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Industrial Hygiene Walk-Through Survey
Report of the Goodyear Tire and Rubber Company
Houston Chemical Plant, Houston, Texas

(U.S.) National Inst. for Occupational
Safety and Health, Cincinnati, OH

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7. Author(s) Fajen, J M, and L J Ungers

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16. Abstract (Limit: 200 words)

A walk through survey was conducted at Goodyear Tire and Rubber Company (SIC-2822), Houston, Texas in November, 1985. The purpose of the survey was to obtain information on production processes for styrene (100425)/butadiene (106990) rubber (SBR), styrene/butadiene latex (SBL) and acrylonitrile (107131)/butadiene rubber (ABR), and to evaluate the potential for 1,3-butadiene exposure. Bulk samples of SBR, SBL, and ABR were analyzed for residual 1,3-butadiene. The products were manufactured by an emulsion process. Pumps in the facility were equipped with single mechanical seals. The acrylonitrile compressor was under negative pressure and used activated carbon filters. The quality control laboratory had a local exhaust hooding system. Quality control sampling was conducted using open/loop bombs. All bulk samples except a SBR sample at 180 degrees-C contained no detectable 1,3-butadiene. Company air monitoring data for 1975 to 1980 and 1982 to 1985 showed mean time weighted average 1,3-butadiene exposures of 4.0 and 5.9 parts per million (ppm), respectively. Tank farm operators, recovery operators, and reactor operators experienced exposures greater than 10ppm. The authors conclude that the facility is suitable for an in depth survey. Recommendations include performing preventive maintenance on pumps in the recovery area and installing closed loop quality control sampling systems.

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Industrial Hygiene Walk-Through Survey Report of The Goodyear Tire and Rubber Company Houston Chemical Plant Houston, Texas

Survey Conducted by:
John M. Fajen
Leslie J. Ungers, C.I.H.

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Industrial Hygiene Section
Industrywide Studies Branch
Division of Surveillance, Hazard Evaluations and Field Studies
National Institute for Occupational Safety and Health
Centers for Disease Control
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DISCLAIMER

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The analysis of the bulk samples was conducted by Ardith A. Grote, Chemist, Division of Physical Sciences and Engineering, National Institute for Occupational Safety and Health.

PURPOSE OF SURVEY:	To perform a walk-through industrial hygiene survey of a 1,3-butadiene polymer using plant and determine the suitability for inclusion in an in-depth exposure survey regarding this substance.
EMPLOYER REPRESENTATIVES CONTACTED:	Les Carnahan, Manager, R&D/Technical Superintendent Oluf Braren, Production Superintendent Bob Folino, Manager, Engineering and Maintenance Dean Cook, Manager, Industrial Relations Wes Muller, Jr., Manager, Environmental Control Kurt Rutz, Manager, Quality Assurance Melvin Lewis, Manager, Safety Bill Gron, Plant Manager Don Bossow, Corporate Industrial Hygienist
EMPLOYEE REPRESENTATIVES CONTACTED:	Don Wake, Production Union Safety Member, International Union of Operating Engineers Jessie Bryant, Maintenance Union Safety Member, International Association of Machinists and Aerospace Workers
STANDARD INDUSTRIAL CLASSIFICATION (SIC) CODE:	2822 - (Synthetic Rubber [Vulcanizable Elastomers])

ABSTRACT

A walk-through industrial hygiene survey was conducted at Goodyear's Houston Chemical Plant on November 13, 1985. The purpose of the survey was to collect information on the production processes for styrene-butadiene rubber (SBR), styrene-butadiene latex, and acrylonitrile-butadiene rubber, and to assess the potential for occupational exposure to 1,3-butadiene at the facility. This information will be used in determining the suitability of including this plant in an indepth industrial hygiene survey.

The plant, which began production in 1943, produces synthetic polymers using an emulsion process. Goodyear has owned the plant since 1955. The plant has a total nameplate capacity to produce 960 million pounds of synthetic polymers annually.

