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IWS-147-23

NIOSH-00163122

**Industrial Hygiene Survey Report
of
Phillips Chemical Company
Philtex Plant
Borger, Texas**

**Survey Conducted by:
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**Dates of Survey:
August 7, 1985**

**Date of Report:
May, 1986**

**Report Number:
147.23**

**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.

ACKNOWLEDGEMENTS

This report was prepared in cooperation with PEI Associates, Inc. Principal authors from PEI were E. Radha Krishnan and Mark Nutter. Their responsibilities were completed under the scope of work of Contract Number 68-02-3976, Task 24, with the U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C.

PURPOSE OF SURVEY:

To perform a walkthrough 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.

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**STANDARD INDUSTRIAL
CLASSIFICATION (SIC) CODE:**

2869 (Industrial Organic Chemicals,
not elsewhere classified)

ABSTRACT

A walkthrough survey was conducted at the Philtex plant of Phillips Petroleum Company in Borger, Texas on August 7, 1985. The purpose of the survey was to obtain information on the production processes related to liquid polybutadiene (Butarez^R), sulfolene/sulfolane, and R-11 insecticide and to assess the potential for occupational exposure to 1,3-butadiene during these processes. 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 liquid polybutadiene by solution polymerization, and produces sulfolene/sulfolane solvents and R-11 insecticide by organic synthesis. According to the company, these products make up a small percentage of the overall company business which produces 200 to 300 chemicals for specialty markets.

Of the 212 Philtex employees, 33 work in areas where there is potential for exposure to 1,3-butadiene. Philtex has conducted personal monitoring for 1,3-butadiene since 1979 in different areas of the plant; seventy-five percent (15/20) of the 8-hour time-weighted average (TWA) exposures were less than 0.1 ppm, and the unweighted mean TWA concentration was 1.7 ppm.

The results of the NIOSH analysis of bulk samples (for 1,3-butadiene) of sulfolane and R-11 were non-detectable (limit of detection was 0.04 ng/mg by weight); a trace amount of 1,3-butadiene (0.04 - 0.2 ng/mg) was detected in the Butarez[®]; greater than 140 ng/mg of 1,3-butadiene was detected in the Sulfolene

Based on the NIOSH bulk analyses of the Philtex 1,3-butadiene based products and a review of company industrial hygiene data which shows individual exposures of greater than 10 ppm for two job categories, it is the decision of NIOSH to include Philtex as a candidate for an indepth industrial hygiene survey.

The company maintains 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 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 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

Phillips Petroleum Company owned and operated three separate chemical plants in the Borger, Texas area that used or produced 1,3-butadiene. These plants were the Butadiene Plant, the Copolymer Rubber Plant, and the Philtex Plant. The only plant still operating is the Philtex Plant.

The Butadiene Plant and the Copolymer Rubber Plant were built by the U.S. Government in the early 1940's. A similar rubber plant was also built by the U.S. Government in Baton Rouge, Louisiana. Phillips Petroleum Company bought the Butadiene Plant and the Copolymer Rubber Plant in Borger after the close of World War II. Phillips Petroleum Company operated the Butadiene Plant until it was shut down in 1978. Phillips operated the Rubber Plant until it was shut down in 1984.

The Philtex Plant was built by Phillips in 1944 as a R&D facility. During the early years the plant did development work on rubber (SBR and others) and researched the use of sulfur compounds, such as mercaptans, to modify the properties of SBR. Philtex Plant became a commercial producing plant in the 1950's but continued R&D development work on rubber until 1956. Transpolybutadiene rubber was produced at Philtex for about five years during the middle 1960's.

Currently, the company manufactures 200 to 300 finished chemicals for specialty markets. 1,3-butadiene is used to produce three products: liquid polybutadiene (Butarez[®]), sulfolene/sulfolane, and R-11 insecticide. R-11 production at the facility started in 1955, and the Butarez[®] and sulfolene/sulfolane plants were installed in 1964-65. Butarez[®] is used primarily as a rocket fuel binder. The company produces approximately 200,000-500,000 pounds of Butarez[®] per year. Sulfolene is an intermediate in the production of sulfolane and is also marketed commercially as an intermediate for lubricant production. Combined production of sulfolene and sulfolane ranges between 5 and 10 million pounds per year. Sulfolane is used as an extraction solvent for numerous applications, including extraction of aromatics and acid gases from refinery streams. It is often sold as a mixture, with 3 percent water and an inhibitor (e.g., monoethanolamine, triethanolamine) to depress its freezing point. The company also produces approximately 50,000 to 100,000 pounds of R-11 per year. R-11 is used as an insect repellent and as a delousing agent for cows in the dairy industry. The concentration of R-11 in commercial insecticide sprays is generally less than 1 percent.

Raw materials used at the plant, in addition to 1,3-butadiene, include propane, butane, hexane, hydrogen sulfide, butene, and other olefins. Other products produced by Philtex include sulfur chemicals, pharmaceutical intermediates, hydrocarbon solvents, reference fuels, and calibration hydrocarbons.

