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Industrial Hygiene Walk-Through Survey Report of Copolymer Rubber and Chemical Corporation, Baton Rouge, Louisiana

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16. Abstract (Limit: 200 words)

A walk through survey was conducted at the Copolymer Rubber and Chemical Corporation (SIC-2822), Baton Rouge, Louisiana. The facility produces 465 million pounds of styrene butadiene rubber (SBR) and 15 million pounds of nitrile butadiene rubber (NBR) annually, requiring 120 million pounds of 1,3-butadiene (106990). Of 470 employees, 143 were directly involved in reaction, recovery, and finishing operations, and were potentially exposed to 1,3-butadiene 8 hours per day. An additional 294 employees were potentially exposed intermittently. Company monitoring data show a weighted mean of the 8 hour time weighted average exposures of 2.4 parts per million (ppm) for these job categories. Engineering controls included dual mechanical seals on newer pumps, single mechanical seals on older pumps, dual mechanical seals on reactor agitators, rail car vapor vents, and locally exhausted lab hoods. Bulk samples of SBR and NBR were 0.2 (NBR) and 0.8ppm (SBR) of 1,3-butadiene by weight. The authors conclude that the company should be included as a candidate for an indepth industrial hygiene survey to develop an extent of exposure profile for all job descriptions associated with the production and distribution of 1,3-butadiene based products. The authors recommend that the company pursue its plan for installing a closed loop sampling system throughout the facility.

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Industrial Hygiene Walk-Through
Survey Report

of

Copolymer Rubber and Chemical Corporation
Baton Rouge, Louisiana

Survey Conducted by:
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Dates of Survey:
July 31, 1985

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

DISCLAIMER

Mention of company or product name in this report does not constitute endorsement by the National Institute for Occupational Safety and Health (NIOSH).

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PURPOSE OF SURVEY:	To perform a walk-through industrial hygiene survey of a 1,3-butadiene polymer producing plant and determine the suitability for inclusion in an indepth exposure survey regarding this substance.
EMPLOYER REPRESENTATIVES CONTACTED:	Hal Ginn, Plant Manager Mack L. Spence, Environmental Manager Steve Kerns, Human Resources Director Robin Pope, Technical Coordinator Will Unruh, Technical Manager Sham L. Sachdev, Ph.D., C.I.H., Industrial Hygiene Consultant, Entek Environmental Laboratories
EMPLOYEE REPRESENTATIVES CONTACTED:	Fred Beasly, Business Agent for Various Crafts Unions
STANDARD INDUSTRIAL CLASSIFICATION (SIC) CODE:	2822 - (Synthetic Rubber [Vulcanizable Elastomers])

ABSTRACT

A walk-through survey was conducted at Copolymer Rubber and Chemical Corporation in Baton Rouge, Louisiana on July 31, 1985. The purpose of the survey was to obtain information on the styrene butadiene rubber (SBR) and nitrile butadiene rubber (NBR) production processes and assess the potential for occupational exposure to 1,3-butadiene. This information will be used in determining the suitability of inclusion of this facility in an indepth survey regarding this substance.

The plant, which opened in 1944, produces SBR and NBR by continuous emulsion polymerization. The polymers produced are sold for use in the manufacture of a wide variety of tire and rubber products.

Of the 470 people employed at the facility, a total of 143 employees work their entire shift in 1,3-butadiene process areas and would be potentially exposed to 1,3-butadiene 8 hours per day. An additional 294 employees are potentially exposed intermittently to 1,3-butadiene. The company has conducted industrial hygiene monitoring for 1,3-butadiene since 1980. The weighted mean of the 8-hour time-weighted average (TWA) exposures for all job categories was 2.4 ppm (n = 163). 1,3-butadiene QC samples are primarily collected by cylinders ("bombs") in an open loop system at the tank farm storage spheres and in the process line; some sampling locations have been converted to closed-loop systems.

The NIOSH analytical results for the bulk samples of SBR were non-detectable; a trace was detected for an NBR sample (BMB3551). The level of detection was 0.04 ng/mg by weight ; trace levels were in the 0.04-0.2 ng/mg range.