The plant employs 658 people, 53 of whom work in the tank farm, reactor and recovery areas, which have the maximum potential for exposure to 1,3-butadiene. Personal and area monitoring for 1,3-butadiene has been conducted at the plant since 1977 by Goodyear's Industrial Hygiene Group. The mean 8-hour time-weighted average of 31 personal samples (collected on activated charcoal tubes) during 1977-80 was 4.0 ppm. A total of 366 personal samples were collected during 1982-85 using passive dosimeters; the mean 8-hour TWA of these samples was 5.9 ppm. The results from 67 area samples collected during 1982-85 (using passive dosimeters) in different plant areas showed a mean 1,3-butadiene concentration of 4.4 ppm.

The personal monitoring data obtained during the period 1977-85 indicate arithmetic mean TWAs of greater than 10 ppm for the tank farm operators, reactor operators, recovery operators, and laborers. Area concentrations greater than 10 ppm were observed in the recovery area.

Sampling of incoming and recycled 1,3-butadiene is performed with open-loop "bombs". Pumps handling 1,3-butadiene are equipped with single mechanical seals.

The NIOSH analytical results of the analysis of bulk samples were all non-detectable with the exception of the SBR bulk sample at 180°C. Mass spectrometry confirmed a trace (0.04-0.2 ng/mg by weight) in the SBR bulk sample. The limit of detection was 0.04 ng/mg by weight.

Goodyear is considered a potential candidate for an in-depth industrial hygiene survey for the determination of the extent of exposure to 1,3-butadiene.

The company conducts pre-employment physical examinations on all employees, and maintains personnel records on terminated as well as current employees.

INTRODUCTION

Inhalation exposure of rats and mice to 1,3-butadiene induced a carcinogenic response at multiple sites. Mammary fibroadenomas/carcinomas, uterine sarcomas, Leydig cell adenomas of the testes, thyroid follicular cell adenomas, exocrine tumors of the pancreas, and Zymbal gland carcinomas were identified in rats exposed at concentrations of 1000 to 8000 ppm of 1,3-butadiene. Mice exposed to 625 or 1250 ppm of 1,3-butadiene developed a high incidence of malignant lymphomas; and increased incidence of other tumors, including hemangiosarcoma; and testicular and ovarian atrophy.[1,2]

The offspring of pregnant rats exposed to 1,3-butadiene at 8000 ppm had major skeletal defects. In addition, fetal toxicity was observed when pregnant dams were exposed at 200 ppm, 1000 ppm, and 8000 ppm.[3]

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

Based on these data, the National Institute for Occupational Safety and Health (NIOSH) recommends that 1,3-butadiene be regarded as a potential occupational carcinogen and teratogen and as a possible reproductive hazard.[6] Due to the number of workers potentially exposed to 1,3-butadiene and the resulting potential health risk, NIOSH researchers are conducting an extent-of-exposure study of workers potentially exposed to the monomer during production of 1,3-butadiene based products.

EXPOSURE EVALUATION CRITERIA

The current Permissible Exposure Limit (PEL) enforced by the Occupational Safety and Health Administration (OSHA) for 1,3-butadiene is 1000 ppm for an 8-hour time-weighted average (TWA).[7] The American Conference of Governmental Industrial Hygienists (ACGIH) has included 1,3-butadiene in their Notice of Intended Changes for the 1984-1985 Threshold Limit Values (TLVs) based upon reported animal carcinogenicity data.[8] The intended change identified 1,3-butadiene as an "A2" industrial substance suspected of carcinogenic potential in man. A numerical TLV of 10 ppm was proposed in connection with the notice.

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

HISTORY AND DESCRIPTION OF THE PLANT

The Goodyear Tire & Rubber Company owns and operates the Houston Chemical Plant in Houston, 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 and final product in the SBR manufacturing process. The plant began production in 1943; Goodyear purchased the facilities in 1955. There have been several process changes and expansions at the facility since it first began operation. The dates of the major changes/additions are as follows:

- 1958 - Expansion of SBR capacity
- 1964 - Construction of antioxidant plant
- 1978 - Addition of SBR foam latex production capability
- 1981 - Shutdown of black SBR production
- 1983 - Modernization of reactor control
- 1984 - Addition of two stripping columns for monomer recovery; shut down of antioxidant plant constructed in 1964

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

The solid rubber products are either used captively in other Goodyear plants or sold to other domestic and international producers of tires and rubber goods. The rubber products are shipped in boxes by rail or truck to customers.

