shift exposures across all generic job categories were less than approximately 5.0 ppm. The highest arithmetic mean full-shift exposure of 4.37 was observed for the process technician in the tank farm. A tank farm operator also received the highest individual full-shift 1,3-butadiene exposure (23.7 ppm) of any worker monitored. A maintenance technician (machinist) received a full-shift exposure of 11.0 ppm during the overhauling of lubricators on 1,3-butadiene compressors. All other individuals received full-shift exposures below 10 ppm. Operators in the finishing area (process technicians: solution and coagulation; crumbing and drying; packaging; and warehouse) had arithmetic mean and geometric mean full-shift exposures below 0.043 and 0.039 ppm, respectively, confirming that the potential for exposure to 1,3-butadiene is minimal past the stripped latex stage. The highest short-term exposure of 38.2 ppm was observed for a hydrocarbon laboratory technician during the collection of a 1,3-butadiene-containing cylinder sample from the process. The data are presented in Table 13.

Area Samples --
Area samples collected during the in-depth survey demonstrate (see Table 13), that, under normal operating conditions, concentrations of 1,3-butadiene measured at the plant perimeter were less than approximately 0.03 ppm. The area monitors were located both upwind and downwind of the SBR production process. The raw data for the area samples (including date, sample ID, air volume, duration, and concentration) are in Appendix B, Table B-2.

Plant B

Personal Sampling--
A total of 39 full-shift personal samples was collected (Table 14) over four shifts during the in-depth survey. These samples represented all of the job categories for the ADN production process (described earlier) with potential for exposure to 1,3-butadiene. Four short-term personal samples were collected during 3 different job tasks. Table 15 presents a summary of these results.

The control room operator was not monitored; area samples, however, were taken in the control room. Table 14 presents a summary of the personal samples collected at Plant B. It includes the number of samples taken, range of measurements, arithmetic mean, median, geometric mean, and geometric standard

Table 14. Summary of NIOSH's full-shift personal samples collected at Plant B (ppm)

Job category	Number of Samples	Arithmetic mean	Median	Range Minimum	Range Maximum	Geometric mean	Geometric standard deviation
Process technician							
unloading area	2	14.6	14.6	0.770	28.5	4.69	12.9
tank farm	8	0.112	0.034	0.009[a]	0.682	0.036	4.01
polymerization or reaction	18	0.057	0.032	<0.006[b]	0.250	0.030	3.45
solutions and coagulation	4	0.051	0.019[a]	<0.006[b]	0.164	0.021	5.09
Laboratory technician	3	0.150	0.016[a]	<0.009[a]	0.429	0.031	10.6
Maintenance technician	4	0.019	0.020[a]	0.011[a]	0.026[a]	0.018	1.41

[a] Laboratory analysis of analyte was below limit of quantitation (1.1 ug/sample).

[b] Laboratory analysis of analyte was below limit of detection (0.3 ug/sample).

Table 15. Summary of NIOSH's short-term personal samples collected at Plant B (ppm)

Job category	Number of Samples	Arithmetic mean	Median	Range Minimum	Range Maximum	Geometric mean	Geometric standard deviation
Process technician							
unloading area	2	116.0	116.0	21.7	210.0	67.4	4.98
Maintenance technician	1	---	---	---	0.306	---	---
Laboratory technician	1	---	---	---	0.682	---	---

Table 16. Summary of NIOSH's full-shift area samples collected at Plant B (ppm)

Location	Number of Samples	Arithmetic mean	Median	Range Minimum	Range Maximum	Geometric mean	Geometric standard deviation
Unloading area	1				0.460		
Polymerization or reaction area	33	0.278	0.074	0.007[a]	2.69	0.083	5.89
Control room	5	0.007	<0.006[b]	<0.006[b]	0.014[a]	0.005	2.32
Perimeter	12	<0.01	<0.006[b]	<0.006[b]	0.016[b]	0.005	1.67

[a] Laboratory analysis of analyte was below limit of quantitation (1.1 ug/sample).

[b] Laboratory analysis of analyte was below limit of detection (0.3 ug/sample).

deviation for each of the job categories monitored. The raw data on personal samples (including date, sample ID, air volume, duration, and concentration) are presented by job category in Appendix B, Table B-3. Samples with duration greater than 8 hours were not weighted to 8 hours.

Area Sampling--
A total of 51 area samples was collected over three shifts during the in-depth survey. These samples characterize four work environments and points along the plant perimeter.

Table 16 summarizes the area samples collected at Plant B. It presents the number of samples taken, the range of measurements, arithmetic mean, median, geometric mean, and geometric standard deviation for each work environment monitored. The raw data for the area samples (including date, sample ID, air volume, duration, and concentration) are presented by work environment in Appendix B, Table B-4.

Plant C

Personal Sampling--
A total of 86 personal samples was collected over four shifts during the in-depth survey. These samples represented all of the job categories described earlier (see section on Description of the Workforce) with potential for exposure to 1,3-butadiene. The VPL production process was not operational at the time of the survey. Table 17 presents a summary of the personal samples collected at Plant C. It includes the number of samples taken, range of measurements, arithmetic mean, median, geometric mean, and geometric standard deviation for each of the categories monitored. The raw data on personal samples (including date, sample ID, air volume, duration, and concentrations) are presented by job category in Appendix B, Table B-5. Four short-term personal samples were obtained and the results are presented in Table 18.

Area Sampling--
A total of 19 area samples was collected over four shifts during the in-depth survey. These samples characterize seven work environments and points along the plant perimeter.

Table 19 summarizes the area samples collected at Plant C. It presents the number of samples taken, the range of measurements, arithmetic mean, median, geometric mean, and geometric standard deviation for each work environment monitored. The raw data for the area samples (including date, sample ID, air volume, duration, and concentration, are presented by work environment in Appendix B, Table B-6.

Plant D

Personal Sampling--
A total of 78 personal samples was collected over three shifts during the in-depth survey. These samples represented all of the job categories for the

Table 17. Summary of NIOSH's full-shift personal samples collected at Plant C (ppm)

Job category	Number of Samples	Arithmetic mean	Median	Range Minimum	Range Maximum	Geometric mean	Geometric standard deviation
Process technician							
tank farm	8	2.37	0.392	<0.006 a	12.0	0.300	15.3
polymerization or reaction	7	0.003	<0.006 a	<0.006 a	<0.008 a	0.003	1.17
solutions and coagulation	3	0.003	<0.006 a	<0.005 a	0.008 a	0.003	1.27
crumbing and drying	13	0.016	0.013 b	<0.005 a	0.081	0.010	2.72
packaging	20	0.006	<0.006 a	<0.005 a	0.026	0.004	1.97
warehouse	11	0.004	<0.006 a	<0.005 a	<0.018 a	0.004	1.50
Laboratory technician	17	0.184	0.069	<0.006 a	0.943	0.058	6.07
Maintenance technician	7	<0.009	<0.006a	0.006 a	0.013 b	0.004	1.77

a Laboratory analysis of analyte was below limit of detection (0.3 ug/sample).

b Laboratory analysis of analyte was below limit of quantitation (1.1 ug/sample).

Table 18. Summary of NIOSH's short-term personal samples collected at Plant C (ppm)

Job category	Number of Samples	Arithmetic mean	Median	Range Minimum	Range Maximum	Geometric mean	Geometric standard deviation
Laboratory technician	1	---	---	---	13.3	---	---
Maintenance technician	3	5.99	3.24	0.088	14.6	1.61	13.8

Table 19. Summary of NIOSH's full-shift area samples collected at Plant C (ppm)

Location	Number of Samples	Arithmetic mean	Median	Range Minimum	Range Maximum	Geometric mean	Geometric standard deviation
Tank farm area	1	---	---	---	0.251	---	---
Purification area	4	0.564	0.312	0.078	1.55	0.299	3.82
Polymerization or reaction area	1	---	---	---	0.018	---	---
Solutions and coagulation area	4	0.003	<0.006 b	<0.006 b	<0.006 b	0.003	1.05
Crumbing and drying area	4	0.003	<0.006 b	<0.006 b	0.008 b	0.003	1.11
Packaging area	2	0.005	<0.006 b	<0.006 b	0.006 a	0.004	1.54
Perimeter	4	0.007	<0.006 b	<0.006 b	0.017 a	0.005	2.38

a Laboratory analysis of analyte was below limit of quantitation (1.1 ug/sample).

b Laboratory analysis of analyte was below limit of detection (0.3 ug/sample).

neoprene production process described earlier (see section on Description of the Workforce) with potential for exposure to 1,3-butadiene. The THPA production process was not operational at the time of the survey. Table 20 presents a summary of the personal samples collected at Plant D. It includes the number of samples taken, range of measurements, arithmetic mean, median, geometric mean, and geometric standard deviation for each of the job categories monitored. The raw data on personal samples (including date, sample ID, air volume, duration, and concentration) are presented by job category in Appendix B, Table B-7. Two short-term personal samples were collected during a job task in polymerization and reaction. Table 20 presents a summary of the results.

Area Sampling-
A total of 36 area samples was collected over three shifts during the indepth survey. These samples characterize five work environments and points along the plant perimeter.

Table 21 summarizes the area samples collected at Plant D. It presents the number of samples taken, the range of measurements, arithmetic mean, median, geometric mean, and geometric standard deviation for each work environment monitored. The raw data for the area samples (including date, sample ID, air volume, duration, and concentration) are presented by work environment in Appendix B, Table B-8.

Plant E

Personal Sampling--

A total of 115 personal samples was collected over three shifts during the in-depth survey. These samples represented all of the job categories for the SBR/NBR production process described earlier with potential for exposure to 1,3-butadiene. Table 22 presents a summary of the personal samples collected at Plant E. It includes the number of samples taken, range of measurements, arithmetic mean, median, geometric mean, and geometric standard deviation for each of the job categories monitored. Two short term personal samples were taken of the laboratory technician. Table 22 presents a summary of the results. The raw data on personal samples (including date, sample ID, air volume, duration, and concentration) are presented by job category in Appendix B, Table B-9.

Area Sampling--

A total of 14 area samples was collected over three shifts during the in-depth survey. These samples characterize the tank farm work area and points along the plant perimeter.

Table 22 summarizes the area samples collected at Plant E. It presents the number of samples taken, the range of measurements, arithmetic mean, median, geometric mean, and geometric standard deviation for each work environment monitored. This approach should again result in an accurate measure of the means and standard deviations. The raw data for the area samples (including date, sample ID, air volume, duration, and concentration) are presented by work environment in Appendix B, Table B-10.

Table 20. Summary of NIOSH's full-shift personal samples collected at Plant D (ppm)

Job category	Number of Samples	Arithmetic mean	Median	Range Minimum	Range Maximum	Geometric mean	Geometric standard deviation
Process technician							
tank farm	3	0.064	0.046	0.023	0.123	0.050	2.34
polymerization or reaction	29	0.077	0.033	<0.008 [a]	0.779	0.038	3.[illegible]
solutions and coagulation	5	0.026	0.028	0.015 [b]	0.038	0.025	1.[illegible]
crumbing and drying	7	0.032	0.027	0.018 [b]	0.052	0.030	1.52
packaging	6	0.033	0.034	0.022 [b]	0.038	0.032	1.23
control room	6	0.028	0.016	< 0.006 [a]	0.070	0.015	3.90
Laboratory technician - analysis	14	0.636	0.044	0.029	4.12	0.094	6.28
Maintenance technician	9	0.030	0.026	0.021 [b]	0.048	0.029	1.33
Process technician							
polymerization or reaction (short-term sample)	2	5.54	5.54	< 0.137 [a]	10.9	1.22	22.2

[a] Laboratory analysis of analyte was below limit of detection (0.3 ug/sample).