Based on a review of industrial hygiene data provided by Copolymer, it has been decided to include Copolymer as a candidate for an indepth industrial hygiene survey.

The company maintains personnel records on some terminated as well as all 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 1,000 or 8,000 ppm of 1,3-butadiene. Mice exposed to 625 or 1,250 ppm of 1,3-butadiene developed a high incidence of malignant lymphomas; an increased incidence of other tumors, including hemangiosarcoma; and testicular and ovarian atrophy.[1,2]

The offspring of pregnant rats exposed to 1,3-butadiene at 8,000 ppm had major skeletal defects. In addition, fetal toxicity was observed when pregnant dams were exposed at 200 ppm, 1,000 ppm, and 8,000 ppm.[3]

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

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

APPLICABLE STANDARDS AND RECOMMENDED LEVELS

The current legally allowable air concentration 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 the Notice of Intended Changes for the 1984-85 Threshold Limit Values (TLV), based upon reported animal carcinogenicity data. The Intended Change identified 1,3-butadiene as an A2 industrial substance suspected of carcinogenic potential for man. A numerical TLV of 10 ppm was proposed in connection with the notice.[8]

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

Copolymer Rubber and Chemical Corporation, a wholly-owned subsidiary of Armstrong Rubber Company, manufacturers styrene-butadiene rubber (SBR) and nitrile (acrylonitrile) butadiene rubber (NBR) at its plant in Baton Rouge, Louisiana. 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 at Copolymer. The production rates of SBR and NBR are 465 million lb per year and 15 million lb per year, respectively. NBR production is block-operated for 30 to 50 days 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.

During the history of the plant, several process changes have been made which have resulted in lower 1,3-butadiene emissions and consequently reduced worker exposure to 1,3-butadiene. In 1970, the undersized absorber/desorber vent unit in the SBR recovery area was replaced with a new unit; this reduced butadiene losses to the atmosphere from 550,000 lbs/yr to 50,000 lb/yr. During 1973, as part of a pollution abatement project at the plant, a smokeless flare tip using steam was installed, thus increasing burning efficiencies to greater than 99 percent. In 1982, the vent stream from the absorber/desorber unit (originally installed in 1970) was routed to the boilers in the plant, essentially eliminating butadiene atmospheric emissions that formerly occurred from the vent unit.

PROCESS DESCRIPTION

Copolymer 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 lbs 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 1,3-butadiene containing 30,000-gallon storage tank in the rubber tank farm, charged from the spheres, 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 Copolymer. 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.