PROCESS DESCRIPTION

Goodyear's Houston Chemical Plant produces SBR, SBR latex and NBR by emulsion co-polymerization. The same process equipment is used for the manufacture of the three products. Figure 1 depicts Goodyear's SBR and SB latex production processes. Production of acrylonitrile-butadiene (NBR) rubber is basically 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. Exxon, Arco, and Texas Petrochemical are the suppliers of 1,3-butadiene monomer.

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 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.

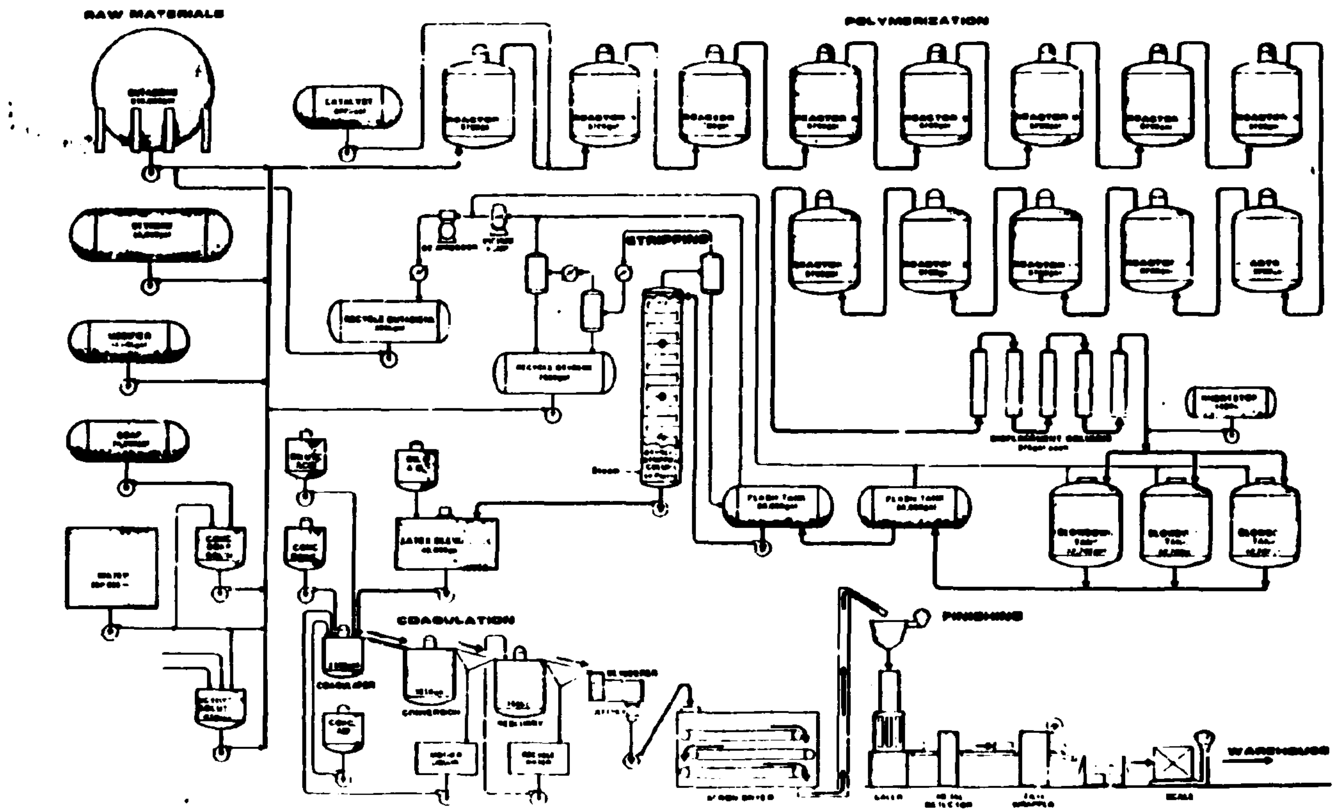

Figure 1. Process flow diagram for production of SBR and SB latex at Goodyear's Houston Chemical Plant.