[b] Laboratory analysis of analyte was below limit of quantitation (1.1 ug/sample).

Table 21. Summary of NIOSH's full-shift area samples collected at Plant D (ppm)

Location	Number of Samples	Arithmetic mean	Median	Range Minimum	Range Maximum	Geometric mean	Geometric standard deviation
Tank farm area	1	---	---	---	0.954	---	---
Polymerization or reaction area	18	0.279	0.068	0.014[a]	1.49	0.097	4.15
Solutions and coagulation area	3	0.020	0.020[a]	0.014[a]	0.026	0.019	1.36
Laboratory	3	3.05	0.034	0.025	9.08	0.199	27.5
Perimeter	11	0.021	0.018[a]	<0.006[b]	0.058	0.016	2.50

[a] Laboratory analysis of analyte was below limit of quantitation (1.1 ug/sample).

[b] Laboratory analysis of analyte was below limit of detection (0.3 ug/sample).

Table 22. Summary of NIOSH's personal industrial hygiene samples collected at Plant E (ppm)

Job category	Number of Samples	Arithmetic mean	Median	Range Minimum	Range Maximum	Geometric mean	Geometric standard deviation
Process technician							
tank farm	6	3.02	2.762	1.066	6.01	2.61	1.83
purification	12	9.52	7.58	2.774	24.13	7.85	1.89
polymerization or reaction	21	1.24	0.451	0.035	11.25	0.419	4.43
solutions and coagulation	12	0.082	0.090	<0.006[a]	0.169	0.060	2.96
crumbing and drying	6	0.055	0.043	0.033	0.116	0.049	1.59
packaging	23	0.058	0.042	<0.014[a]	0.144	0.049	1.92
warehouse	7	0.045	0.039	0.033	0.068	0.043	1.36
Laboratory technician	10	8.08	5.13	0.100	37.37	3.26	5.84
Maintenance technician	18	3.86	0.861	0.072	43.15	0.966	4.79
Laboratory technician (short-term sample)	2	63.5	63.5	26.3	101.1	51.4	2.58
Tank farm area	2	0.959	0.959	0.142	1.77	0.502	5.96
Perimeter area	12	0.073	0.050	0.027	0.166	0.061	1.82

[a] Laboratory analysis of analyte was below limit of detection (0.3 ug/sample).

DISCUSSION

Personal Monitoring Data

A total of 451 personal samples (comprised of 437 full-shift and 14 short-term samples) were collected during the five 1,3-butadiene polymer facility in-depth surveys.

Tables 23 and 24 provide a breakdown by job category/work activity of the full-shift and short-term personal monitoring results, respectively, and present averages, ranges, and standard deviations for the measured 1,3-butadiene concentrations. Full-shift exposures for the different job categories range from a low of <0.005 to a high of 43.2 ppm (Table 23), whereas the short-term exposures range from 0.088 to a high of 210 ppm (Table 24). The highest full-shift personal exposure was 43.2 ppm for a maintenance technician working on a 1,3-butadiene compressor. The highest short-term exposure was 210 ppm for a process technician (unloading area) sampling a barge for 1,3-butadiene. The short-term personal monitoring was conducted with the intention of identifying peak exposures during operation or activities that were considered to have a potential for exposure to 1,3-butadiene. However, because continuous, real-time monitors were not available for measuring 1,3-butadiene concentrations, it was not possible to ensure that the short-term sampling would succeed in detecting peak concentrations over the entire workshift. The short-term sampling results in Table 24 shows, at least one exposure to 1,3-butadiene greater than 10 ppm for all four types of periodic inplant activities.

Table 23 clearly shows that the six job categories that experience full-shift (personal) 1,3-butadiene exposures greater than 10 ppm (at least one sample) are the process technician in unloading, tank farm, purification, polymerization or reaction, laboratory technician, and maintenance technicians. These job categories had geometric mean exposures of 4.69, 0.270, 6.10, 0.062, 0.213, and 0.122 ppm, respectively. Geometric mean exposures for all other job categories were below 0.03 ppm. Maximum full shift exposures for laboratory and maintenance technicans exceeded 35 ppm (at least one sample).

Area Monitoring Data

A total of 132 area samples were obtained during the 5 in-depth industrial hygiene surveys. Table 25 provides a breakdown by work environment of the full-shift area monitoring results and presents averages, ranges, and standard deviations for the 1,3-butadiene concentrations. Full-shift 1,3-butadiene concentrations in the work areas ranged from 0.006 to 9.08 ppm. The maximum average full-shift area concentration was observed in the 1,3-butadiene quality control laboratory near the gas chromatograph, with an arithmetic mean of 9.08 ppm. A total of 51 samples were taken at the plant perimeter and a geometric mean of 0.013 ppm was reported.

Table 23. Summary of NIOSH's full-shift personal samples collected at the five polymer plants (ppm)

Job category	Number of Samples	Arithmetic mean	Median	Range Minimum	Range Maximum	Geometric mean	Geometric standard deviation
Process technician							
unloading area	2	14.6	14.6	0.770	28.5	4.69	13
tank farm	31	2.08	0.362	<0.006[a]	23.7	0.270	10
purification	18	7.80	6.40	1.33	24.1	6.10	2
polymerization or reaction	81	0.414	0.047	<0.006[a]	11.3	0.062	6
solutions and coagulation	33	0.048	0.028	<0.005[a]	0.169	0.029	3
crumbing and drying	35	0.033	0.028	0.005[a]	0.116	0.023	3
packaging	79	0.036	0.029	<0.005[a]	0.154	0.022	3
warehouse	20	0.020	0.008[b]	0.005[a]	0.068	0.010	3
control room	6	0.030	0.016[b]	<0.012[a]	0.070	0.019	3
Laboratory technician	54	2.27	0.103	<0.006a	37.4	0.213	12
Maintenance technician	72	1.37	0.089	<0.006[a]	43.2	0.122	9
Utilities operator	6	0.118	0.075	<0.006[a]	0.304	0.054	5

[a] Laboratory analysis of analyte was below limit of detection (0.3 ug/sample).

[b] Laboratory analysis of analyte was below limit of quantitation (1.1 ug/sample).

Table 24. Summary of NIOSH's short-term personal samples for 1,3-butadiene collected at the five polymer plants (ppm)

Job category	Number of Samples	Arithmetic mean	Median	Range Minimum	Range Maximum	Geometric mean	Geometric standard deviation
Process technician							
unloading area	2	116.0	116.0	21.7	210.0	67.4	5
polymerization or reaction	2	5.54	5.54	<0.137[a]	10.90	1.22	22
Laboratory technician	6	30.2	19.8	0.682	101.0	10.8	7
Maintenance technician	4	4.57	1.77	0.088	14.6	1.06	10

[a] Laboratory analysis of analyte was below limit of detection (0.3 ug/sample).

Table 25. Summary of NIOSH's full-shift area samples for 1,3-butadiene collected at five polymer plants (ppm)

Location	Number of Samples	Arithmetic mean	Median	Range		Geometric mean	Geometric standard deviation
				Minimum	Maximum		
Unloading area	1				0.460		
Tank farm area	4	0.780	0.602	0.142	1.77	0.496	3
Purification area	4	0.564	0.312	0.078	1.55	0.299	4
Polymerization or reaction area	52	0.274	0.072	0.007[a]	2.70	0.085	5
Solutions and coagulation area	6	0.011	<0.009 b	<0.006 b	0.026	0.008	3
Crumbing and drying area	4	0.003	<0.006 b	<0.006 b	0.008 b	0.003	1.1
Packaging area	2	0.005	<0.005 b	<0.006 b	0.006 a	0.004	1.5
Laboratory	3	3.05	0.034	0.025	9.08	0.199	28
Control room	5	0.007	<0.006 b	<0.006 b	0.014 b	0.005	2
Perimeter	51	0.027	0.017 a	<0.006 b	0.166	0.013	3

a Laboratory analysis of analyte was below limit of quantitation (1.1 ug/sample).

b Laboratory analysis of analyte was below limit of detection (0.3 ug/sample).

CONCLUSIONS

In summary, the monitoring results from the present NIOSH study for the 1,3-butadiene polymer industry show that full-shift exposures for all job categories are well below the current OSHA PEL of 1000 ppm. Geometric mean full-shift exposures for all job categories are also below the ACGIH TLV of 10 ppm. Maximum full-shift exposures, however, did exceed 10 ppm for six job categories. A total of 19 of the 451 industrial hygiene samples taken (4.2%) had results exceeding 10 ppm. Those so exposed were in the unloading area, tank farm, purification unit, polymerization or reaction area, and laboratory and maintenance technicians.

The polymer industry is confronted with the same engineering design problems as the 1,3-butadiene monomer production industry in control of 1,3-butadiene emissions, i.e., the loading and unloading of 1,3-butadiene, taking quality control samples, and the maintenance of pumps and equipment that handle 1,3-butadiene. The process technology for handling 1,3-butadiene on the front end of the polymer process is the same in the monomer industry.

RECOMMENDATIONS

In the context of the current OSHA PEL for 1,3-butadiene (1000 ppm) and the ACGIH TLV of 10 ppm, the NIOSH study results indicate that the control programs in the polymer industry generally appear to maintain personal exposures below the applicable limits. However, because of certain job-related exposures and the concern that 1,3-butadiene may present both a carcinogenic and teratogenic risk, the following additional control measures are recommended for polymer production plants that may not already be implementing such controls:

1. For obtaining quality control cylinder samples, plants should consider conversion to a closed-loop sampling system to lower the mean exposure of process technicians working in process areas and to lab technicians.

2. Leaking pumps present an exposure potential to process technicians in the process areas. The release of 1,3-butadiene from such equipment can be controlled through the use of dual mechanical seals. Plants should consider retrofittng of pumps having single mechanical seals with the more effective dual mechanical seals.

3. Because magnetic gauges are known to limit the release of 1,3-butadiene (and hence exposure to process technicians in the loading area) during the loading of rail cars, plants should consider a program to convert to magnetic gauges for monitoring rail car filling operations.

4. As evident from the monitoring results for laboratory technicians conducting cylinder voiding, workers assigned to this task may be exposed to relatively high levels of 1,3-butadiene. Consideration should be given to the use of a laboratory hood or a vacuum exhaust with an enclosure for cylinder voiding. Furthermore, workers should be trained in the proper conduct of tasks such as cylinder voiding and cylinder sampling.

5. Maintenance technicians should follow appropriate decontamination procedures when working on process equipment. However, if it is not possible to completely decontaminate a process prior to the procedure then respirators with organic vapor cartridges should be worn.

As evident from the results of the NIOSH monitoring study, the use of analytical methods specific to 1,3-butadiene is preferred for assessing 1,3-butadiene exposures. The new NIOSH sampling and analytical method (NIOSH Method 1024) for 1,3-butadiene is recommended in areas of potentially low exposures and where there is a potential for interference with other C_4 compounds.