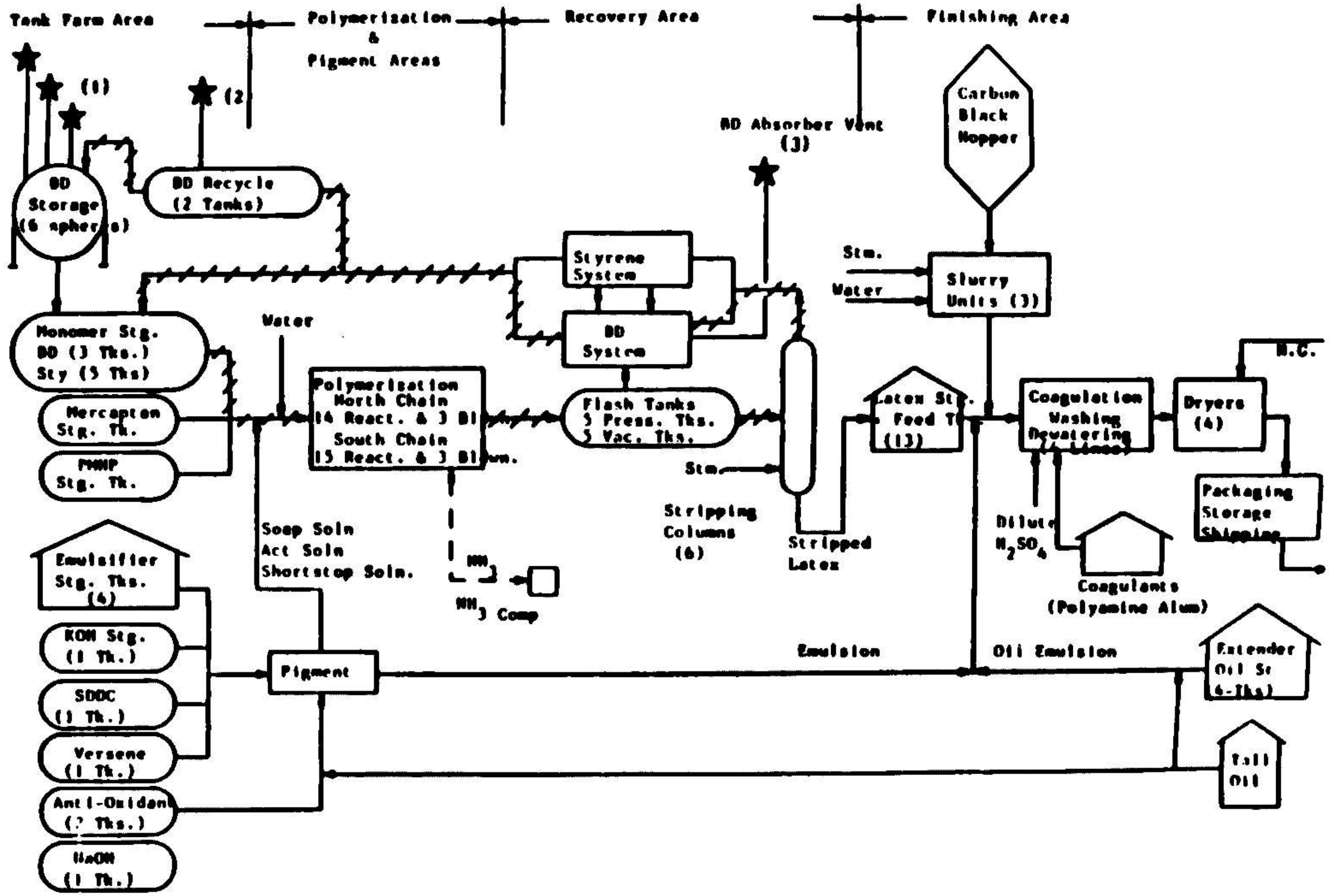

Figure 1. Process flow diagram for production of SBR at Copolymer Rubber and Chemical Corporation, Baton Rouge, Louisiana.