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 postreatment, 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. The stripped latex is an intermediate product of the Goodyear Houston Chemical Plant.

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 bailing portions of the process. The rubber product is boxed and stored in the plant warehouse.

Quality Control (QC)

Quality control for the 1,3-butadiene monomer received at the plant is based upon vendor analysis certification, as well as laboratory testing by Goodyear at the plant. Purity and level of inhibitor are tested daily on each shift. 1,3-butadiene that is recycled from the recovery system is also analyzed once per shift. Samples are collected by laboratory technicians using sampling cylinders ("bombs") in an open-loop mode.

DESCRIPTION OF THE WORKFORCE

There are a total of 658 employees at Goodyear's Houston Chemical Plant. The plant operates 24 hours a day, 7 days a week, 52 weeks a year. Four shifts work on a 28-day rotation schedule. Goodyear estimates 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.

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

Tank Farm Operators, Reactor and Recovery Operators, and Relief Operators:	Employees are in the area 100 percent of the time; however, 1,3-butadiene is contained in pipes or vessels in their work areas. Incidental exposure through leaks or spills is the major source of potential exposure.
Pigment Preparation Operators:	Prepare soap and other charges.
Clean-up Crew:	Clean vessels, dryers, and other process equipment. Wear protective clothing and fresh air mask when performing their duties.
Finishing Area Operators:	Coagulate, dry and bale product. Have incidental exposure to latex and coagulated rubber in water or in drying stages.
Baler Helpers:	Package rubber, and clean up finishing area. Potentially exposed to finished product, but for the most part, all bales are film wrapped. Exposures to products can occur during wrapper failures or clean-up of crumb spillage.
Laboratory Technicians:	Responsible for collecting and analyzing QC samples.
Mechanics:	Conduct maintenance on process equipment. Have potential for intermittent exposure to 1,3-butadiene.

DESCRIPTION OF PAST WORKER EXPOSURES

The synthetic emulsion polymer manufacturing process used at the Houston Chemical Plant has undergone a series of updates (engineering controls, process modifications) since it first began operation in 1943.

The Goodyear Corporate Hygiene staff has conducted personal and area monitoring for 1,3-butadiene since 1977. Table 1 and Table 2 present the results of Goodyear's personal air monitoring for the periods of 1977-80 and 1982-85, respectively. The data for these two periods are presented separately because Goodyear 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

TABLE 1. SUMMARY OF GOODYEAR'S PERSONAL MONITORING DATA FOR 1,3-BUTADIENE AT THE HOUSTON PLANT, 1977-80

Job category	8-hour TWA[a]		
	No. of samples	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

[a] Time-weighted average.

TABLE 2. SUMMARY OF GOODYEAR'S PERSONAL MONITORING DATA FOR 1,3-BUTADIENE AT THE HOUSTON PLANT, 1982-85

Job category	8-hour TWA[a]		
	No. of samples	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	0.25 - 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

[a] Time-weighted average.

detector (NIOSH Method S-91[9]). The majority (92 percent) of Goodyear's personal samples was collected during 1982-85. Table 3 presents Goodyear's results for area monitoring conducted during 1982-85. The mean 8-hour time-weighted average of 31 personal samples collected during 1977-80 was 4.00 ppm, while that for 366 personal samples during 1982-85 was 5.87 ppm. The mean of 67 area samples (see Table 3) collected in different process area during 1982-85 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 1977-80 period and for the recovery operators and laborers during the 1982-85 period. Finishing operators had mean TWAs of less than 1 ppm for both monitoring time frames, indicating that the potential for exposure to 1,3-butadiene exists primarily before the stripped latex stage. Mean area concentrations greater than 10 ppm of 1,3-butadiene were observed in the recovery area of the plant.