PROCESS DESCRIPTION

Process lines for Butarez[®], sulfolene/sulfolane, and R-11 are separate and independent; however, all process lines are supplied with fresh 1,3-butadiene from the same storage facilities in the tank farm. Until 1978, the Phillips 1,3-butadiene monomer plant was the supplier of 1,3-butadiene for the processes. Since the shutting down of the monomer plant, Philtex has used several suppliers. Shell is currently a major supplier of 1,3-butadiene for the Philtex plant. A rail tank car of 1,3-butadiene is delivered every one to two weeks. 1,3-butadiene is weighed when delivered to the storage facilities and metered out when transferred to

the process. The fresh 1,3-butadiene is transferred from the rail tank cars to two designated storage tanks. Transfer is done in a closed system with vapors from the receiving tank being compressed and sent to the tank car.

Butarez[®] (Liquid Polybutadiene)

Figure 1 is a process flow diagram for the production of Butarez[®] (liquid polybutadiene). Batch production of polybutadiene occurs throughout the year. Fresh 1,3-butadiene is first prepared for polymerization by entry into a flash unit and a dryer: heat is applied in the flash unit, volatilizing 1,3-butadiene and freeing it from inhibitors which are left behind in a liquid state; purified 1,3-butadiene is sent through a dryer unit packed with hydrophilic materials which absorb water. 1,3-butadiene which has been purified and dried is sent to temporary storage. From short-term storage, 1,3-butadiene is charged to a 1000-gallon reactor containing a catalyst and solvent. Solution polymerization occurs under "hot" (50°C) conditions. In the blowdown tank following the reactor, the polymer is neutralized by addition of hydrochloric acid. Polymer is then transferred to a holding tank and subsequently to the filter feed tank. After leaving the filter feed tank, the polymer undergoes further processing whereby the polymerization solvent is dispersed or volatilized from the polymer. Treatment in the final concentrator removes any residual solvent. Solvent from the filter tank and concentrator is collected in the solvent recovery system and recycled to the reactor. The final product (Butarez[®]) is drummed for storage or shipment. The Butarez[®] is a black viscous liquid with a molecular weight of approximately 8000 and a viscosity of 300 poise.

Sulfolene/Sulfolane

Production of sulfolene and sulfolane, shown in Figure 2, occurs as a continuous operation, 365 days per year. In the process, liquid sulfur dioxide (SO₂) is fed to the reactor from a storage tank. 1,3-butadiene is pumped from the tank farm to a metering tank. From this tank, a measured amount of 1,3-butadiene is fed to the sulfolane reactor which contains an excess of SO₂. 1,3-butadiene constitutes approximately 50 percent of the feed to the reactor. Vapors from the reactor, which contain SO₂ and minor amounts of 1,3-butadiene, are vented and absorbed in a caustic scrubber. From the reactor, molten sulfolene (2,5-dihydrothiophene-1,1-dioxide) is transferred to a flaker. The process is a closed system until it reaches this point; the flaker is under negative pressure and is vented to a scrubber which removes SO₂. The flaker has a chill roller bathing in molten sulfolene; sulfolene which comes in contact with the roller solidifies. A doctor blade cuts the quasi-crystallized (white) sulfolene into weighed bags for shipment. Sulfolene has a freezing point of 65-68°C, and is unstable at elevated temperatures.

Production of sulfolane begins by dissolving sulfolene in water. The mixture is reacted with hydrogen gas, reducing sulfolene to sulfolane. The sulfolane product, containing byproducts and water, is distilled through a series of three columns. Two of these remove lower molecular weight