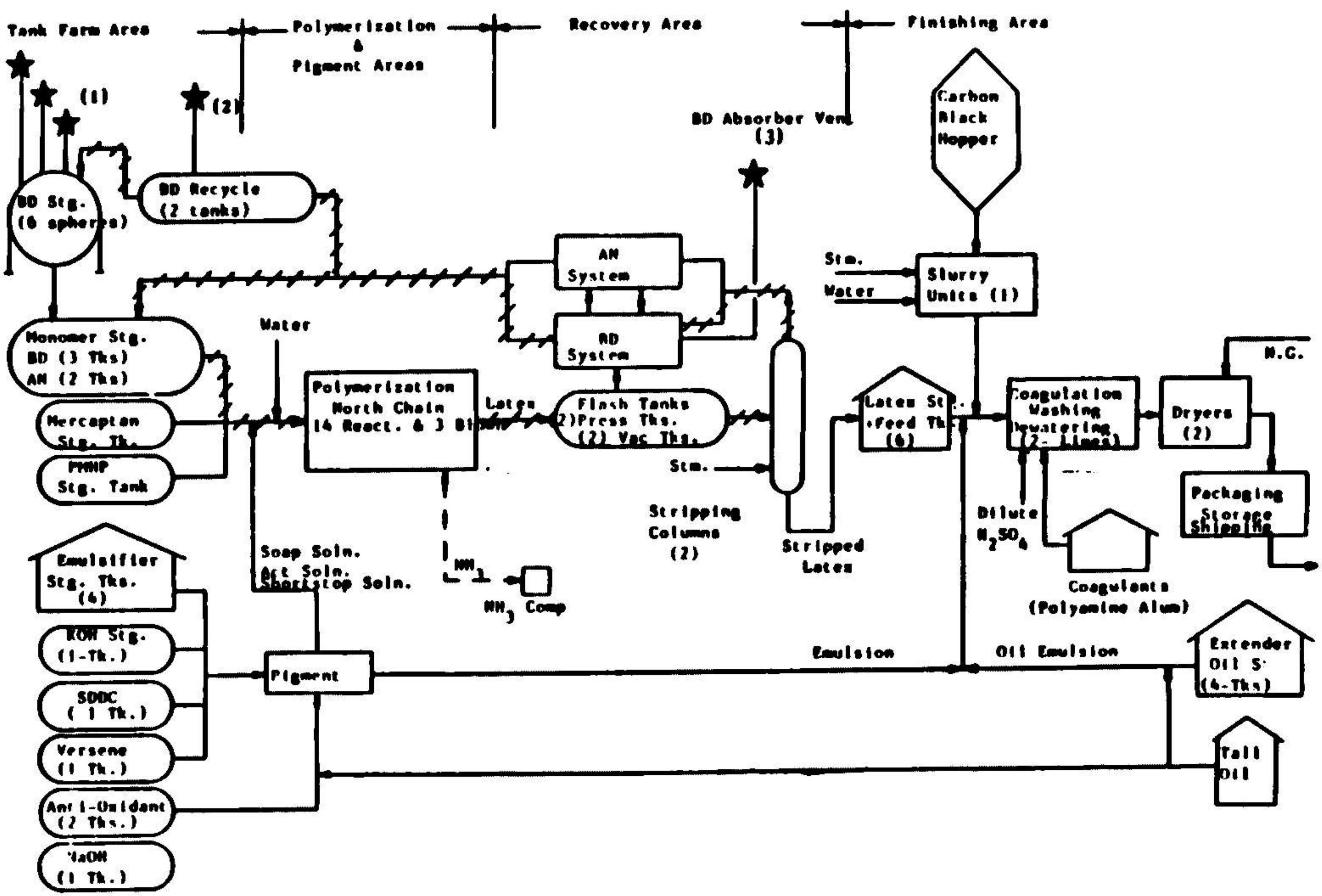

Figure 2. Process flow diagram for production of NBR at Copolymer Rubber and Chemical Corporation, Baton Rouge, Louisiana

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 flash tank, and then to the vacuum 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 butadiene from the knockout tanks to the butadiene compressors which then feed it to the butadiene recycle tower. The butadiene recycle tower also scrubs out styrene. The 1,3-butadiene is then condensed and returned to the recycle butadiene tanks in the tank farm. The absorber/desorber unit purges air from the recycle butadiene tanks, into a vapor stream returning 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.

1,3-butadiene recovery from NBR production is similar to the SBR recovery system 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.

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 product in crumb form. The product 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 has 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 UPS.

Quality Control (QC)

Two plant laboratories (hydrocarbon [HC] support laboratory and the rubber laboratory) conduct analyses of QC samples. The HC laboratory conducts analysis of 1,3-butadiene samples. A sample is collected from each rail tank car for QC analysis. The blended 1,3-butadiene monomer feed is sampled as it enters the reactor chain. Employees collect 1,3-butadiene QC samples using cylinders, or "bombs", in an open-loop configuration with quick disconnect fittings. Some sample locations have been converted to a closed-loop configuration. After analysis, bombs are voided in a laboratory hood equipped with local exhaust ventilation before subsequent use.

The rubber laboratory conducts tests on the finished rubber for viscosity and percent heat loss.

The company has conducted analysis of the SBR and NBR for residual 1,3-butadiene. The company reported that results from 24 samples of SBR showed free 1,3-butadiene content ranging from non-detectable to 1.6 ppm by weight, with an arithmetic mean of 0.8 ppm. The results from 9 samples of NBR showed a range of 0.1 to 0.3 ppm by weight for residual 1,3-butadiene, with an arithmetic mean of 0.2 ppm. Due to the levels of butadiene typically found by Copolymer's survey method, 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 butadiene was routinely present and being handled for all purposes. In brief, the analytical procedure included dissolution of 0.075 - 0.100 g of the product sample in 5 ml of carbon disulfide, followed by analysis with gas chromatography with flame ionization detection. Tetrahydrofuran was also tried as the extraction solvent, but all lots tested showed interference with the 1,3-butadiene peak.