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

Sampling of 1,3-butadiene is performed by laboratory technicians using cylinders ("bombs") in an open-loop mode.

Engineering Controls

The plant has single mechanical seals on pumps that handle 1,3-butadiene in the tank farm and process areas. The plant is contemplating retrofitting to dual mechanical seals on these pumps. The compressor handling acrylonitrile is under negative pressure and uses activated carbon filters. The 1,3-butadiene monomer is delivered by pipeline; therefore gauges or other means for measuring the delivered product are not needed.

The laboratory has a local exhaust hooding system. The building enclosing the indoor process equipment has a local air conditioning system (window).

DESCRIPTION OF MEDICAL, SAFETY, AND INDUSTRIAL HYGIENE PROGRAMS

Medical Program

The Houston Chemical Plant has a physician 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)

TABLE 3. SUMMARY OF GOODYEAR'S AREA MONITORING DATA FOR 1,3-BUTADIENE AT THE HOUSTON PLANT, 1982-85

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

* 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.

<u>Safety Program</u>
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 & Laboratory	30
Warehouse and Shipping	50
Latex Plant	67

The plant provides coveralls for employees working in certain areas of production. Impermeable and full protection waders or slicker suits are required for some maintenance operations. Safety glasses are required throughout the production areas of the plant. Safety glasses and prescription glasses meet ANSI Standard Z 87 for industrial safety. Hard hats required to be worn by employees are Bullard safety caps with dihedral suspension systems, and meet ANSI Z 89.1. Electricians wear electrician caps for electrical insulation resistance as specified by ANSI Z 89.1. Safety shoes are recommended for all employees in the plant, but are mandatory for maintenance and laborers. Impermeable PVC gloves are used in specific process operations and during maintenance operations. Cotton gloves are also used in certain areas.

Respirators are used throughout the plant whenever needed. Types of respirators available include organic vapor, hose line, ammonia, chlorine, positive pressure CESCO air hoods, acid gas, particulate and mist.

The plant provides showers and clothing change areas. Eating and smoking are permitted only in designated areas.

<u>Industrial Hygiene Program</u>
Industrial hygiene sampling at the Houston Chemical 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 is available from 1977 on 1,3-butadiene. There is one industrial hygienist at the Houston Chemical

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.

Goodyear's Houston Chemical Plant has a series of films and training materials that deal with health monitoring and hygiene in the work place. The information is presented to new employees as part of the New Employee Safety Training (NEST) program. The training materials are also discussed during 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".

DESCRIPTION OF PERSONNEL RECORD SYSTEM

The Houston Chemical Plant 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:

- Home address
- Telephone number
- Social Security number
- Education
- Previous employment

The union also maintains membership records.

SAMPLING AND ANALYTICAL METHOD FOR BULK POLYMER SAMPLES

Because polymers are further processed into finished products, it was one of the intentions of this study 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 used the polymer. Therefore, a bulk polymer sample(s) was obtained at each site and then analyzed for emanation of free monomer at three predetermined temperatures: 1) ambient, 2) highest polymer process temperature, and 3) highest estimated end use temperature.

The method for analysis of the bulks was developed by the Measurement Research Support Branch of the Division of Physical Sciences and Engineering at NIOSH.

Sampling System Description

A Tekmar Model 4000 Automatic Dynamic Headspace Concentrator combined with the Model 4100 Heated Sampler Module and Model 1000 Capillary Interface was used throughout this study for the bulk sample analysis. The basic operating principle of this system is as follows: residual organic compounds diffusing from the bulk matrix (placed in an enclosed sampling tube) are removed by purging the enclosed sampling tube with inert gas (helium) followed by analysis via gas chromatography. The Heated Sampler Module allows the bulk matrix to be heated at a specified controlled temperature variable from ambient to 200°C. The organics removed from the sampling tube are next swept to a porous polymer adsorbent (Tenax) and trapped. The adsorbent is then heated and backflushed to release the organics, which are then swept onto the head of a capillary column via the Capillary Interface Unit. This capillary interface operates on the principle of cryofocusing. The interface freezes (using liquid nitrogen) the desorbed sample from the Concentrator into a narrow band on the injection end of a fused silica precolumn. The focused sample is then flash heated and injected into a gas chromatograph.