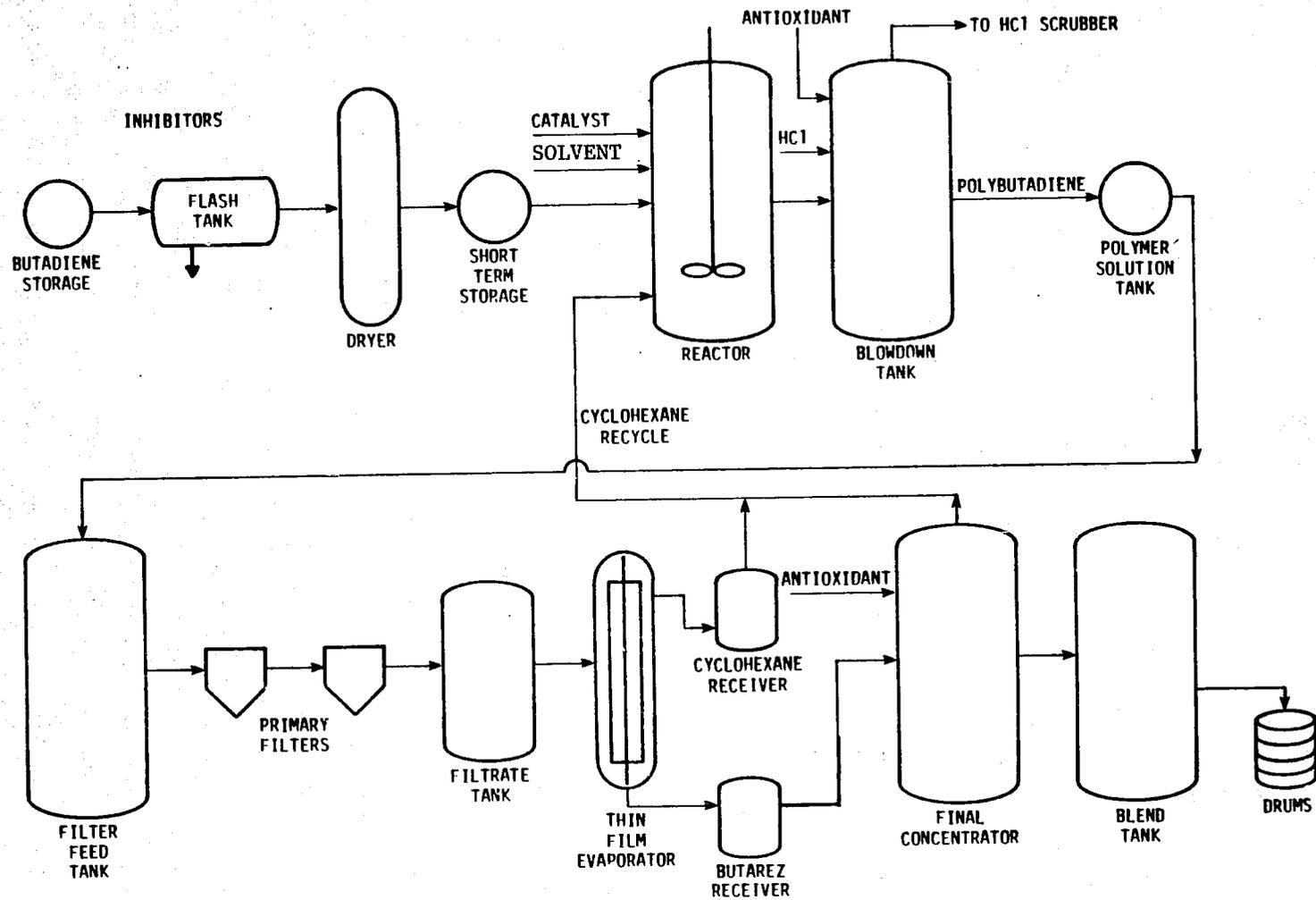


Figure 1. Process flow diagram for production of liquid polybutadiene (Butarez^R) at the Philtex Plant, Borger, Texas.