DESCRIPTION OF THE WORKFORCE

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.

The 143 employees spend their entire workshift in the vicinity of 1,3-butadiene monomer or 1,3-butadiene polymers and are potentially exposed to 1,3-butadiene 8 hours per day. An additional 294 employees are potentially exposed intermittently to 1,3-butadiene. Table 1 shows the distribution of the production, maintenance, and laboratory personnel at Copolymer.

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 operations personnel are as follows:

<u>Reactor/recovery area</u>

Leaderman	Senior operator and lead operator for area; monitors all area operations.
Tank farm operator	Loads and unloads raw materials.
Reactor No. 1 Operator	Monitors process at control panel; inside control room for 60 percent of the shift.

TABLE 1. DISTRIBUTION OF PRODUCTION, MAINTENANCE, AND LABORATORY EMPLOYEES AT COPOLYMER, BATON ROUGE, LOUISIANA

Location/job title	Estimation of percentage of work shift in area of 1,3-butadiene monomer/polymers
Reactor/Recovery Area	
Leaderman	100
Tank farm operator	100
Reactor No. 1 operator	100
Reactor No. 2 operator	100
Pigment operator	100
Recovery No. 2 operator	100
Recovery b operator	100
Vacation relief/shift breaker	100
Utility A operator	100
Finishing Process Area	
Leaderman	100
Finishing A operator	100
Carbon black operator	100
Dryer operator	100
Baler	100
Packager (utility person)	100
Vacation, relief operator	100
Lift truck operator	100
Maintenance	
Craftsman	0-10
Utility Personnel	50
Rubber Laboratory	
Technician	0-10
Utility person	0-1-
Hydrocarbon Laboratory	
Technician	0-30
Utility person	0-10
Research and Development Laboratory	
Technician	0-10
Utility person	0-10
Other (Powerhouse and Pumphouse Operator)	10
Supervisor (exempt)	0-5

Reactor No. 2 operator	Outside operator; checks reaction conditions, pump seals, etc. Takes process equipment in and out of service.
Pigment operator	Prepares emulsifiers and charge makeup solutions. Spends 98 percent of the shift in a pressurized building.
Recovery No. 2 operator	Assists leaderman in the recovery area. Takes equipment in and out of service. Conducts pressure tests.
Recovery B operator	Assists in recovery area. Oils compressors; collects QC samples of stripped latex for analysis of residual styrene, 1,3-butadiene, etc.
Vacation relief/shift breaker	Area janitor; performs housekeeping duties

<u>Finishing Process Area</u>

Leader man	Lead operator in latex coagulation area; monitors all area operations.
Finishing A operator	Inspects process equipment; assists in finishing process.
Carbon black operator	Unloads carbon black and extender oil; operates carbon black unit.
Dryer operator	Operates 2 fluid bed units and 2 tray/apron driers; spends majority of shift in the panel room.
Baler	Compresses polymer crumb into 75 and 90 pounds bales; applies coating and thin wrap.
Packager	Packages and palletizes rubber.
Vacation relief	Trained in all jobs.
Lift truck operator	Transports product package to warehouse.

DESCRIPTION OF PAST WORKER EXPOSURES

Since opening in 1944, the plant has produced synthetic rubber (SBR, NBR) exclusively by emulsion polymerization. Over the years the process, however, has changed from batch to continuous operation.

Since 1980, Copolymer has had an ongoing program to monitor personal exposures and area concentrations of 1,3-butadiene. Table 2 summarizes personal monitoring data collected 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 = 163).

While no area data were obtained from Copolymer, 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 butadiene typically found by Copolymer's survey method, 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 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.[9]

Pumps, columns and lines are cleaned when required. Storage tanks are inspected for leaks every 2 years. Prior to maintenance activities on equipment, decontamination is conducted by water displacement and stream cleaning (optional).