Sampling System Conditions

The system described involves the setting of numerous temperature and time parameters that had to be predetermined before any analytical work could be accomplished. After preliminary work with the 1,3-butadiene standard the settings listed in Table 4 were chosen and used throughout the study.

TABLE 4
SAMPLING TIME AND TEMPERATURE VARIABLES
USING THE DYNAMIC HEADSPACE CONCENTRATOR, TEKMAR MODEL 4000

Sample Chamber Temperature	Variable 30°C (ambient) to 200°C
Sample Transfer Lines & Valves	150°C
Sample Chamber Preheat Time	0 min (ambient); 5 min (heated samples)
Sample Wet Purge Time	5 min
Purge Flow	40 cc/min
Trap Desorb Temperature	200°C
Trap Desorb Time	4 min
Trap Bake Out Temperature	220°C
Trap Bake Out Time	15 min

Due to the high sensitivity of this system, sample size, especially with heated samples, had to be kept small to avoid overloading or contaminating the Tenax trap irreversibly with generated organic compounds. Twenty to 30-mg portions of the bulk polymers were weighed and used for sampling. (Even with these small amounts the system was often found to be heavily contaminated with higher boiling organic material after analysis of a sample.)

Analytical Instrumentation and Conditions

All bulks were initially screened using the Dynamic Headspace Concentrator interfaced directly to an HP 5840 gas chromatograph (GC) equipped with a flame ionization detector (FID). A 30-meter DB-1 fused silica capillary column, 0.25 mm I.D., and 1.0 um film thickness was used for all analyses.

The column was temperature programmed from 35°C to 260°C at a rate of 15°/min after an initial hold time of 2 minutes. 1,3-butadiene eluted at about 2.0-2.2 minutes under these analytical conditions.

Positive identification of the presence of butadiene in selected samples was accomplished by interfacing the headspace unit and GC column directly into an HP 5982A mass spectrometer (MS). Samples were reanalyzed under the same concentrator conditions except that the GC effluent was passed into the mass spectrometer ion source rather than a FID. Samples were scanned from 35 to 200 atomic mass units (amus) to obtain the mass spectra. The presence of 1,3-butadiene was specifically look for by monitoring for the m/e 54 ion. A 1,3-butadiene gas standard was run by mass spectrometry to obtain a standard reference spectrum and GC/MS retention time data for comparison. Standards in the same range as used for the GC/FID calibration were also analyzed by GC/MS.

Calibration and Standards

Quantitation of 1,3-butadiene released from the polymer bulks was performed by GC-FID. GC/MS was used for confirmation and identification only. Certified (± 2%) 37-liter Scotty IV cylinders of 1,3-butadiene in nitrogen were used for standards (obtained from Scott Specialty Gases). A one-liter Tedlar bag was filled from this cylinder for use in obtaining the standard aliquots. This bag was evacuated and refilled with new 1,3-butadiene standard every 2-5 days. The 1,3-butadiene standard appeared stable in the Tedlar bag for at least 5 days. Various 0.1-5.0 cc aliquots of 1,3-butadiene from the bag were taken using gas tight syringes and injected directly into the purge stream of the heated module sample tube. Standards were subjected to the same purge and trap conditions as the samples. An initial calibration curve was constructed using multiple runs of varying amounts of a 9.51 ppm calibrated 1,3-butadiene gas standard. Each day at least two standard runs were made and amounts calculated against this curve to make sure the system was performing satisfactorily.

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). These limits were calculated from the statistics of the calibration curve.