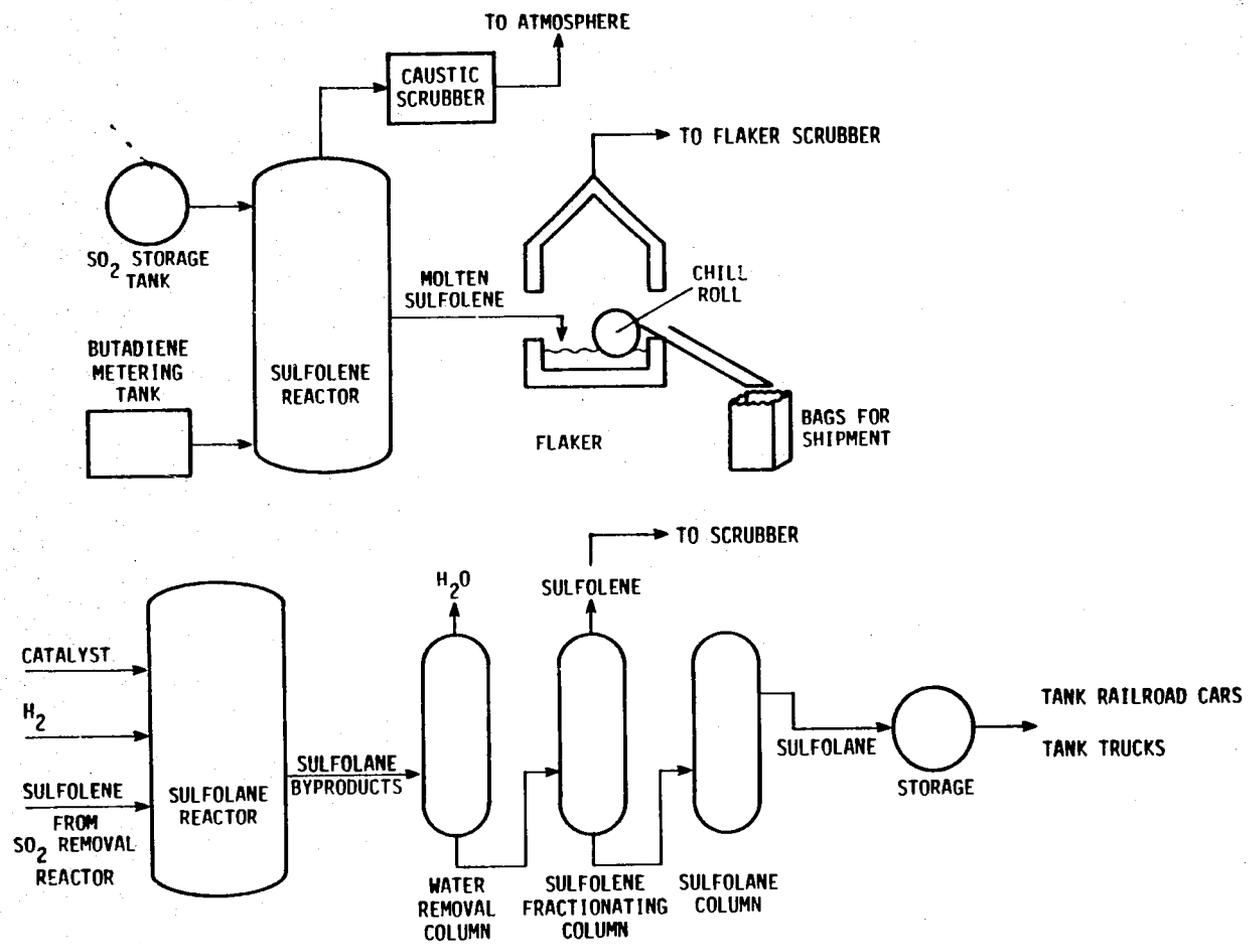


Figure 2. Process flow diagram for production of Sulfolene and Sulfolane at the Philtex Plant, Borger, Texas.

compounds such as water and sulfolene; and the third column recovers sulfolane as the overhead product which is then stored in tanks at atmospheric pressure for subsequent shipment. Sulfolane is a white colloidal suspension at room temperature. It has a melting point of 27°C and a boiling point of 288°C.

R-11

Production of R-11 occurs intermittently throughout the year. R-11 was not being produced at the time of the survey. The production process for R-11 is a continuous operation.

Figure 3 shows a diagram of the R-11 production process. In the process, 1,3-butadiene reacts with an excess of furfural in a liquid-phase reactor; the reaction proceeds under moderate conditions of temperature and pressure. The reaction consumes 1 mole of furfural for 2 moles of 1,3-butadiene. After a period of 4 to 5 hours, the reaction mixture is transferred to the reactor effluent surge tank. The mixture proceeds to a vertical column which separates butadiene dimer by distillation. Butadiene dimer, or 4-vinyl cyclohexane, is recovered from the column and later transported to a refinery for reprocessing in crude catalytic cracking units. Furfural is removed from the reaction products by distillation in a similar column and recycled to the reactor. The last column in the R-11 process is run batch wise, and separates R-11 from the polymer kettle product (K.P.). The K.P. is a crystalline solid which is disposed of in an onsite landfill. R-11 is transferred to storage tanks and is shipped to customers in drums. R-11, or 2,3,4,5-bis (2-butadiene)-tetrahydrofurfural, is in the form of a yellow liquid.

Quality Control (QC)

a. Butarez[®]

QC samples are obtained at four points on the Butarez[®] process line: after the polymerization reactor; at the filtration step; after the semi-concentration step; and at the final product stage. Product sample analyses include tests for viscosity, cis/trans vinyl ratio, and antioxidant concentration. The company believes that the vacuum applied in the concentrator would remove any latent 1,3-butadiene from the Butarez[®] product. Philtex has not conducted analysis of Butarez[®] bulk samples for free 1,3-butadiene.

b. Sulfolene/sulfolane

QC samples are not obtained at intermediate process points in the production of sulfolene/sulfolane. Periodic samples of the end products are collected for product quality assurance. The company has not analyzed either product for levels of free 1,3-butadiene.