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APPENDIX A

NEW NIOSH SAMPLING AND ANALYTICAL METHOD FOR 1,3-BUTADIENE

FORMULA: C_4H_6, $CH_2=CHCH=CH_2$

M.W.: 54.09

1,3-BUTADIENE

METHOD: 1024
ISSUED: 5/15/86

OSHA: 1000 ppm
NIOSH: potential carcinogen [1]
ACGIH: 10 ppm; suspect carcinogen
(1 ppm = 2.21 mg/m³ @ NTP)

PROPERTIES: gas; vapor density 1.9 (air = 1);
BP -4.4 °C; VP 280 kPa (26 psig) @ 25 °C;
explosive range 2.0 to 11.5% v/v in air

SYNONYMS: CAS #106-99-0

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut charcoal, 400- and 200-mg in separate tubes)

FLOW RATE: 0.01 to 0.5 L/min

VOL-MIN: 3 L
-MAX: 25 L @ 100 ppm

SHIPMENT: separate front and back tubes, chill below -4 °C

SAMPLE STABILITY: at least two months for quality assurance blind spikes stored in a freezer

BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 0.19 to 19 mg/m³
(25-L samples)

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION (s_r): 0.060

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 1,3-butadiene

DESORPTION: 4 mL methylene chloride; 30 min

INJECTION: 1 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 250 °C
-COLUMN: see APPENDIX A

CARRIER GAS: Helium

MAKEUP GAS: Nitrogen, 30 mL/min

COLUMNS: fused silica, 10-m x 0.50-mm ID
1.8-µm CP WAX 57 CB (backflushable pre-column), and 50-m x 0.32-mm ID
Al_2O_3/KCl PLOT (see APPENDIX A)

CALIBRATION: vapor-spiked sampling media

RANGE: 1.1 to 480 µg per sample

ESTIMATED LOD: 0.2 µg per sample

PRECISION (s_r): 0.025

APPLICABILITY: Assuming 25-L sampling volumes: the upper limit of the sampler is 220 mg/m³ (100 ppm); the analytical range covers 0.04 to 18 mg/m³ (0.02 to 8 ppm); at higher levels, desorbed samples may require dilution; below 0.9 mg/m³ (0.4 ppm), the desorption efficiency falls below 75% and allowance should be made for decreased accuracy.

INTERFERENCES: Pentane, methyl acetylene, or vinylidene chloride may chromatographically interfere at high levels. High humidity (>80% RH) or other hydrocarbons present at permissible levels may significantly decrease the sampler's capacity for 1,3-butadiene.

OTHER METHODS: This method revises S91 [2].

A-2

REAGENTS:
1. Methylene chloride,* chromatographic quality with hydrocarbon (cyclohexene) preservative.
2. 1,3-Butadiene,* 99.5%, in cylinder equipped for gas withdrawal, with needle valve.
3. Helium, purified.
4. Hydrogen, purified.
5. Air, purified.
6. Nitrogen, purified.
7. Water, distilled.

*See Special Precautions.

EQUIPMENT:
1. Sampler: Tandem charcoal tubes. Each tube is flame-sealed glass (8.5 cm long, 8-mm OD, 6-mm ID), has plastic caps for resealing, and contains activated coconut shell charcoal (such as SKC Lot 120) preceded by silylated glass wool and followed by a 3-mm urethane foam plug. The front tube holds 400 mg charcoal. The back tube holds 200 mg.
2. Personal sampling pump, 0.01 to 0.5 L/min, with flexible connecting tubing.
3. Refrigerant, bagged (e.g., Blue Ice or dry ice), and insulated shipping container.
4. Gas chromatograph, flame ionization detector, integrator, and column (see APPENDIX A).
5. Ice, wet.
6. Vials, 5-mL, 2-mL, 1-mL, and other convenient sizes, with PTFE-lined septum caps.
7. Pipettes, TD, 4-, 2-, and 1-mL.
8. Syringes, gas-tight, 250-, 100-, 25-, and 10-µL.
9. Beaker, 150-mL.
10. Gas drying tube with serum cap to fit stem and 2-cm piece of plastic tubing to fit over serum cap.

SPECIAL PRECAUTIONS: 1,3-Butadiene is a potential carcinogen, teratogen, and reproductive hazard [1]. Methylene chloride is toxic, very volatile, and a suspect carcinogen [3]. Work should be performed in a well-ventilated fume hood.

SAMPLING:
1. Calibrate each personal sampling pump with a representative sampler in line.
2. Immediately before sampling, break ends of sampler tubes. Connect smaller tube to personal sampling pump with flexible tubing and to larger tube with a short piece of plastic tubing.
3. Sample at an accurately known flow rate of 0.01 to 0.5 L/min for a sample size of 3 to 25 L.
4. Separate the tubes, cap, and pack securely for shipment. Chill below -4 °C during shipment and storage.

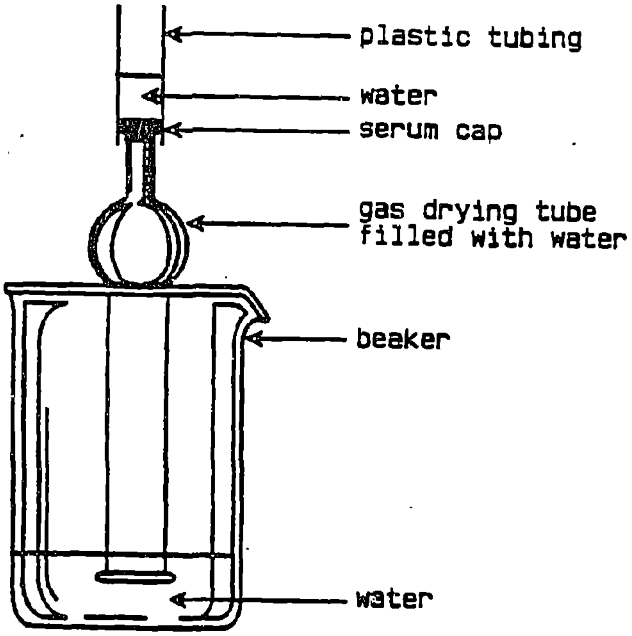
SAMPLE PREPARATION:

5. Add 4.0 mL methylene chloride to 5-mL vials and 2.0 mL to 2-mL vials. Loosely cap vials and thoroughly chill in ice.
6. Place front sorbent sections in 5-mL vials and back sections in 2-mL vials. Discard glass wool and foam plugs. Immediately cap each vial.
7. Remove from ice and allow to stand 30 min with occasional agitation.
8. Transfer sample solution to appropriate vial and cap if using an autosampler. Thoroughly chill solution and vial before making transfer.

CALIBRATION AND QUALITY CONTROL:

NOTE: The accurate measurement of pure 1,3-butadiene gas by gas-tight syringe is a critical step in the calibration. Even a slight obstruction (e.g., flakes of PTFE from the plunger tip which obstruct the needle) can cause 1,3-butadiene to be liquified as the plunger is depressed, making delivery incomplete. Bracketing gas samples with water, as described below, allows the volume taken to be approximately verified, and assures complete delivery. The precision of the analysis of multiple independent standards is another indicator of the accuracy of the volumes taken.

9. Make up stock solutions in triplicate at three concentration levels, e.g., 200 µL of 1,3-butadiene gas in 1 mL solution, and both 200 and 50 µL of gas in 4 mL solution:
   a. Prepare a beaker and drying tube assembly as shown below. Bubble 1,3-butadiene under the lower edge of the drying tube so that water is displaced and the gas is trapped in the tube.



   b. Pipet 1 or 4 mL of methylene chloride into a 1- or 5-mL vial, cap, and thoroughly chill.
   c. Take a known amount (50 or 200 µL) of 1,3-butadiene from the drying tube with a 100- or 250-µL gas-tight syringe. Bracket the gas in the syringe with small amounts of water (5 to 10% of syringe volume) taken from the area above the serum cap before and after withdrawing the gas. Do not take water from inside the drying tube, since it may contain a significant amount of dissolved 1,3-butadiene.
   d. Slowly inject the 1,3-butadiene and water below the surface of the methylene chloride.
   e. Agitate and continue to chill the vial to complete dissolution.
10. Calibrate daily with media blanks and triplicate independent media standards of at least five levels ranging from, e.g., 0.5 to 200 µL 1,3-butadiene gas per sample:
    a. Break ends of larger sampler and attach to personal sampling pump with flexible tubing.
    b. Take pure gas (50 or 200 µL, as in step 9.c) for the higher levels, or 40 µL of stock solution for lower levels.
    c. Inject the gas and surrounding water plugs or the stock solution at a point inside the sampler near the glass wool plug while drawing clean air through tube at 0.05 L/min. Continue to draw air through the tube for 5 min or just until the stock solution evaporates.
    d. Seal tube with plastic caps.
    e. Store at temperature below -4 °C overnight, then desorb (steps 5 through 8).
    f. Analyze media standards and blanks together with samples (steps 13 and 14).
    g. Convert gas volumes to masses, correcting for compressibility and water vapor (see APPENDIX B), and prepare a calibration graph (peak areas or heights vs. concentration of 1,3-butadiene taken in µg/mL).

11. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in calibration range (step 10).
    a. Dilute the stock solutions (step 9) with methylene chloride to extend the range of standards down to 0.1 µg/mL. Avoid including water in the portions diluted.
    b. Transfer solutions as in step 8 if using an autosampler, and analyze together with media standards (steps 13 and 14).
    c. Convert gas volumes to masses, correcting for compressibility and water vapor (see APPENDIX B), and prepare DE calibration graph of peak area or height vs. µg/mL 1,3-butadiene.
    d. Read the concentrations, µg/mL, in media standards and blanks from DE calibration graph and multiply by the desorption volume to calculate the masses recovered.
    e. Prepare a graph of DE vs. µg taken. DE = (mass found - blank mass)/(mass taken).
12. Analyze three quality control blind spikes to insure that calibration graph (step 10) is in control.

MEASUREMENT:

13. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1024-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If detector response is above range of working standards, dilute with methylene chloride, reanalyze, and apply appropriate dilution factor in calculations.
14. Measure peak area or height.
    NOTE: Vinylidene chloride, an impurity in methylene chloride, elutes just after 1,3-butadiene and may be used as an internal standard.

CALCULATIONS:

15. Determine the concentration, µg/mL, of 1,3-butadiene found in each sample front (W_f) and back (W_b) sorbent section from calibration graph (step 10), and multiply by desorption volume and dilution factor, if any, to calculate the mass, µg, found.
    NOTE 1: This calibration method corrects for media blank and DE. Do not duplicate corrections.
    NOTE 2: For any sampler with $W_b > W_f/10$, report breakthrough and possible sample loss.
16. Calculate concentration of analyte in the volume of air sampled, V (L):

$$C = \frac{(W_f + W_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The detector responses determined for triplicate standard solutions at each of five levels were linear over the range 0.3 to 440 µg per sample. The pooled s_r was 0.038. The estimated limit of detection was 0.02 µg/mL.

The capacity of a 400-mg charcoal sorbent section was 31 L for a sample at 80% RH and approximately 56 ppm 1,3-butadiene. When exposed to 0.7 and 2.5 mL of pure 1,3-butadiene gas followed by 80% RH air, breakthrough occurred after 35 L and 28.5 L, respectively. The corresponding respective time-weighted average concentrations were 20 and 88 ppm.

For the analysis of media standards at levels of 1.1, 4.4, 18, 125, and 480 µg per sample, the pooled s_r was 0.025, and the desorption efficiencies were 67%, 68%, 75%, 102%, and 97%, respectively. Adding water to media standards just after spiking or during desorption had no significant effect on desorption efficiencies.

In a study of temperature effects on storage stability, 400-mg charcoal tubes were spiked with 26 µg 1,3-butadiene and stored either at ambient temperature or in a freezer below -4 °C. Recoveries were measured relative to media standards stored overnight in the freezer. The recoveries (and days stored) were 94% (7), 93% (14), and 98% (21) for the frozen samples, and 95% (1), 76% (7), 61% (14), and 65% (21) for the ambient samples.