Engineering Controls

Reactor agitators are equipped with dual mechanical seals with 145 psig pressure between the seals. All new 1,3-butadiene pumps are equipped with dual mechanical seals. The older 1,3-butadiene handling pumps are equipped with single mechanical seals; the company replaces single mechanical seals with dual seals when an opportunity arises. Compressors are of the reciprocating-type and are equipped with packed seals.

Tank farm vessels for storage of 1,3-butadiene, including 3 non-working bulk storage tanks and 3 process storage tanks, vent directly to the atmosphere; all other process equipment vent to scrubbers or absorbers 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.

TABLE 2. SUMMARY OF COPOLYMER'S PERSONAL MONITORING FOR 1,3-BUTADIENE AT BATON ROUGE, LOUISIANA 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 cperator	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

Vapor space in the rail car head is vented to a flare when unloading 1,3-butadiene. Sampling connections located at the inlet to 1,3-butadiene storage spheres and before the polymerization chains have been equipped with quick-disconnect fittings and check valves. Some rail cars may still be equipped with non-venting magnetic gauges, but all recent shipments have been made in tank cars equipped with the magnetic gauges.

Employees sample 1,3-butadiene with sampling bombs primarily in an open-loop arrangement. The plant is evaluating conversion to a closed-loop purged system with quick-disconnect bomb fittings at all sampling points. Closed-loop systems had been installed at the 5 most used sample locations at the time of the survey. Positive displacement-type "Strahman" valves are used at latex sampling locations, which eliminate the purge volume requirements of some other valve and line configurations.

Airborne concentrations of acrylonitrile and 1,3-butadiene will be monitored by fixed-point area monitors when installation and start-up of the new equipment is completed.

Employees in the hydrocarbon support and rubber laboratories conduct analyses under laboratory hoods equipped with exhaust ventilation.

DESCRIPTION OF MEDICAL, SAFETY AND INDUSTRIAL HYGIENE PROGRAMS

Medical

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-ray, audiometric hearing tests, Snelin vision tests, pulmonary function test, blood test, 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 facilities, 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.

The company requires the wearing of safety glasses and hard hats at all times. Chemical splash goggles and face shields are required when needed, especially where caustic alkalies or acids are used. Steel-toe shoe covers, knee-high rubber boots, and rubber shoe covers are provided as needed. Operators in certain process related job categories, maintenance employees and utility persons, are provided uniformed coveralls which are company laundered. PVC and other chemical-protective gloves are used in material handling and maintenance jobs. Respirators available for employee use include self-contained breathing apparatus, airline respirators, air-purifying respirators and disposable respirators. Respirators are primarily used around NBR processing to avoid exposure to acrylonitrile. The company did not report the existence of a formal respirator program. The central change house is available to employees for showers, clothing change, and for lunch break. Separate lunchrooms are also located in other areas of the plant. Process areas are equipped with safety showers and eye-wash stations. Smoking is permitted only in areas which have been designated as non-hazardous.

Industrial Hygiene Program

Copolymer 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.

DESCRIPTION OF THE PERSONNEL RECORD SYSTEM

The company maintains personnel records on some terminated as well as all 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 information on personal history, education, family status, date of employment and/or transfer, hourly rate, job position, absentee records, vacations, and pension status. Several unions (e.g., operating engineers, pipefitters, painters, machinists) represent employees in the company workforce. These unions maintain separate membership records.

SAMPLING AND ANALYTICAL METHOD FOR BULK POLYMER SAMPLES

Because polymers are further processed into finished products, it was one of the purposes 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 use 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 (situated in an enclosed sampling tube) are removed by purging the enclosed sampling tube with inert gas (helium) followed by subsequent 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 for a period of time. 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 3 were chosen and used throughout the study.

TABLE 3
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. Portions of the bulk polymers ranging in weight from 20-30 mg 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. 1,3-butadiene was also run by mass spectrometry to obtain a standard reference spectrum for comparison.

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 Scott 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 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 this portion at 30°C. If little or no butadiene was detected at this temperature, this 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 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 was 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. Because no 1,3-butadiene was found in the bulks using Dynamic headspace analysis (see following discussion) it was not necessary to do GC/MS.