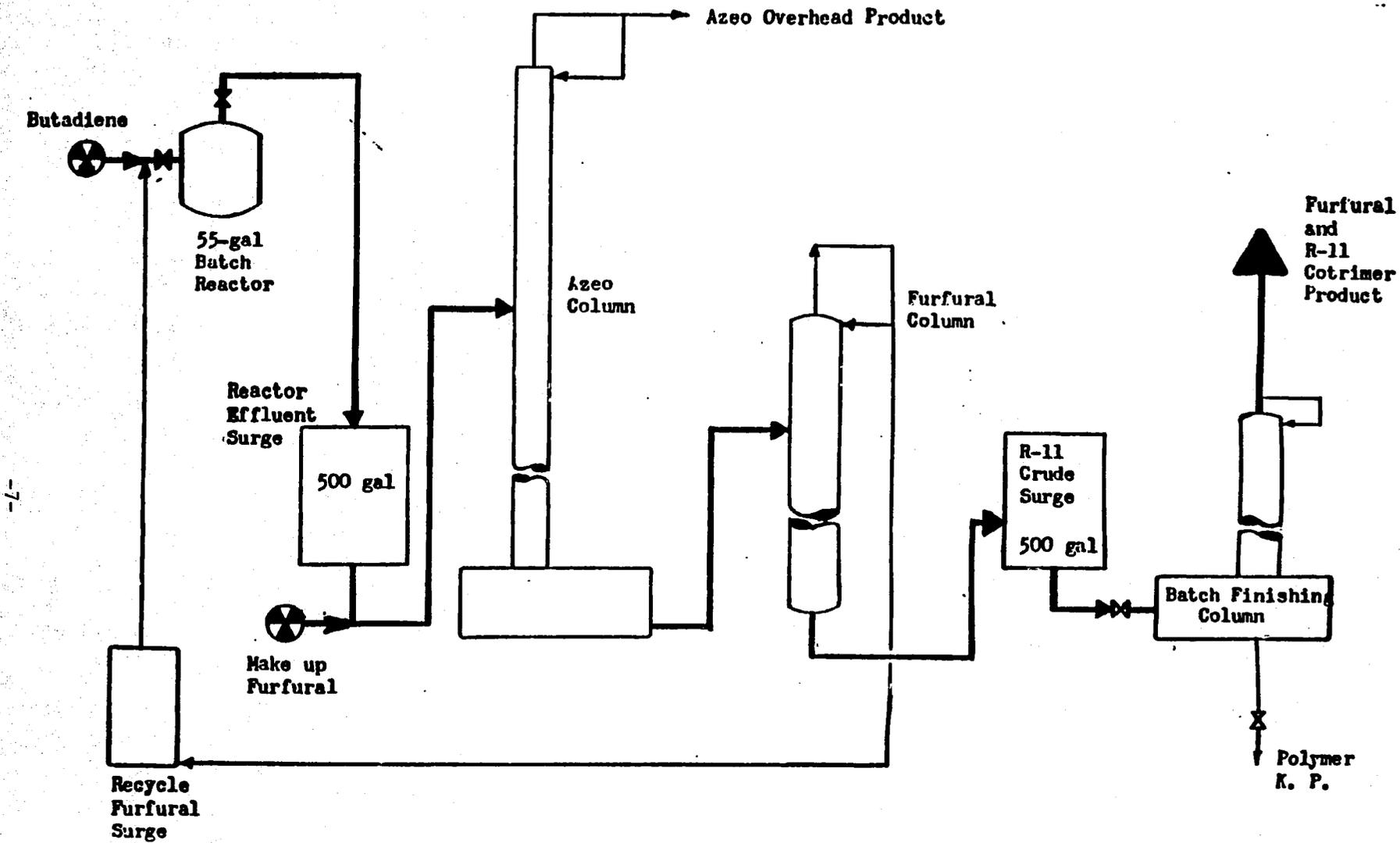


Figure 3. Process flow diagram for production of R-11 cotrimer at Philtex, Borger, Texas.

c. R-11

QC sampling is conducted on the final R-11 product only; no samples are taken of the feed streams to the process or at intermediate process points. Analysis of R-11 product bulk samples for 1,3-butadiene has not been conducted by Philtex.

DESCRIPTION OF THE WORKFORCE

The Philtex facility employs approximately 300 workers including contract personnel. A total of 212 employees are on the Philtex payroll as full-time employees. The plant operates 24 hours/day, 365 days/year. Process operations and the laboratory operate over three 8 hour shifts per day. Maintenance employees work only day shift, but work other shifts when necessary. Shipping operators work day shift only.

Table 1 shows employee distribution in 1,3-butadiene areas. The table also shows the estimated percentage of time different workers spend in proximity to 1,3-butadiene. A total of 33 employees work in 1,3-butadiene areas over three shifts. The day shift includes maintenance and shipping employees. Tank cars delivering 1,3-butadiene arrive every one to two weeks; shipping employees load product material as well as unload pure 1,3-butadiene. One quality assurance laboratory services all three product lines. Certification analysis are usually run on the day shift; 6 to 7 employees may work during such times.

The employees who have potential exposure to 1,3-butadiene are divided into the following job categories:

Process Operator	Monitors control room instrumentation. Takes process samples.
Supervisor	Supervises all process areas. Spends 20% of time in Butarez [®] /Sulfolane areas, 15% in R-11 areas, 65% in office and other areas.
Maintenance Mechanics	Repair/replaces process pumps and related equipment.
Lab Technician	Analyzes process samples.
Shipping Operator	Unloads tank cars. Loads final products on shipping vehicle.

DESCRIPTION OF PAST WORKER EXPOSURES

The processes which use 1,3-butadiene have remained essentially unchanged since their inception: R-11 has been made since 1955, Butarez[®] production started in the mid-1960s' and sulfolene/sulfolane production

TABLE 1. WORKFORCE DISTRIBUTION IN 1,3-BUTADIENE
AREAS AT PHILTEX PLANT, BORGER, TEXAS

Job category	Percent of time exposed to 1,3-butadiene	Number of employees per shift
Process Operator - °Multipurpose area (Butarez/Sulfolene/ Sulfolane)	100	3
°R-11	50	1-2
Supervisor (all areas)	35	1
Maintenance	Intermittent	2-4 ^a
Laboratory	10	2-3
Shipping	15	1-2 ^a
TOTAL		10-15

^a Day shift only.

began in 1964. The last revisions to the equipment in the Butarez[®] process were made in 1982.