In a preliminary evaluation of precision and accuracy, charcoal tubes were spiked with 125 µg 1,3-butadiene via calibrated sampling valve. The recovery was 102.2% versus media standards (corrected for desorption efficiency) and 96.8% versus standard solutions (uncorrected for desorption efficiency); the s_r of the response was 0.016. Subsequently, simulated samples were exposed to known amounts of approximately 10% 1,3-butadiene in helium, followed by 25 L of air at 80% RH. The 1,3-butadiene concentration was independently determined by packed column gas chromatography with thermal conductivity detection. Media standards were prepared via calibrated sampling valves. The recovery from six simulated samples at 463 µg per sample was 101.6% versus media standards and 91.3% versus standard solutions; the s_r of the response was 0.047. At 45.3 µg per sample, the recovery was 112.3% versus media standards and 102.9% versus standard solutions; the s_r of the response was 0.048. At 4.64 µg per sample, the recovery was 80.3% versus media standards and 103.8% versus standard solutions; the s_r of the response was 0.011. In the latter experiment, the two lowest levels of media standards appeared to be high, possibly due to absorption and release of 1,3-butadiene by internal parts of the sampling valve. The study was repeated at 4.71 µg, with the three lowest levels of media standards prepared as in step 10. The recovery was 129.5% versus media standards and 91.2% versus standard solutions; the s_r of the response was 0.023. The s_r of the response pooled for all levels was 0.033. Assuming a sampling pump error of 0.05, the precision of the total sampling and analytical method was 0.060. For levels at and above 45 µg (0.8 ppm in 25 L), apparent biases may be attributed to experimental errors in the preparation and analysis of standards and samples rather than a true bias in the method. At lower levels, based on the linear response and near-zero intercept observed for the standard solution calibrations and the higher than expected desorption efficiencies for the samples, there appeared to be a positive bias in the preparation of the simulated samples.

The method has been used in six industrial hygiene surveys, for a total of 621 samples, most of which were collected under conditions of high ambient temperature and humidity. Only two samples showed severe breakthrough ($W_b > W_f/10$). Results for field samples at levels as high as 7.3 mg per sample were not significantly changed by dilution and reanalysis. In all, over 2000 analyses were made over a period of six months without any deterioration of the chromatographic columns. During the course of the analyses, twenty sets of standard solutions and media standards were prepared and analyzed, each set consisting of triplicates at each of five levels corresponding to 1.08 to 1.10, 4.32 to 4.40, 17.3 to 17.6, 108 to 110, and 432 to 441 µg per sample. For the five levels of standard solutions, the respective pooled relative standard deviations of the observed responses were 0.093, 0.074, 0.059, 0.055, and 0.071. For each set of standard solutions, the deviations of the responses were determined relative to the line resulting from a weighted linear regression of response on concentration. The 95% confidence intervals for the mean relative deviations from linearity for the five levels were -0.002 ± 0.003, 0.000 ± 0.003, -0.020 ± 0.002, 0.002 ± 0.002, and -0.019 ± 0.002, respectively. For the media standards, the respective pooled relative standard deviations for the observed responses at the five levels were 0.109, 0.080, 0.050, 0.064, and 0.037; the respective 95% confidence intervals for the mean percent recoveries relative to the standard solution calibrations were 60.4 ± 0.4, 66.4 ± 0.3, 70.5 ± 0.2, 86.2 ± 0.3, and 91.2 ± 0.2.

The analysis of quality assurance blind spikes provided additional data indicating that samples were stable when stored below -4 °C, and that average recoveries, calibrated against media standards, ranged from 96 to 107%. Seventy-seven blind spikes were prepared at six levels, 19.9 to 21.9, 48.6 to 52.6, 104 to 110, 199 to 219, 398 to 438, and 663 µg per sample, stored in a freezer, and analyzed along with the field samples. The storage times ranged from 3 to 134 days; the average was 59 days. For the six levels of blind spikes, the respective relative standard deviations for recoveries were 0.210, 0.092, 0.054, 0.091, 0.126, and 0.056; the respective 95% confidence intervals for the mean recoveries were 0.986 ± 0.032, 0.961 ± 0.014, 0.994 ± 0.008, 1.029 ± 0.015, 1.064 ± 0.021, and 1.074 ± 0.021. Prior to linear regression of the recoveries versus the amounts spiked and/or days stored, three results, two high and one low, were determined to be outliers by application of one-sided Grubbs tests [4] at the 2.5% significance level and were dropped from the data set. Linear regression of percent recovery on days stored for the data segregated by level resulted in respective slopes and 95% confidence intervals of 0.060 ± 0.080, 0.005 ± 0.128, -0.003 ± 0.092, 0.060 ± 0.179, 0.249 ± 0.188, and 0.018 ± 0.247 percent per day. Thus, the only statistically significant correlation between recovery and days stored was at the next to highest level, for a gain rather than loss over time. Over all levels, the slopes and 95% confidence intervals for recovery versus amounts spiked and days stored were 0.017 ± 0.009 percent per µg and 0.045 ± 0.051 percent per day, respectively. Thus, according to the latter model: the recovery for the blind spikes increased at a rate corresponding to approximately 11% over the range prepared; as stored, the blind spikes appeared to be stable — the 95% confidence interval of the slope over time indicated a maximum gain of 5.7% or loss of 0.4% during the average 59-day storage period.

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METHOD WRITTEN BY: R. Alan Lunsford, Ph.D., Yvonne T. Gagnon, and John Palassis, NIOSH/DPSE.

APPENDIX A. GAS CHROMATOGRAPH COLUMN SELECTION, INSTALLATION, AND OPERATION:

Any column which separates 1,3-butadiene from the other substances present, and which otherwise provides satisfactory chromatographic performance, is acceptable. The column specified in NIOSH Method S91 [2] is 6-m x 3-mm OD stainless steel, packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS. It provides a convenient separation of 1,3-butadiene from the desorbing solvent. However, if other C_4 to C_6 hydrocarbons are present, interferences are likely. For the development of this method, a 50-m x 0.32-mm ID fused-silica porous-layer open-tubular (PLOT) column coated with Al_2O_3/KCl (Cat. # 7515, Chrompack, Bridgewater, NJ) was chosen as the analytical column because it provides a very efficient separation at temperatures above ambient. However, water from the samples deactivates the aluminum oxide, reducing retention times, and high-boiling or polar substances may accumulate on the column and irreversibly degrade the separation. The degradation was eliminated by using a backflushable pre-column, i.e., 10-m x 0.5-mm ID fused-silica CP Wax 57 CB (Cat. # 7648, Chrompack, Bridgewater, NJ). The pre-column allows light hydrocarbons to pass through, but water, methylene chloride, and polar or high boiling components are retained and can be backflushed. Eliminating the solvent peak significantly reduces the time required to complete the analysis.

Figures 1 and 2 schematically illustrate the installation and operation of the recommended columns in a Hewlett-Packard 5880A gas chromatograph with split-splitless capillary inlet systems installed in the "B" and "C" injector positions. The only change to the "B" system involves the normally closed (NC) port of the "B" solenoid valve. Originally, it was connected to the capped port of the tee in the "B" septum purge line. (If desired, switching between normal operation of the "B" system and backflushable pre-column operation could be easily achieved by adding a manually operated three-way valve.) Replumb the components of the "C" system as shown, and extend lines from the normally open (NO) port of the "C" solenoid and the "C" backpressure regulator into the oven. Connect the lines and columns with a zero-dead-volume cross (e.g., Part # ZX1, Valco, Houston, TX) and graphite ferrules.

Set the initial oven temperature to 50 °C and the "C" backpressure regulator to 185 kPa. With the solenoid valves activated (inject mode), set the "C" flow control to 20 mL/min and the "B" controls so that the effluent from the analytical column and the "C" split vent total 10 mL/min. Then, with the solenoid valves deactivated (backflush or normal mode), adjust the "B" backpressure regulator until the flow from the "C" split vent returns to the value previously measured. This establishes a reverse flow of 10 mL/min through the pre-column. Program the oven to hold the initial temperature (50 °C) for 2 min, ~~then~~ rise to 120 °C at 20 °C/min, and hold for 8 min. Adjust the time from injection to backflush by injecting standards and progressively decreasing the time from 2 min until the methylene chloride peak is removed without attenuating the butadiene response. It may be necessary to clear higher hydrocarbons from the analytical column by programming the oven to 200 °C at 30 °C/min and holding 4 min. Program the solenoid valves to be activated at the end of each run to prepare for the next injection.

Using the backflushable pre-column, there remains a slight problem with retention drift. While in inject mode, the pre-column strips residual water from the carrier gas. This activates the aluminum oxide surface of the analytical column and causes retention to increase. The effect is most noticable when starting up after the system has been idle. When beginning a sequence of samples, it is advisable to analyze solvent blanks until the retention drift (e.g., of vinylidene chloride) becomes tolerable.

APPENDIX B. CONVERSION OF 1,3-BUTADIENE VOLUME TO MASS:

MacCallum and McKetta [5] determined the compressibility factor, Z, which corrects for non-ideal behavior, for 1,3-butadiene at temperatures, T, ranging from 10 to 75 °C, and pressures, P, from approximately 420 to 1050 mm Hg. Multiple regression of the observed values against P, PT, and PT^2, yields the following equation (standard error of the estimated Z is 0.000635 for 13 degrees of freedom):

$$Z = a + bP + cPT + dPT^2.$$

where: $a = 1.00095$
$b = -4.84089 \times 10^{-5}$
$c = 4.44816 \times 10^{-7}$
$d = -1.15744 \times 10^{-9}$

The mass, M, of 1,3-butadiene, corrected for compressibility and the presence of water vapor (when the gas is stored above water), may be calculated by the following equation:

$$M = \frac{(P - P_v)\cdot V\cdot 54.09}{Z\cdot 62.36\cdot (T + 273.2)},\ \mu g.$$

where: P_v = vapor pressure of water @ T °C (mm Hg)
V = volume of 1,3-butadiene (µL)
54.09 = molecular weight of 1,3-butadiene ($g\cdot mol^{-1}$)
62.36 = gas constant ($mm\ Hg\cdot L\cdot mol^{-1}\cdot K^{-1}$)
273.2 = absolute temperature of 0 °C (K)

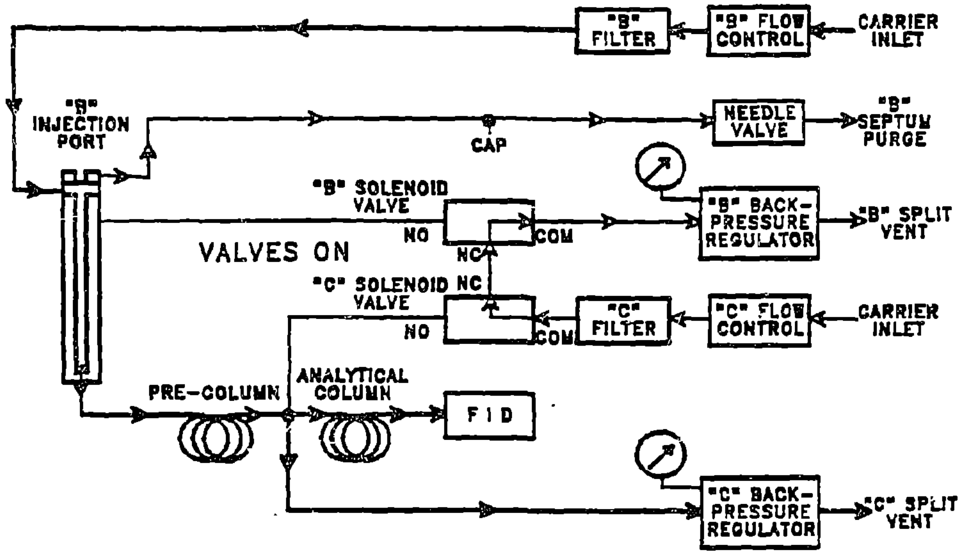

Figure 1. Flow diagram for pre-column system in inject mode.