Under the analytical conditions previously described the limit of detection (LOD) for 1,3-butadiene was approximately 1 ng per injection. Based on an initial sample weight of 25 mg (actual weights used varied from about 20 to 30 mg for solids), the LOD per sample was about 0.04 ng/mg or 0.04 ppm by weight. The limit of quantitation (LOQ) was 0.2 ppm by weight.

Sample Analysis

The following general procedure was used for the bulk samples: One 20-30 mg portion of the bulk was weighed out and put into the sample tube. An initial ambient run was made on all samples at 30°C. If little or no butadiene was detected at this temperature, the same portion of the bulk was subjected to the next higher predetermined temperature and reanalyzed. The procedure was repeated for a third temperature if applicable.

If 1,3-butadiene was detected in the sample at a certain temperature, that same portion of the bulk was then reanalyzed at the same temperature again, two or three times if necessary, until little or no additional butadiene was evolved. The sample then progressed to the next higher temperature and the process repeated if necessary.

Only samples suspected of containing 1,3-butadiene at a level above the LOQ (0.2 ppm) were reanalyzed at a later date using GC/MS to positively confirm the presence of 1,3-butadiene.

Analytical Results

The analytical results of the bulk sample analysis of the SBR, SB latex and NBR samples are shown in Table 5. The mass spectra confirmation of the bulk analysis of SBR at 180°C is shown in Figure 2.

TABLE 5
ANALYTICAL RESULTS OF POLYMER BULK SAMPLES

Sample	SAMPLE HEATING TEMP. (°C)	BULK SAMPLE ANALYSIS (ng/mg)
SBR	30	N.D.[a]
	95	N.D.
	180	Trace[b,c]
NBR	30	N.D.
	95	N.D.
SB Latex	30	N.D.

[a]N.D. = limit of detection 0.04 ng/mg by weight
[b]Trace = 1,3-butadiene present at low levels in range of 0.04-0.2 ng/mg by weight
c = mass spectrometry confirmation