Philtex has conducted industrial hygiene sampling for 1,3-butadiene since 1979. Table 2 presents the results of personal monitoring. The data show that most employees are exposed to relatively low levels of 1,3-butadiene; 75 percent (15/20) of the samples are below 0.1 ppm. There were, however, several relatively high exposures reported. Three of four samples obtained in the control rooms of the multipurpose plant (Butarez[®]/sulfolene) area and the packaged products area were at or above 3 ppm. An employee in the packaged products area had an eight-hour time-weighted average (TWA) concentration of 11.5 ppm. The highest value for the personal samples, 12.6 ppm could not be identified by location. Overall, the mean TWA concentration for the 20 personal TWA samples was 1.7 ppm. Table 3 presents the results of area monitoring. Sample data were not time weighted to 8 hours. The mean concentration for 10 area samples was 6.7 ppm; relatively high area concentrations were reported in the packaged products area. These concentrations appear to correlate with the personal sample results obtained in this area. Samples were collected on standard charcoal tubes and analyzed by gas chromatography with flame ionization detection, a method similar to NIOSH Method P&CAM 127⁸.

Process operators are potentially exposed to 1,3-butadiene during collection of process quality control (QC) samples. Samples are collected using pressure cylinders. Routine QC samples in the tank farm area are collected by operators using pressure cylinders, or sample containers in an open-loop configuration. Operators connect the sample container to a process line, then open valves to fill the cylinder. 1,3-butadiene fills the container and is purged out of the rear of the cylinder before the employee closes the valve. This results in exposure to airborne concentrations of 1,3-butadiene during sampling. At the conclusion of QC analysis the technician vacuum exhausts the sample container in a laboratory hood.

Maintenance occurs on an as-needed basis; shutdowns are not scheduled beforehand due to the batch operation nature of some of the processes. Maintenance employees frequently need to repair process equipment on the Butarez[®] line. Polymer buildup occurs on the heating coils in the reactor and this must be removed periodically. The frequency of maintenance is less on other pieces of equipment; cleaning of pumps and columns usually occurs once per year. Maintenance work on pumps, reactors, lines, columns and tanks is a source of employee exposure to process materials which may contain 1,3-butadiene. Before repair begins, however, equipment is decontaminated by standard procedures. Pumps are blocked off from the process line, vapors are bled to the atmosphere, and liquids are pumped off. Columns, reactors, lines, and tanks are depressurized, purged with nitrogen gas, and steam cleaned.

Engineering Controls

Process equipment is engineered to control leaks of 1,3-butadiene. 1,3-butadiene handling pumps have single mechanical seals; the company has considered retrofitting the pumps with dual mechanical seals but does not

TABLE 2. PERSONAL MONITORING DATA FOR 1,3-BUTADIENE
AT PHILTEX PLANT, BORGER, TEXAS*

Location	Sample time, minutes	8-h TWA ^a concentration, ppm
Multipurpose area (Butarez/sulfolane)	424	0.003
	424	0.003
	421	0.021
	422	0.028
	422	0.763
	429	0.028
Control room (Multipurpose plant area)	434	3.523
	433	3.040
Packaged products area	402	11.546
Control room (packaged products)	424	0.093
	424	3.907
R-11 Plant	447	0.039
	458	0.002
Maintenance area	427	0.010
	428	0.011
	431	0.010
	425	0.013
	414	0.009
Other	452	0.021
	418	12.562
		Mean = 1.70 ppm

^a Time-weighted average.

* Job title for all sample locations with the exception of Maintenance is process operator; job titles for Maintenance is maintenance mechanic.

TABLE 3. AREA MONITORING FOR 1,3-BUTADIENE AT
PHILTEX, BORGER, TEXAS

Location	Sample time, minutes	Concentration, ppm
Packaged products area	455	0.015
	451	0.014
	218	40.055
	403	4.884
	404	19.228
	399	0.518
	403	2.160
Multipurpose area (Butarez/sulfolane)	467	0.015
	Other	435
427		0.021
		Mean = 6.69 ppm

plan to do so in the near future. 1,3-butadiene tank cars are equipped with spew stick or slip-tube gauges for monitoring the unloading process.

Reactor agitators are equipped with dual mechanical seals. The polymerization reactor and 1,3-butadiene storage tanks are equipped with rupture disks and relief valves. Reciprocating compressors (with rings) are used on the vapor recompression system; this system prevents leakage of 1,3-butadiene during transfer to storage tanks. A vapor line supplements the primary transfer line (liquid). The vapor line captures escaping 1,3-butadiene vapors; they are then pressurized and returned to the tank car. The Philtex plant has two flares, one for the hydrogen sulfide system in the plant and the other for the hydrocarbon system. QC operations, including sample cylinder purging and sample injection for wet analysis, are conducted under a laboratory hood with local exhaust ventilation.