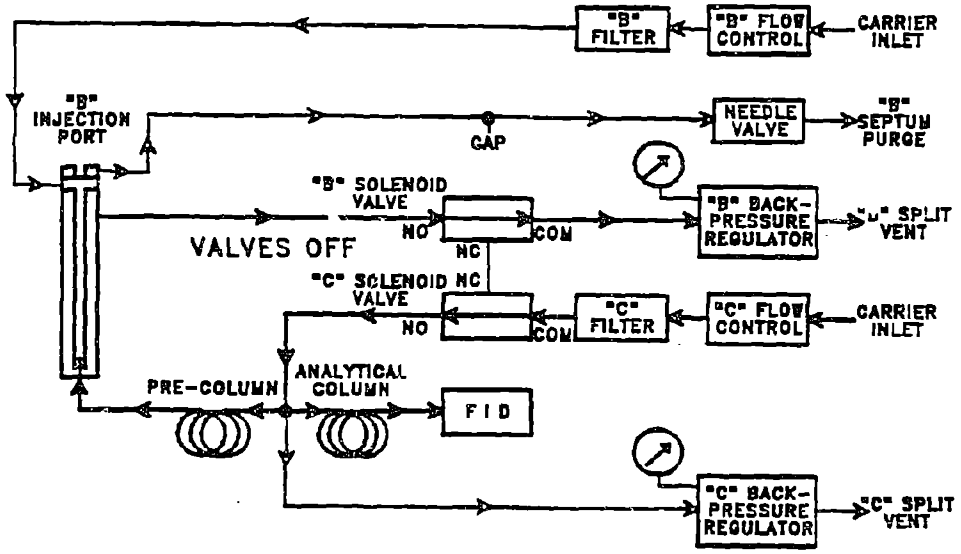

Figure 2. Flow diagram for pre-column system in backflush (normal) mode.

APPENDIX B

NIOSH PERSONAL AND AREA MONITORING DATA COLLECTED AT PLANTS, A, B, C, D, AND E

TABLE B-1. PERSONAL SAMPLING DATA COLLECTED BY NIOSH AT PLANT A

Job category	Date (1986)	Sample ID	Air volume, liters	Duration, min	Concentration, ppm[a]
Reactor/Recovery Area					
Leaderman	9/23	C2	23.85	477	6.02
Tank farm operator	9/23	C9	24.60	473	0.690
Tank farm operator	9/23	C13	22.61	471	23.7
Tank farm operator	9/24	C48	24.48	510	0.362
Tank farm operator	9/24	C54	24.48	510	0.436
Tank farm operator	9/25	C103	24.25	485	0.113
Tank farm operator	9/25	C95	24.25	485	0.962
Reactor No. 1 operator	9/23	C10	22.51	469	1.26
Reactor No. 1 operator	9/24	C51	23.08	491	0.047
Reactor No. 1 operator	9/25	C98	23.47	489	0.068
Recovery No. 2 operator	9/24	C55	23.41	509	2.71
Recovery No. 2 operator	9/23	C12	26.43	472	5.59
Recovery No. 2 operator	9/24	C57	23.45	499	1.33
Recovery No. 2 operator	9/25	C97	22.72	494	1.80
Reactor/recovery operator	9/23	C6	22.66	472	6.95
Reactor/recovery operator	9/25	C106	23.09	481	4.46
Pigment operator	9/23	C8	22.56	470	0.052
Pigment operator	9/24	C53	23.46	510	0.035
Finishing Process Area					
Coagulation operator	9/23	C20	22.32	465	0.028
Coagulation operator	9/23	C23	15.60	325	0.046
Coagulation operator	9/24	C56	26.98	509	0.032
Coagulation operator	9/24	C61	22.32	475	0.020[b]
Coagulation operator	9/25	C107	22.17	482	0.025
Coagulation operator	9/25	C99	23.52	490	0.023
Carbon black operator	9/23	C32	23.31	457	0.027
Carbon black operator	9/24	C59	21.71	468	0.019[b]
Carbon black operator	9/25	C116	21.29	453	0.024
Dryer operator	9/23	C7	23.75	475	0.040
Dryer operator	9/23	C26	21.71	458	0.031
Dryer operator	9/23	C34	22.18	462	0.053
Dryer operator	9/24	C58	23.05	501	0.071[b]
Dryer operator	9/24	C63	23.04	480	0.014
Dryer operator	9/24	C76	22.59	491	0.069
Dryer operator	9/25	C101	23.38	487	0.039
Dryer operator	9/25	C109	23.28	475	0.028
Dryer operator	9/25	C102	23.35	467	0.043

TABLE B-1 (continued)

Job category	Date (1986)	Sample ID	Air volume, liters	Duration min	Concen-tration, ppm[a]
Baler operator	9/23	C16	21.50	448	0.036
Baler operator	9/23	C21	19.83	422	0.018[b]
Baler operator	9/23	C29	24.95	462	0.025
Baler operator	9/24	C50	22.13	481	0.056
Baler operator	9/24	C64	22.63	492	0.012[b]
Baler operator	9/24	C65	22.43	492	0.026
Baler operator	9/25	C96	24.60	492	0.050
Baler operator	9/25	C104	23.52	490	0.012[b]
Baler operator	9/25	C112	22.04	469	0.025
Packager (utility)	9/23	C17	22.22	463	0.061
Packager (utility)	9/23	C24	21.71	462	0.075
Packager (utility)	9/23	C25	22.54	460	0.014[b]
Packager (utility)	9/23	C33	22.49	459	0.020[b]
Packager (utility)	9/23	C35	23.05	461	0.031
Packager (utility)	9/24	C67	22.68	493	0.024
Packager (utility)	9/24	C69	22.54	490	0.014[b]
Packager (utility)	9/24	C72	22.00	489	0.039
Packager (utility)	9/24	C74	22.54	490	0.154
Packager (utility)	9/25	C108	23.09	481	0.067
Packager (utility)	9/25	C113	22.85	476	0.102
Packager (utility)	9/25	C118	22.98	469	0.022
Packager (utility)	9/25	C119	22.42	477	0.014[b]
Packager (utility)	9/25	C122	23.92	469	0.119[b]
Hogman	9/23	C18	22.27	464	0.045
Hogman	9/24	C75	25.27	486	0.031
Hogman	9/25	C114	21.85	475	0.029
Fork lift operator	9/23	C19	22.74	464	0.014[b]
Fork lift operator	9/23	C22	22.13	461	0.020[b]
Clean-up operator (utility)	9/23	C27	22.49	459	0.038
Clean-up operator (utility)	9/23	C28	22.13	461	0.213
Clean-up operator (utility)	9/23	C30	20.63	439	0.149
Clean-up operator (utility)	9/24	C60	21.85	475	0.138
Clean-up operator (utility)	9/24	C66	21.34	464	0.081
Clean-up operator (utility)	9/24	C68	22.54	490	0.034
Clean-up operator (utility)	9/24	C73	22.61	471	0.018[b]

TABLE B-1 (continued)

Job category	Date (1986)	Sample ID	Air volume, liters	Duration min	Concentration, ppm[a]
Clean-up operator (utility)	9/25	C105	23.09	481	0.089
Clean-up operator (utility)	9/25	C117	21.67	461	0.021[b]
Clean-up operator (utility)	9/25	C121	22.56	470	0.045
Clean-up operator (utility)	9/25	C125	19.40	388	0.080
Clean-up operator (utility)	9/25	C129	21.46	438	0.077
Clean-up operator (utility)	9/25	C130	20.98	456	2.62
Vacation relief operator	9/23	C31	23.10	462	0.020[b]
Vacation relief operator	9/24	C78	21.12	431	0.024
Vacation relief operator	9/25	C102	22.61	481	0.069
Vacation relief operator	9/25	C115	21.99	478	0.037
Utilities					
Power house operator	9/23	C4	21.89	456	0.023
Utility pump house operator	9/23	C5	21.94	457	<0.006[c]
Environmental control unit operator	9/23	C3	21.10	449	0.056
Fireman	9/23	C1	20.83	434	0.304
Fireman	9/24	C62	22.84	486	0.094
Fireman	9/25	C123	22.89	487	0.230
Laboratories					
Hydrocarbon laboratory technician	9/23	C11	21.69	443	0.858
Hydrocarbon laboratory technician	9/24	C52	22.04	469	1.56
Hydrocarbon laboratory technician - cylinder sampling	9/24	C91	0.75	2	1.70[d]
Hydrocarbon laboratory technician	9/25	C100	21.48	457	5.86
Hydrocarbon laboratory technician - cylinder sampling	9/25	C138	0.50	1	38.2[d]
Control laboratory technician	9/23	C15	22.18	462	8.33
Control laboratory technician	9/24	C71	21.98	458	4.36

TABLE B-1 (continued)

Job category	Date (1986)	Sample ID	Air volume, liters	Duration min	Concentration, ppm[a]
Control laboratory technician	9/25	C128	20.79	452	0.253
Rubber laboratory technician	9/23	C14	21.66	442	0.015[b]
Rubber laboratory technician	9/24	C49	24.65	503	0.081
Rubber laboratory technician	9/25	C110	23.28	483	0.057
Rubber laboratory technician	9/25	C111	20.10	437	7.71
Maintenance					
Pipefitter	9/23	C37	23.97	470	0.967
Pipefitter	9/23	C39	23.35	467	0.252
Pipefitter	9/25	C126	18.34	382	0.426
Pipefitter	9/25	C132	20.74	432	0.198
Boilermaker	9/24	C77	25.06	522	0.036
Boilermaker	9/25	C124	15.36	320	0.423
Machinist	9/23	C36	22.98	469	11.0
Machinist	9/23	C38	22.56	470	0.060
Machinist	9/23	C40	21.17	441	0.680
Machinist	9/24	C79	21.24	452	2.45
Machinist	9/24	C80	21.95	467	0.015[b]
Machinist	9/25	C131	21.22	442	8.04
Electrician	9/24	C70	20.15	438	0.027
Electrician	9/24	C86	21.34	464	0.045
Utility man	9/24	C81	21.16	460	0.108
Utility man	9/24	C82	21.60	450	0.093
Utility man	9/24	C83	22.18	462	0.185
Utility man	9/24	C84	21.76	463	0.168
Utility man	9/24	C85	21.81	464	0.169
Utility man	9/25	C127	18.48	385	0.084
Utility man	9/28	C133	20.63	439	0.089

[a] Samples were not time-weighed to 8-hour concentrations.

[b] Laboratory analysis of analyte was below limit of quantitation (1.1 ug/sample).

[c] Laboratory analysis of analyte was below limit of detection (0.3 ug/sample).

[d] Short-term samples; values were not time-weighed to 8-hour concentrations.

TABLE B-2. AREA SAMPLING DATA COLLECTED BY NIOSH AT PLANT A

Job category	Date (1986)	Sample ID	Air volume, liters	Duration, min	Concentration, ppm
Perimeter					
North	9/23	C42	20.93	455	0.022[a]
North	9/24	C90	19.93	424	0.025
North	9/25	C137	22.60	451	0.022
East	9/23	C44	23.60	472	<0.006[b]
East	9/24	C87	20.12	428	<0.007[b]
East	9/25	C134	22.40	457	0.010[a]
South	9/23	C43	23.30	466	<0.006[b]
South	9/24	C88	19.60	426	<0.007[b]
South	9/25	C135	22.90	457	<0.010[a]
West	9/23	C41	21.98	458	0.023
West	9/24	C89	20.30	423	0.025
West	9/25	C136	23.30	466	0.022

[a] Laboratory analysis of analyte was below limit of quantitation (1.1 ug/sample).