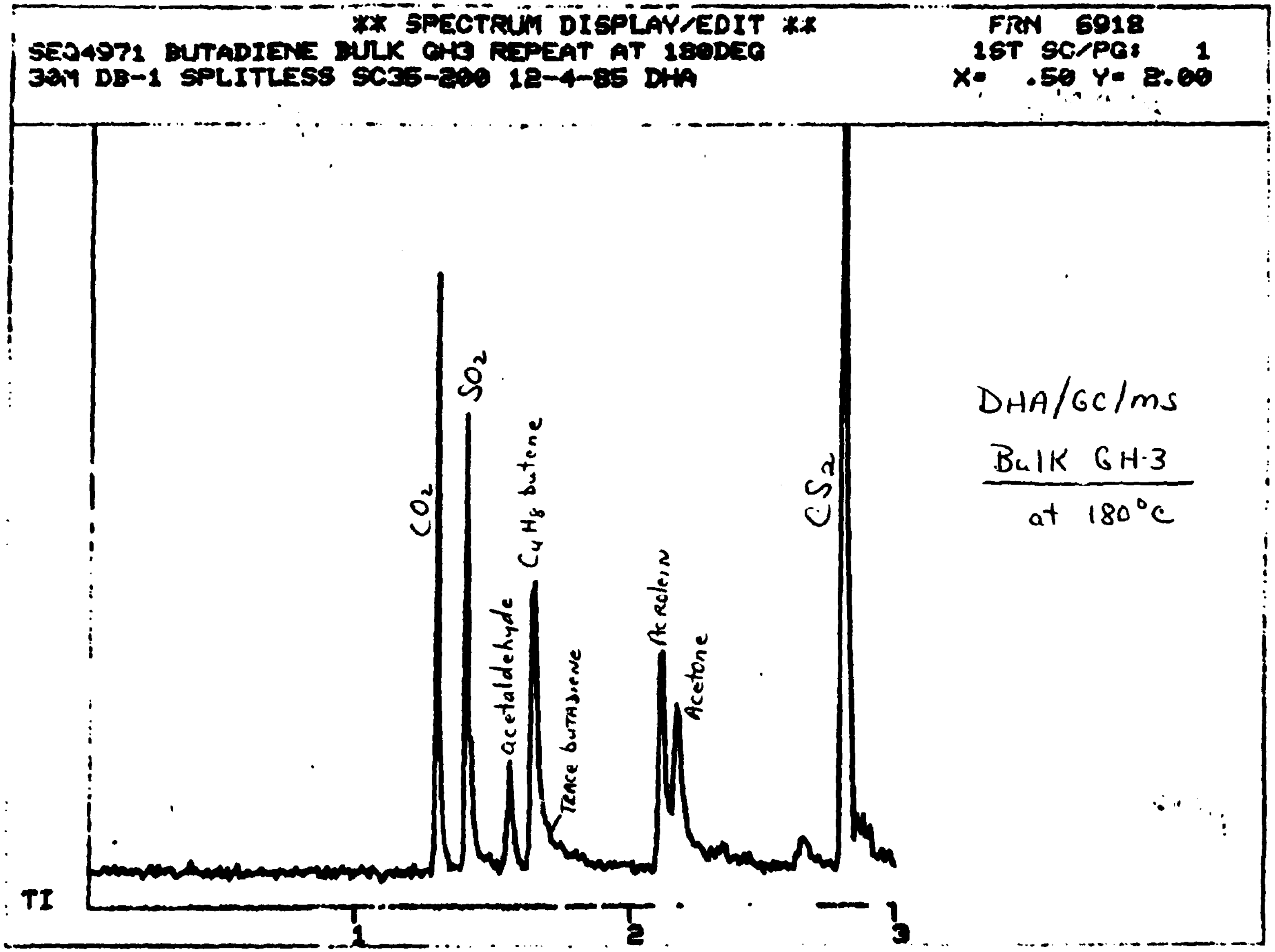

Figure 2. Mass Spectra of SBR bulk at 180°C

DISCUSSION

Goodyear produces SBR, SB latex, and NBR at the Houston Chemical Plant using a synthetic emulsion polymerization process.

Extensive personal and area monitoring has been conducted at the plant since 1977 by the Goodyear corporate industrial hygiene staff. Mean 8-hour TWA exposures for all job categories during 1977-80 and 1982-85 were 4.0 ppm and 5.9 ppm, respectively. The mean 8-hour TWA concentration of the area samples was 4.4 ppm. Tank farm operators, recovery operators, reactor operators (1977-80 data) and laborers had mean 8-hour TWAs greater than 10 ppm. The mean area concentration in the recovery area was above 10 ppm.

Pumps in the plant are equipped with single mechanical seals. The acrylonitrile compressor is under negative pressure and uses activated carbon filters. The plant laboratory has a local exhaust hooding system. Sampling of 1,3-butadiene delivered to the plant and within the process is conducted using open-loop bomb sampling.

CONCLUSION

Based on the historical industrial hygiene information provided by Goodyear, the Houston Chemical Plant is a candidate for site selection for an indepth industrial hygiene survey. The purpose of the survey, if Goodyear is selected, would be to develop an extent of exposure profile for all job descriptions associated with the production and distribution of 1,3-butadiene based polymers.

RECOMMENDATIONS

Based on an analysis of Goodyear's industrial hygiene data for 1,3-butadiene, it is suggested that Goodyear evaluate engineering control techniques to reduce the potential of exposure to operators and other personnel. Goodyear should pursue its plans to evaluate the effectiveness of dual vs. single mechanical seals on 1,3-butadiene handling pumps in the tank farm and process area. Consideration should also be given towards installing a closed-loop system for collecting QC samples in the tank farm and recovery areas of the plant. Preventative maintenance is suggested for minimizing leaks from pumps and compressors in the recovery area. Specific attention should be given to the pump house where the NIOSH researcher detected a noticable odor of 1,3-butadiene. The pump house environment can probably be improved through engineering controls or modification in the design of the building. Removing the exterior walls of the building would make it an open process and greatly reduce the potential for exposure.

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