DESCRIPTION OF MEDICAL, SAFETY AND INDUSTRIAL HYGIENE PROGRAMS

Medical Program

There are no doctors or nurses employed at the Philtex plant. Phillips Petroleum, however, employs one licensed nurse at its refinery (adjacent to Philtex) who is on call for medical problems at Philtex. Approximately 30 employees receive "Medic" safety training including first-aid and CPR training. Eighty employees received fire brigade training. Physicals are provided by the company through contracted physicians in the city of Borger. The company provides pre-employment physicals to all employees except office workers. Periodic physicals are given to all employees every 5 years; the frequency of periodic exams increases to once every 3 years based on age. Special physicals are given to fire brigade members. Annual physicals are required of maintenance workers with potential for asbestos exposure. Radiography exams are offered to all employees at the time of the periodic exam. Hearing tests are offered to approximately 25 people employed in high-noise occupations such as maintenance, truck driving, and welding. Fire brigade members receive lung function tests. Vision tests, blood tests, and urine tests are conducted during pre-employment and periodic physicals.

The company maintains an ambulance on standby 24 hours per day. The nearest hospital is located 4 miles from the plant.

Safety Programs

In 1984, the company and its employees conducted 752 safety meetings and 562 safety audits. The Philtex plant is in its fifth year without a lost time accident.

The safety program is administered by a central safety Department; the safety manager handles safety audits and industrial hygiene sampling. There is also a Safety Committee headed by the Philtex plant manager, and a safety subcommittee which schedules audits, meetings, and safety training activities.

Safety equipment required plantwide includes safety glasses and hard hats. Maintenance employees wear coveralls. Some jobs require chemical suits; these suits, however, are not required for handling 1,3-butadiene. Safety glasses are required as a basic form of eye protection; some operations, however, require the use of a face shield. The company recommends, but does not require, the use of steel-toed safety shoes. Process operators are required to wear chemical (vinyl-coated) gloves. Maintenance personnel wear cotton gloves. Air purifying respirators are available but not widely used. The company maintains 65 Scott Air-Paks and 128 full-face air-supplied respirators; this equipment is used when SO₂ levels from the sulfolene unit become excessive. There is a formal respiratory protection program at the plant. Operators are given respiratory protection training twice a year; maintenance is trained yearly. Records are kept on this training. There are 46 combination safety shower/eye wash stations in the plant. Clothing change rooms are available. Smoking is permitted in designated areas only.

Industrial Hygiene Program

Industrial hygiene assessment is coordinated by the industrial hygiene staff at the corporate office; monitoring is conducted by the plant safety staff. Three persons at Philtex are trained in air sampling techniques. The sampling equipment is located at Philtex. Since 1979, over 5000 samples have been taken by Philtex for a wide variety of chemicals, such as n-propylbenzene, paradichlorobenzene, butane, 1,3-butadiene and 2-methyl pentane. The company does not have a periodic monitoring schedule for 1,3-butadiene; monitoring is conducted when problems occur, and occasionally to update monitoring records.

DESCRIPTION OF PERSONNEL RECORD SYSTEM

Personnel records are maintained on terminated as well as current employees. Old records are microfilmed and actual hard copies are destroyed. The personnel file contains approximately 1500 records dating back to 1944. The records specify the period of employment in a specific job category or title but do not provide a complete description of the tasks involved in a job. Standard personnel forms are used which, for each employee indicate job title, reports of accidents, foreman's appraisal information, and information on the employee's benefits. The union maintains 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. 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. 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- μ m film thickness was used for all analyses. The column was temperature programmed from 350°C to 260°C at a rate of 150/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 ($\pm 2\%$) 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.

Analytical Results

Trace amounts (0.04 - 0.2 ng/mg) of 1,3-butadiene were detected in the Butarez® sample (30°C) collected at Philtex and greater than 140 ng/mg was reported for sulfolene (30°C). 1,3-butadiene was not detected in Sulfolane and R-11 at any analytical temperatures.

To positively confirm that 1,3-butadiene was actually present at the low levels indicated, the Butarez® sample was reanalyzed by GC/MS at 140°C. The analysis showed the presence of 1,3-butadiene in the 0.04 - 0.2 ng/mg range. The chromatogram for this sample is presented in Appendix A.

DISCUSSION

The Philtex plant uses 1,3-butadiene to produce several products, including liquid polybutadiene (Butarez®) by solution polymerization, and sulfolene/sulfolane, and R-11 insecticide by organic synthesis. The company has conducted occasional industrial hygiene monitoring for 1,3-butadiene since 1979. The mean TWA for all job categories was 1.7 ppm; seventy-five percent (15/20) of the TWA exposures are less than 0.1 ppm. However, several relatively high exposures were reported. Three of four personal samples in the control rooms of the multipurpose Butarez®/sulfolene and the packaged product areas were 3 ppm or above. Also, there was a personal TWA exposure of 11.5 ppm in the packaged products area, and 12.6 ppm in an unknown area of the process.

The pumps in 1,3-butadiene service are equipped with single mechanical seals, and the reactor agitators have dual mechanical seals. 1,3-butadiene vapors are contained during transfer from rail car to storage facilities by a vapor recompression system. Exposure to 1,3-butadiene occurs primarily during maintenance operations and quality control (QC) sampling. Pressure cylinders are used in an open-loop mode to collect QC samples.