[b] Laboratory analysis of analyte was below limit of detection (0.3 ug/sample).

TABLE B-3. PERSONAL SAMPLING DATA COLLECTED BY NIOSH AT PLANT B

Job category	Date (1986)	Sample ID	Air volume, liters	Duration, min	Concentration, ppm[d]
Tank farm operator	8/26	DP8	21.48	467	0.011[a]
	8/27	DP50	23.77	466	0.013[a]
	8/27	DP60	22.82	496	0.036
	8/28	DP91	17.86	406	0.048
Outside operator	8/26	DP18	21.84	455	0.033
	8/27	DP47	21.57	469	0.682
	8/27	DP71	23.86	487	0.063
	8/28	DP86	20.20	396	0.009[a]
Synthesis Operator A (Step I operator)	8/26	DP16	24.16	493	0.043
	8/27	DP51	23.60	472	0.079
	8/27	DP55	21.91	498	0.250
	8/28	DP85	19.65	401	0.200
Synthesis Operator B (Step II operator)	8/26	DP20	23.47	489	0.033
	8/27	DP52	22.80	475	0.028
	8/27	DP65	24.26	495	0.105
	8/28	DP81	20.40	408	0.091
ADN recovery operator	8/26	DP9	22.04	469	<0.006[b]
	8/27	DP38	23.10	462	0.018[a]
	8/27	DP59	23.18	483	0.164
	8/28	DP84	19.55	399	0.021[a]
ADN refining operator	8/26	DP15	24.00	480	0.009[a]
	8/27	DP40	23.10	462	0.014[a]
	8/27	DP42	23.25	465	0.021[a]
	8/27	DP61	24.38	508	0.032
	8/28	DP99	20.35	424	0.033
	8/28	DP87	21.30	426	0.036
HCN boiler operator	8/26	DP10	23.18	473	<0.006[b]
	8/27	DP39	23.08	471	0.012[a]
	8/27	DP69	24.35	497	<0.006[b]
	8/28	DP98	19.15	399	0.026[a]
Tankerman	8/28	DP79	15.78	30	210.0[c]
	8/28	DP88	10.99	229	28.5[d]
	8/28	DP92	15.72	31	21.7[c]
	8/28	DP94	11.52	245	0.770
Laboratory technician	8/28	DP75	15.50	310	<0.009[b]
	8/28	DP83	16.99	354	0.429
	8/28	DP93	17.04	355	0.016[a]
	8/28	DP101	71.06	141	0.682[c]
Maintenance technician	8/26	DP3	19.34	403	0.026[a]
	8/26	DP4	19.70	402	0.011[a]
	8/26	DP6	19.65	401	0.021[a]
	8/28	DP7	19.25	401	0.019[a]
	8/27	DP58	11.09	22	0.306[c]

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[a] Laboratory analysis of analyte was below limit of quantitation (1.0 ug/sample).

[b] Laboratory analysis of analyte was below limit of detection (0.3 ug/sample).

[c] Short-term samples; values were not time-weighted to 8-hour concentrations.

[d] Values were not time-weighted to 8-hour concentrations.

TABLE B-4. AREA SAMPLING DATA COLLECTED BY NIOSH AT PLANT B

Job category	Date (1986)	Sample ID	Air volume, liters	Duration, min	Concentration, ppm[c]
Control room	8/26	DP17	24.10	482	<0.006[a]
	8/26	DP19	23.62	482	<0.006[a]
	8/27	DP46	22.13	461	<0.006[a]
	8/27	DP67	24.91	519	0.013[b]
	8/28	DP96	18.96	395	0.014[b]
1,3-butadiene incoming pipe, 1st floor - synthesis area	8/26	DP5	21.60	450	0.069
	8/27	DP48	19.54	444	0.185
	8/27	DP62	24.11	492	0.015[b]
	8/28	DP90	11.09	231	0.102
1,3-butadiene Sundyne pumps, 1st floor - synthesis area (east)	8/26	DP21	17.43	379	0.273
1,3-butadiene Sundyne pumps, 1st floor - synthesis area (west)	8/26	DP24	17.11	372	0.064
1,3-butadiene Sundyne pumps, 1st floor - synthesis area	8/26	DP25	17.66	368	0.074
1,3-butadiene Sundyne pumps, 1st floor - synthesis area (east)	8/27	DP43	20.74	461	0.059
1,3-butadiene Sundyne pumps, 1st floor - synthesis area (west)	8/27	DP49	20.88	464	0.063
1,3-butadiene Sundyne pumps, 1st floor - synthesis area (east)	8/27	DP68	23.52	490	0.010[b]
1,3-butadiene Sundyne pumps, 1st floor - synthesis area (west)	8/27	DP70	24.65	493	0.184
1,3-butadiene Sundyne pumps, 1st floor - synthesis area (west)	8/28	DP100	17.86	397	0.426
1,3-butadiene Sundyne pumps, 1st floor - synthesis area (east)	8/28	DP95	20.70	398	0.348

(continued)

TABLE B-4 (continued)

Job category	Date (1986)	Sample ID	Air volume, liters	Duration min	Concentration, ppm
1,3-butadiene molecular sieve, 2nd floor - synthesis area (east)	8/26	DP22	17.01	362	0.439
1,3-butadiene molecular sieve, 2nd floor - synthesis area (west)	8/26	DP23	16.42	357	2.69
1,3-butadiene molecular sieve, 2nd floor - synthesis area	8/26	DP26	17.62	367	0.033
	8/26	DP29	18.41	354	0.057
	8/27	DP45	19.96	434	0.238
	8/27	DP64	24.30	486	0.632
	8/28	DP89	19.50	390	0.200
1,3-butadiene vent header, 2nd floor - synthesis area	8/26	DP27	16.10	350	0.427
	8/27	DP44	18.14	432	0.651
	8/27	DP66	22.03	479	0.956
	8/28	DP73	18.48	385	0.380
Step II column, 1st floor - synthesis area	8/27	DP41	20.68	440	0.530
ADN refining area	8/26	DP2	15.44	315	<0.009[a]
	8/26	DP28	14.81	322	<0.009[a]
	8/26	DP30	13.90	316	<0.010[a]
	8/27	DP34	21.02	438	0.015[b]
	8/27	DP57	23.81	486	0.013[b]
	8/27	DP63	24.55	501	0.022
	8/28	DP82	18.24	380	0.007[b]
HCN boiler area	8/26	DP11	24.90	498	0.007[b]
Barge unloading area	8/28	DP77	10.72	233	0.460
Perimeter					
North	8/26	DP12	22.42	467	<0.006[a]
	8/27	DP36	23.85	477	<0.006[a]
	8/28	DP74	8.70	174	<0.016[a]
East	8/26	DP1	20.88	454	<0.007[a]
	8/27	DP35	21.55	449	<0.006[a]
	8/28	DP76	8.87	181	<0.015[a]
South	8/26	DP13	23.45	469	0.010[b]
	8/27	DP33	23.40	468	<0.006[b]
	8/28	DP78	8.95	179	<0.015[a]

TABLE B-4 (continued)

Job category	Date (1986)	Sample ID	Air volume, liters	Duration, min	Concentration, ppm
West	8/26	DP14	22.51	469	<0.006[a]
	8/27	DP37	24.20	484	<0.006[a]
	8/28	DP80	8.98	176	<0.015[a]

[a] Laboratory analysis of analyte was below limit of detection (0.3 ug/ sample).

[b] Laboratory analysis of analyte was below limit of quantitation (1.0 ug/ sample).

[c] Values were not time-weighted to 8-hour concentrations.

TABLE B-5. PERSONAL SAMPLING DATA COLLECTED BY NIOSH AT PLANT C

Job category	Date (1986)	Sample ID	Air volume, liters	Duration, min	Concentration, ppm
A Operator - 200 area	06/24	F2	23.8	477	0.201
	06/25	F44	24.6	491	1.37
	06/25	F77	23.4	464	0.072
	06/26	F93	22.4	447	0.035
B Operator - 200 area	06/24	F1	23.6	472	0.584
	06/25	F8	23.3	485	<0.006[a]
	06/25	F43	21.5	501	12.0
	06/26	F117	18.4	383	4.63
A Operator -reactor area	06/25	F58	24.4	487	<0.006[a]
	06/26	F91	22.7	473	<0.006[a]
B Operator - reactor area	06/25	F51	16.4	335	<0.008[a]
	06/25	F67	23.6	472	<0.006[a]
	06/25	F71	17.5	349	<0.008[a]
	06/25	F74	21.6	432	<0.006[a]
	06/26	F104	23.6	470	<0.006[a]
B Operator - process area	06/25	F65	16.2	367	<0.008[a]
	06/25	F78	22.5	450	<0.006[a]
	06/26	F97	26.1	522	<0.005[a]
B Operator - crumbing area	06/24	F4	25.1	513	0.013[b]
	06/24	F5	26.2	523	0.019
	06/24	F6	24.9	509	0.017[b]
	06/24	F14	25.0	501	0.081
	06/24	F15	23.9	478	0.015[b]
	06/24	F17	23.4	467	0.014[b]
	06/24	F24	23.9	478	0.017[b]
	06/25	F50	27.0	483	0.010[b]
	06/25	F61	24.4	498	<0.006[a]
	06/25	F86	23.7	483	<0.006[a]
	06/25	F87	25.1	501	0.009[b]
	06/26	F103	25.3	496	<0.005[a]
	06/26	F108	22.5	449	<0.006[a]
Baler operator	06/24	F27	23.0	461	0.012[b]
	06/25	F48	24.8	497	<0.006[a]
	06/26	F99	23.7	473	<0.006[a]
	06/26	F126	19.6	392	<0.007[a]
Hogman	06/24	F3	25.6	511	<0.005[a]
	06/24	F11	13.9	278	0.026[b]
	06/25	F45	22.7	463	<0.006[a]
	06/25	F55	22.9	477	<0.006[a]
	06/25	F76	23.4	465	<0.006[a]
	06/26	F113	21.0	449	<0.007[a]

(continued)

TABLE B-5 (continued)