Analytical Results

The analytical results of the bulk analysis of both SBR samples and one NBR sample were below the limit of detection of 0.04 ng/mg by weight at all analytical temperatures. Trace amounts (0.04 - 0.2 ng/mg) of 1,3-butadiene were detected at 160°C in one NBR (BMB 3551) sample. The temperatures at which all the bulk samples were analyzed were: ambient, 30°C; process, 90°C; and end use 160°C. The copolymer products collected and analyzed by NIOSH were: SBR 1520; SBR 1500; NBR 35-8; and BMB 3551.

DISCUSSION

Copolymer Rubber and Chemical Products Corporation produces SBR and NBR by emulsion polymerization at its plant in Baton Rouge, Louisiana. The plant, which opened in 1944, produces 465 million pounds of SBR and 15 million pounds of NBR annually. Approximately 120 miilion pounds of 1,3-butadiene is used annually. The 1,3-butadiene monomer for the process is delivered primarily by pipeline and occasionally by rail tank cars.

Of 470 people employed at the facility, 143 are directly involved in the reaction, recovery, and finishing operations. These employees are potentially exposed to 1,3-butadiene 8 hours per day. An additional 294 employees are potentially exposed to 1,3-butadiene intermittently. Copolymer's personal monitoring data show a weighted mean of the 8-hour TWA exposures of 2.4 ppm (n = 163) for job categories measured.

Engineering controls employed in the process include dual mechanical seals on newer pumps, single mechanical seals on older pumps, dual mechanical seals on reactor agitators, rail car vapor vents, and locally exhausted laboratory hoods. QC sampling for 1,3-butadiene is primarily performed by open-loop cylinders ("bombs"); the company is evaluating conversion to closed-loop systems with quick disconnects for the entire plant.

Bulk samples of SBR and NBR have been evaluated by Copolymer for residual 1,3-butadiene. Arithmetic means were 0.2 (NBR) and 0.8 ppm (SBR) of 1,3-butadiene by weight.

CONCLUSIONS

Based on a review of the Copolymer historical industrial hygiene data, Copolymer will be included as a candidate for an indepth industrial hygiene survey. However, the designation as a candidate does not mean that Copolymer is certain to be included in the indepth survey sites selected. The purpose of the indepth surveys will be to develop and extent of exposure profile for all job descriptions associated with the production and distribution of 1,3-butadiene based products.

RECOMMENDATIONS

It is recommended that the company pursue its plan for installation of a closed-loop sampling system throughout the plant.

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SUPPLEMENT

COSTS OF CONTROLS

Copolymer Rubber and Chemical Corporation
Baton Rouge, Louisiana

COSTS OF CONTROLS

During the walk-through survey at Copolymer's Baton Rouge plant, PEI Associates, Inc., requested information from Copolymer personnel on costs of controls employed by the plant to minimize worker exposures to 1,3-butadiene. Table 1 presents cost estimates for several types of engineering controls at the plant. The associated year of the cost quotation is also indicated. It should be noted that most of the controls were instituted by the plant to control exposures to acrylonitrile pursuant to OSHA regulations; however, these controls are also effective in controlling exposures to 1,3-butadiene.

TABLE 1. COPOLYMER'S COST ESTIMATES OF ENGINEERING CONTROLS EMPLOYED AT THE BATON ROUGE, LOUISIANA, PLANT

Type of control	Cost, $	Year
Leak detection system, to monitor acrylonitrile and 1,3-butadiene concentrations in different plant areas (including equipment and labor)	150,000	1985
Connection of Absorber/Desorber Vent Stream to Plant Boilers (instrumentation for safety loop compressor, knockout drum, etc.)	250,000	1982
Conversion to closed-loop sampling system with check-valved quick disconnects (equipment, plumbing, etc.)	1,500 per location	1985
Positive Displacement - type "Strahman" valves at latex sampling points	800 per valve	1985
Dual mechanical seals ("duraseals") on pumps handling 1,3-butadiene (new)	1000 per pump	1985
Double-sealed agitator shafts on 28 reactors (installed)	450,000	1985
- Operation and maintenance on agitator seals	50,000/yr	1985
Local exhaust hoods in Rubber Laboratory	5,000 per hood	1985