CONCLUSIONS

Based on a review of the industrial hygiene data provided by Philtex in which 1,3-butadiene exposures exceeded 10 ppm for two job classifications (i.e., packaged products and other), and the presence of 1,3-butadiene in the bulk samples, Philtex will be included as a candidate for an indepth industrial hygiene survey. However, the designation of candidate does not mean that Philtex is certain to be included in the indepth survey sites selected. The purpose of the indepth survey will be to develop an extent of exposure profile for all job descriptions associated with the product and distribution of 1,3-butadiene based products produced at Philtex.

RECOMMENDATIONS

The Philtex plant should consider installation of a closed-loop system for collecting 1,3-butadiene quality control samples; and installation of double mechanical seals in place of single seals, on 1,3-butadiene handling pumps, when replacements are needed. In addition, regular industrial hygiene monitoring 1,3-butadiene should be conducted, especially for personnel in the packaged products area.

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APPENDIX A

CHROMATOGRAM OF PHILTEX BULK SAMPLE OF BUTAREZ

** SPECTRUM DISPLAY/EDIT **

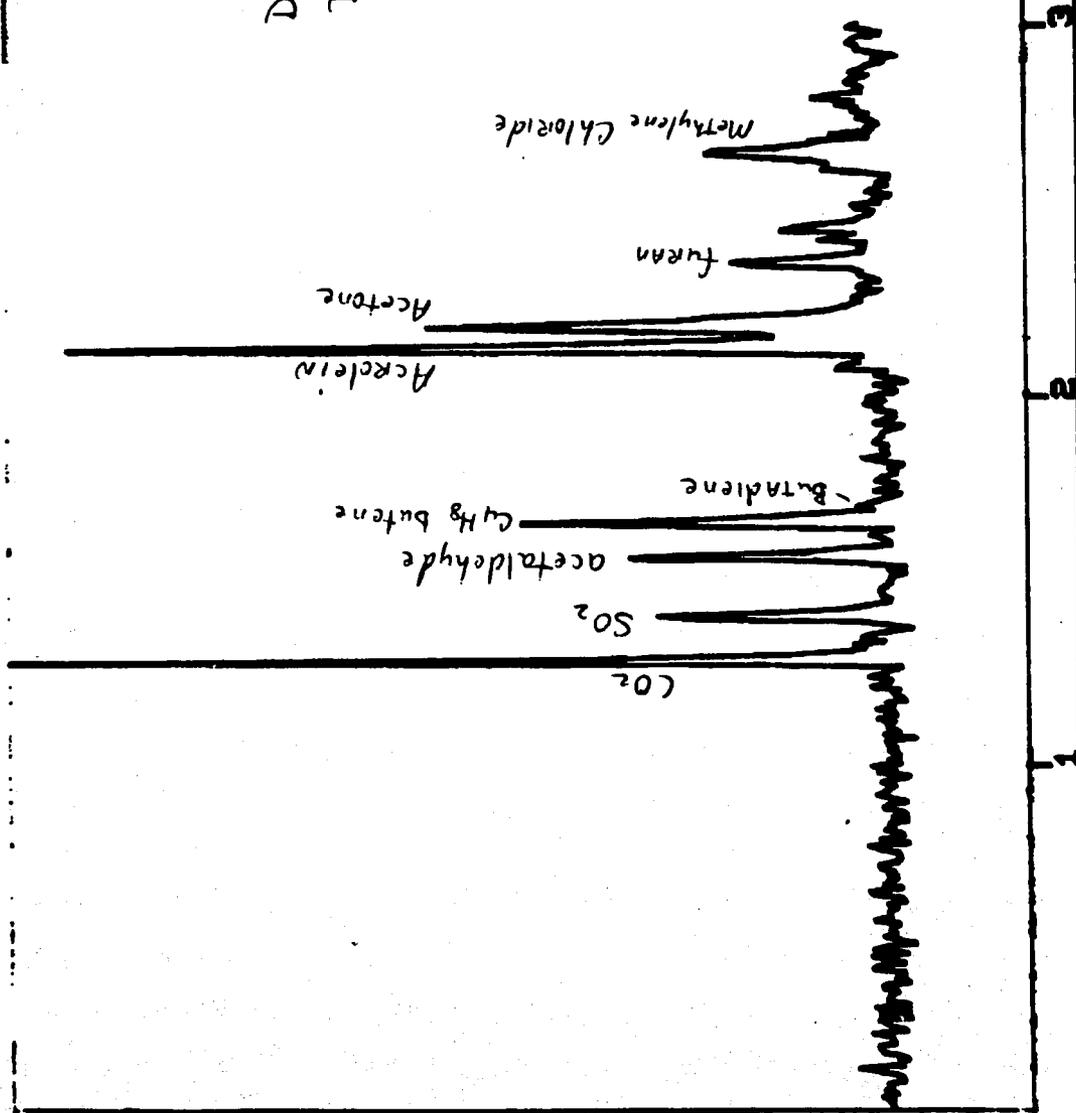
FAN 6866

1ST SC/PQ: 1

X= .50 Y= 1.00

SEQ4971 FAJEN BULK PH2 30DEG DHA
30M DB-1 DUAL COLS SC35-200 10-25-85

DHA/GC/MS
Bulk Ph-2
at 30°C



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