Job category	Date (1986)	Sample ID	Air volume, liters	Duration, min	Concentration, ppm
Sumpman	06/24	F10	24.5	489	<0.006[a]
	06/25	F62	23.2	483	<0.006[a]
	06/25	F72	24.5	489	<0.006[a]
	06/25	F81	24.6	492	<0.006[a]
	06/26	F96	23.7	474	<0.006[a]
	06/26	F107	24.2	483	<0.006[a]
Crate driver	06/24	F21	24.0	479	<0.006[a]
	06/25	F52	25.9	518	<0.005[a]
	06/25	F60	23.4	469	<0.006[a]
	06/25	F63	24.4	488	<0.006[a]
	06/25	F82	17.0	394	<0.008[a]
	06/25	F83	7.5	150	<0.018[a]
	06/26	F94	21.1	430	<0.007[a]
	06/26	F98	24.1	473	<0.006[a]
Crate maker	06/26	F92	19.7	448	0.007[b]
Rubber loader	06/24	F19	24.4	488	0.013[b]
	06/25	F68	21.3	444	<0.006[a]
	06/25	F73	21.7	441	<0.006[a]
	06/25	F75	21.9	467	<0.006[a]
	06/26	F88	22.9	458	<0.006[a]
	06/26	F95	16.2	463	<0.008[a]
	06/26	F101	23.4	468	<0.006[a]
Production puller	06/25	F85	22.7	483	<0.006[a]
	06/25	F53	17.2	476	<0.008[a]
Film wrap operator	06/24	F16	24.2	494	0.013[b]
	06/25	F59	24.8	496	<0.006[a]
	06/26	F119	20.7	406	<0.007[a]
Chemical laboratory technician	06/24	F9	24.0	481	0.023
	06/24	F12	23.5	473	0.782
	06/24	F18	19.2	385	0.943
	06/24	F20	24.3	488	0.336
	06/25	F47	14.5	295	0.176
	06/25	F54	23.5	480	0.142
	06/25	F64	23.7	483	0.069
	06/25	F66	24.0	481	0.103
	06/26	F90	22.5	500	0.057
	06/26	F102	23.5	469	0.286
	06/26	F105	24.4	478	0.098
Field laboratory technician	06/24	F7	24.2	483	<0.006[a]
	06/25	F46	23.7	483	0.062
Field laboratory technician	06/24	F42	7.0	14	13.3[c]

TABLE B-5 (continued)

Job category	Date (1986)	Sample ID	Air volume, liters	Duration, min	Concentration, ppm
Water laboratory technician	06/25	F56	23.7	474	0.023
	06/26	F89	24.2	484	<0.006[a]
Physical laboratory technician	06/24	F13	13.6	272	<0.010[a]
	06/25	F57	24.3	486	0.009[b]
Pipefitter	06/24	F36	31.8	63	3.24[c]
	06/24	F37	31.8	63	0.088[c]
	06/24	F38	43.4	86	14.6[c]
Boilermaker	06/24	F25	21.4	428	0.013[b]

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[a] Laboratory analysis of analyte was below limit of detection (0.3 ug/sample).

[b] Laboratory analysis of analyte was below limit of quantitation (1.1 ug/sample).

[c] Short-term samples; values were not time-weighed to 8-hour concentrations.

TABLE B-6. AREA SAMPLING DATA COLLECTED BY NIOSH AT PLANT C

Job category	Date (1986)	Sample ID	Air volume, liters	Duration, min	Concentration, ppm
Tank farm area	06/24	F33	21.8	436	0.251
Purification unit area	06/24	F28	22.5	450	0.488
	06/24	F29	22.4	448	1.55
	06/24	F31	22.4	448	0.135
	06/24	F32	21.7	434	0.078
Reactor area	06/24	F30	23.0	460	0.018[a]
Dewatering area	06/24	F8	23.6	472	<0.006[b]
	06/26	F122	21.4	446	<0.006[b]
	06/26	F129	21.6	440	<0.006[b]
Dryer area	06/26	F115	17.5	437	<0.008[b]
	06/26	F123	21.9	438	<0.006[b]
Crumb spreader area	06/26	F106	21.5	448	<0.006[b]
	06/26	F124	21.8	444	<0.006[b]
Baler area	06/24	F26	23.4	469	0.006[a]
	06/26	F114	21.5	429	<0.006[b]
Perimeter					
North	06/24	F23	22.8	455	<0.006[b]
East	06/24	F35	20.4	410	<0.007[b]
South	06/24	F22	24.1	491	<0.006[b]
West	06/24	F34	21.2	425	0.017[a]

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[a] Laboratory analysis of analyte was below limit of quantitation (1.1 ug/sample).

[b] Laboratory analysis of analyte was below limit of detection (0.3 ug/sample).

TABLE B-7. PERSONAL SAMPLING DATA COLLECTED BY NIOSH AT PLANT D

Job category	Date (1986)	Sample ID	Air volume, liters	Duration, min	Concentration, ppm
Tank farm operator	07/15	D29	23.09	444	0.123
Tank farm operator	07/16	D46	24.20	436	0.023
Tank farm operator	07/17	D103	21.90	438	0.046
Tank farm operator	07/15	D21	22.25	445	0.070
Head Operator-Monomer Area	07/16	D48	17.93	366	<0.008[a]
Head Operator-Monomer Area	07/17	D98	22.70	445	0.062
Dry End Man-Monomer Area	07/15	D25	22.48	450	0.194
Dry End Man-Monomer Area	07/15	D39	22.35	447	0.779
Dry End Man-Monomer Area	07/16	D47	21.61	441	0.191
Dry End Man-Monomer Area	07/16	D51	16.5[b]	384	0.050
Dry End Man-Monomer Area	07/17	D100	21.20	451	0.138
Dry End Man-Monomer Area	07/17	D102	22.30	455	0.055
Dry End Man-Monomer Area	07/17	D125	1.00	2	<0.137[a,c]
Wet End Man-Monomer Area	07/15	D24	18.41	449	0.112
Wet End Man-Monomer Area	07/16	D45	17.25	345	<0.008[a]
Wet End Man-Monomer Area	07/16	D84	1.01	2	10.9[c]
Wet End Man-Monomer Area	07/17	D101	22.10	451	0.033
Head Operator-Polymerization Area	07/15	D12	22.60	452	0.022[b]
Head Operator-Polymerization Area	07/16	D58	23.05	452	<0.006[a]
Head Operator-Polymerization Area	07/17	D120	24.96	531	0.009[b]
Assistant Operator-Polymerization Area	07/15	D11	24.02	462	0.073
Assistant Operator-Polymerization Area	07/15	D15	23.36	458	0.022[b]
Assistant Operator-Polymerization Area	07/15	D16	22.44	458	0.031
Assistant Operator-Polymerization Area	07/15	D34	23.31	457	0.047
Assistant Operator-Polymerization Area	07/16	D59	22.55	451	0.022[b]
Assistant Operator-Polymerization Area	07/16	D66	22.45	449	0.041
Assistant Operator-Polymerization Area	07/16	D68	22.44	458	0.016[b]
Assistant Operator-Polymerization Area	07/16	D70	17.30	346	<0.008[a]
Assistant Operator-Polymerization Area	07/16	D72	22.15	443	0.079

TABLE B-7 (continued)

Job category	Date (1986)	Sample ID	Air volume, liters	Duration min	Concentration, ppm
Assistant Operator-Polymerization Area	07/17	D91	21.41	437	0.015[b]
Assistant Operator-Polymerization Area	07/17	D108	22.85	457	0.052
Assistant Operator-Polymerization Area	07/17	D115	21.94	457	0.012[b]
Assistant Operator-Polymerization Area	07/17	D121	20.84	453	0.031
Helper-Polymerization Area	07/15	D20	22.20	453	0.041
Helper-Polymerization Area	07/15	D40	18.94	462	0.027[b]
Helper-Polymerization Area	07/16	D61	21.02	438	0.068
Helper-Polymerization Area	07/16	D63	22.75	455	0.016[b]
Helper-Polymerization Area	07/17	D105	23.20	455	0.012[b]
Helper-Polymerization Area	07/17	D106	19.15	456	0.031
Helper-Polymerization Area	07/17	D122	19.32	460	0.028
Head Operator-Finishing Area	07/15	D6	14.90	298	0.052
Head Operator-Finishing Area	07/17	D116	20.35	407	0.018[b]
Assistant Operator-Finishing Area	07/15	D10	19.57	435	0.042
Assistant Operator-Finishing Area	07/15	D33	20.35	407	0.025[b]
Assistant Operator-Finishing Area	07/16	D52	16.85	337	0.027[b]
Assistant Operator-Finishing Area	07/16	D54	8.88	185	0.041[b]
Assistant Operator-Finishing Area	07/17	D96	19.36	412	0.019[b]
Front End Helper-Finishing Area	07/15	D9	23.05	461	0.038
Front End Helper-Finishing Area	07/16	D56	23.21	463	0.032
Front End Helper-Finishing Area	07/16	D57	24.65	474	0.028
Front End Helper-Finishing Area	07/17	D99	21.10	422	0.015[b]
Front End Helper-Finishing Area	07/17	D112	20.50	410	0.018[b]
Back End Helper-Finishing Area	07/15	D1	23.25	465	0.037
Back End Helper-Finishing Area	07/15	D2	22.70	445	0.038
Back End Helper-Finishing Area	07/15	D7	21.61	441	0.034

(continued)

TABLE B-7 (continued)

Job category	Date (1986)	Sample ID	Air volume, liters	Duration min	Concentration, ppm
Back End Helper-Finishing Area	07/16	D55	22.45	449	0.031
Back End Helper-Finishing Area	07/16	D73	23.50	470	0.033
Back End Helper-Finishing Area	07/17	D111	21.05	421	0.022[b]
Head Shift Tester-QC Laboratory	07/15	D17	21.41	437	2.40
Head Shift Tester-QC Laboratory	07/15	D30	20.38	392	0.034
Head Shift Tester-QC Laboratory	07/16	D74	19.70	394	1.95
Head Shift Tester-QC Laboratory	07/16	D76	12.26	438	0.052
Head Shift Tester-QC Laboratory	07/17	D107	21.66	442	0.029
Head Shift Tester-QC Laboratory	07/17	D123	19.40	441	4.12
Special Laboratory Tester QC Laboratory	07/15	D14	21.61	432	0.038
Special Laboratory Tester QC Laboratory	07/15	D28	20.89	435	0.050
Special Laboratory Tester QC Laboratory	07/16	D71	22.29	437	0.029
Special Laboratory Tester QC Laboratory	07/16	D78	21.85	437	0.029
Special Laboratory Tester QC Laboratory	07/16	D124	22.25	445	0.029
Laboratory Tester QC Laboratory	07/15	D26	20.99	447	0.050
Laboratory Tester QC Laboratory	07/16	D80	21.56	440	0.032
Laboratory Tester QC Laboratory	07/17	D119	20.63	439	0.058
Maintenance Man-Monomer Area	07/16	D67	19.33	379	0.026[b]
Maintenance Man-Monomer Area	07/16	D81	18.75	375	0.037
Pipefitter-Polymerization Area	07/15	D3	18.70	374	0.022[b]
Pipefitter-Polymerization Area	07/15	D4	18.23	380	0.025[b]
Pipefitter-Polymerization Area	07/15	D13	21.80	436	0.023[b]
Pipefitter-Polymerization Area	07/15	D19	19.55	391	0.021[b]
Pipefitter-Polymerization Area	07/16	D82	17.30	368	0.048
Pipefitter-Polymerization Area	07/16	D83	18.23	372	0.038
Utility ManPolymerization Area	07/15	D8	22.74	464	0.030

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[a] Laboratory analysis of analyte was below limit of detection (0.3 ug/sample).

[b] Laboratory analysis of analyte was below limit of quantitation (1.1 ug/sample).

[c] Short-term samples; values were not time-weighed to 8-hour concentrations.

TABLE B-8. AREA SAMPLING DATA COLLECTED BY NIOSH AT PLANT D

Job category	Date (1986)	Sample ID	Air volume, liters	Duration, min	Concentration, ppm
1,3-butadiene Header Area Tank Farm	07/17	D85	21.71	443	0.954
Dry End - Monomer Area	07/15	D31	22.10	442	1.34
Dry End - Monomer Area	07/15	D35	19.10	398	1.49
Dry End - Monomer Area	07/16	D42	23.65	473	0.644
Dry End - Monomer Area	07/16	D49	21.46	438	0.650
Dry End - Monomer Area	07/17	D95	22.49	441	0.138
Dry End - Monomer Area	07/17	D97	21.17	441	0.153
Wet End - Monomer Area	07/16	D41	21.56	440	0.083
Wet End - Monomer Area	07/17	D92	18.48	385	0.042
Wet End - Monomer Area	07/17	D94	19.60	392	0.054
Wet End - Monomer Area	07/17	D104	21.55	449	0.040
1st Floor-Polymerization Area	07/16	D64	22.20	453	0.043
1st Floor-Polymerization Area	07/17	D89	21.95	439	0.025
2nd Floor-Polymerization Area	07/16	D62	21.65	451	0.095
2nd Floor-Polymerization Area	07/17	D87	22.93	441	0.040
3rd Floor-Polymerization Area	07/15	D5	24.91	470	0.109
3rd Floor-Polymerization Area	07/16	D65	23.05	461	0.020[a]
3rd Floor-Polymerization Area	07/17	D110	22.45	449	0.014[a]
4th Floor-Polymerization Area	07/15	D18	22.79	469	0.032
Front End - Finishing Area	07/15	D37	21.30	426	0.026
Front End - Finishing Area	07/16	D53	20.74	461	0.020[a]
Front End - Finishing Area	07/17	D113	22.90	458	0.014[a]
1,3-butadiene GC-QC Laboratory	07/17	D114	22.00	440	9.08
NIOSH Work Area-QC Laboratory	07/16	D79	23.52	480	0.025
NIOSH Work Area-QC Laboratory	07/17	D117	21.47	488	0.034
Perimeter					
North	07/15	D27	16.66	476	0.058
North	07/17	D90	22.90	458	0.018[a]
East	07/15	D38	23.90	466	0.026
East	07/16	D75	23.03	470	0.018[a]
East	07/17	D86	22.05	441	0.012[a]
South	07/15	D23	22.35	447	0.029
South	07/16	D69	23.52	480	0.031
South	07/17	D93	22.05	441	0.012[a]
West	07/15	D22	24.43	479	0.021[a]
West	07/16	D60	22.00	468	<0.006[b]
West	07/17	D88	23.00	460	<0.006[b]

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[a] Laboratory analysis of analyte was below limit of quantitation (1.1 ug/sample).

[b] Laboratory analysis of analyte was below limit of detection (0.3 ug/sample).

TABLE B-9. PERSONAL SAMPLING DATA COLLECTED BY NIOSH AT PLANT E

Job category	Date (1986)	Sample ID	Air volume, liters	Duration, min	Concentration, ppm[a]
Tank Farm Operator	9/09	G24	22.66	472	6.01
Tank Farm Operator	9/09	G30	22.56	470	1.70
Tank Farm Operator	9/10	G56	21.67	471	2.85
Tank Farm Operator	9/10	G71	14.21	290	1.07[a]
Tank Farm Operator	9/11	G124	22.99	479	2.67
Tank Farm Operator	9/11	G134	23.50	470	3.82
Material (pigment) Preparation Operator	9/09	G26	22.65	453	0.125
Material (pigment) Preparation Operator	9/09	G27	20.68	470	0.156
Material (pigment) Preparation Operator	9/09	G28	21.57	469	0.135
Material (pigment) Preparation Operator	9/10	G57	23.45	469	0.343
Material (pigment) Preparation Operator	9/10	G59	21.76	463	0.524
Material (pigment) Preparation Operator	9/10	G76	20.68	440	0.064
Material (pigment) Preparation Operator	9/11	G111	22.25	445	0.614
Material (pigment) Preparation Operator	9/11	G113	22.57	434	0.035
Material (pigment) Preparation Operator	9/11	G129	22.08	460	0.066
Reactor Operator	9/09	G20	21.55	449	0.082
Reactor Operator	9/09	G23	16.65	362	2.55
Reactor Operator	9/09	G25	21.85	446	0.544
Reactor Operator	9/09	G29	25.70	476	1.47
Reactor Operator	9/10	G51	22.32	475	11.3
Reactor Operator	9/10	G58	22.85	474	2.30
Reactor Operator	9/10	G78	23.33	432	0.451
Reactor Operator	9/10	G80	19.58	435	0.348
Reactor Operator	9/11	G116	20.78	433	0.467
Reactor Operator	9/11	G118	21.55	431	0.196
Reactor Operator	9/11	G119	23.40	468	2.80
Reactor Operator	9/11	G120	23.55	471	1.52
Monomer Recovery and Purification Operator	9/09	G18	24.48	480	5.08
Monomer Recovery and Purification Operator	9/09	G19	22.45	449	9.69
Monomer Recovery and Purification Operator	9/09	G21	10.44	227	21.9[a]

TABLE B-9 (continued)

Job category	Date (1986)	Sample ID	Air volume, liters	Duration, min	Concentration, ppm[a]
Monomer Recovery and Purification Operator	9/09	G22	22.51	469	6.78
Monomer Recovery and Purification Operator	9/10	G53	19.76	449	5.88
Monomer Recovery and Purification Operator	9/10	G55	21.25	462	2.77
Monomer Recovery and Purification Operator	9/10	G74	19.40	441	10.8
Monomer Recovery and Purification Operator	9/10	G75	21.85	446	24.1
Monomer Recovery and Purification Operator	9/11	G112	22.40	448	8.25
Monomer Recovery and Purification Operator	9/11	G114	21.41	437	8.39
Monomer Recovery and Purification Operator	9/11	G115	20.74	432	3.69
Monomer Recovery and Purification Operator	9/11	G117	21.07	458	6.92
Solutions Operator	9/09	G4	22.80	456	<0.006[b]
Solutions Operator	9/10	G67	19.92	433	0.087
Solutions Operator	9/11	G136	19.27	419	0.169
Solutions Operator	9/11	G138	18.72	416	0.095
Coagulation Operator	9/09	G2	22.20	453	0.037
Coagulation Operator	9/09	G12	21.06	448	0.028
Coagulation Operator	9/09	G13	20.38	443	0.042
Coagulation Operator	9/10	G48	23.15	463	0.109
Coagulation Operator	9/10	G68	21.15	443	0.080
Coagulation Operator	9/11	G130	20.93	436	0.092
Coagulation Operator	9/11	G133	22.25	412	0.107
Coagulation Operator	9/11	G139	19.49	406	0.134
Dryer Operator	9/09	G3	21.79	454	0.038
Dryer Operator	9/09	G8	23.50	470	0.033
Dryer Operator	9/10	G50	22.70	454	0.048
Dryer Operator	9/10	G65	21.90	438	0.059
Dryer Operator	9/10	G69	20.21	430	0.036
Dryer Operator	9/11	G123	20.63	439	0.116
Baling Operator	9/09	G14	19.32	420	0.028
Baling Operator	9/09	G15	21.80	436	0.036
Baling Operator	9/09	G16	21.60	432	0.076
Baling Operator	9/09	G17	20.65	413	0.033
Baling Operator	9/10	G45	21.62	460	0.076
Baling Operator	9/10	G61	9.55	191	<0.014[a,b]
Baling Operator	9/10	G64	22.95	459	0.042

TABLE B-9 (continued)

Job category	Date (1986)	Sample ID	Air volume, liters	Duration, min	Concentration, ppm[a]
Baling Operator	9/11	G127	21.31	444	0.112
Baling Operator	9/11	G128	20.02	417	0.144
Sacker	9/09	G1	19.89	452	0.044
Sacker	9/09	G6	22.22	463	0.039
Sacker	9/09	G9	21.20	471	0.032
Sacker	9/09	G10	23.65	473	0.033
Sacker	9/09	G11	23.75	475	0.029
Sacker	9/10	G49	22.22	463	0.058
Sacker	9/10	G62	19.92	433	0.037
Sacker	9/10	G63	21.66	442	0.051
Sacker	9/10	G66	20.88	435	0.037
Sacker	9/10	G70	21.46	438	0.036
Sacker	9/11	G102	22.90	458	0.100
Sacker	9/11	G104	22.55	451	0.100
Sacker	9/11	G105	22.45	449	0.100
Sacker	9/11	G125	21.95	439	0.088
Clean-up Operator	9/09	G34	21.36	445	0.333
Clean-up Operator	9/09	G35	21.85	437	1.75
Clean-up Operator	9/09	G37	21.55	449	0.795
Clean-up Operator	9/09	G38	14.20	284	0.927[a]
Clean-up Operator	9/09	G39	22.20	444	2.71
Clean-up Operator	9/10	G72	17.54	358	7.07
Clean-up Operator	9/10	G77	22.65	453	3.89
Clean-up Operator	9/10	G79	22.13	461	3.74
Clean-up Operator	9/10	G84	17.03	334	0.406[a]
Clean-up Operator	9/11	G101	22.93	468	0.516
Clean-up Operator	9/11	G103	21.50	448	0.072
Clean-up Operator	9/11	G108	21.99	478	0.421
Clean-up Operator	9/11	G92	23.80	476	0.204
Warehouseman	9/09	G5	22.90	458	0.034
Warehouseman	9/09	G7	23.40	468	0.033
Warehouseman	9/10	G52	21.45	429	0.034
Warehouseman	9/10	G54	20.95	419	0.039
Warehouseman	9/10	G60	21.15	423	0.043
Warehouseman	9/11	G122	20.11	419	0.068
Warehouseman	9/11	G125	19.92	415	0.064
Laboratory Technician	9/09	G33	23.28	475	37.4
Laboratory Technician	9/10	G86	21.50	430	6.13
Laboratory Technician	9/11	G94	21.07	439	4.92
Laboratory Technician	9/11	G107	21.66	442	11.7
Process Chemist	9/09	G31	23.80	476	1.90
Process Chemist	9/10	G85	20.34	415	0.272

TABLE B-9 (continued)

Job category	Date (1986)	Sample ID	Air volume, liters	Duration, min	Concentration, ppm[a]
Instrument Lab Chemist	9/09	G32	23.28	475	8.87
Instrument Lab Chemist	9/10	G82	21.00	420	5.36
Instrument Lab Chemist Cylinder Sampling	9/10	G91	19.50	15	101.0[c]
Instrument Lab Chemist	9/11	G93	20.55	411	0.100
Instrument Lab Chemist	9/11	G96	22.05	441	4.24
Instrument Lab Chemist Cylinder Sampling	9/11	G131	3.70	7	26.3[c]
Pipefitter	9/09	G40	22.62	435	43.2
Pipefitter	9/09	G41	18.95	379	0.130
Pipefitter	9/10	G73	21.22	442	1.74
Mechanic	9/10	G81	22.70	454	1.29
Electrician	9/11	G106	23.52	490	0.275

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[a] Values were not time-weighed to 8-hour concentrations.

[b] Laboratory analysis of analyte was below limit of detection (0.3 ug/sample).

[c] Short-term samples; values were not time-weighed to 8-hour concentrations.

TABLE B-10. AREA SAMPLING DATA COLLECTED BY NIOSH AT PLANT E

Job category	Date (1986)	Sample ID	Air volume, liters	Duration, min	Concentration, ppm[a]
Pumphouse Area	9/10	G88	22.85	476	0.142
Pumphouse Area	9/11	G99	22.10	442	1.77
Perimeter					
North	9/09	G36	22.80	456	0.078
North	9/10	G83	24.39	469	0.158
North	9/11	G109	20.00	400	0.124
East	9/09	G44	20.07	386	0.027
East	9/10	G87	22.36	486	0.039
East	9/11	G110	19.61	467	0.051
South	9/09	G43	20.37	463	0.034
South	9/10	G89	22.56	470	0.049
South	9/11	G97	21.26	443	0.043
West	9/09	G42	22.18	472	0.166
West	9/10	G90	23.25	465	0.059
West	9/11	G95	22.35	447	0.047

[a] Values were not time-weighted to 8-hour concentrations.