U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
CENTER FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
CINCINNATI, OHIO 45226

HEALTH HAZARD EVALUATION DETERMINATION
REPORT NO. 77-1-426

FIRESTONE SYNTHETIC RUBBER COMPANY
AKRON, OHIO

SEPTEMBER 1977

I. TOXICITY DETERMINATION

A Health Hazard Evaluation was conducted by the National Institute for Occupational Safety and Health (NIOSH) in the Firestone Synthetic Rubber Company, in Akron, Ohio. Sampling was conducted on March 2-4, 1977, to determine concentrations of styrene, butadiene, vinyl cyclohexene, toluene, dimethylpyridine, cyclooctadiene, benzene and vinyl pyridine. Based on the results of that sampling, it was determined that employees in this plant are not exposed to toxic concentrations of those substances. However, one welder is thought to suffer occasionally from metal fume fever based on symptomology.

A previous study concerning leukemia among styrene butadiene rubber workers, conducted by the University of North Carolina, is referenced in Section III of this report. No additional investigation was undertaken on this subject by this Health Hazard Evaluation.

II. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report are currently available upon request from NIOSH, Division of Technical Services, Information and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days the report will be available through the National Technical Information Service (NTIS), Springfield, Virginia. Information regarding its availability through NTIS can be obtained from NIOSH, Publications Office at the Cincinnati address.

Copies of this report have been sent to:

a) Firestone Synthetic Rubber Company, Akron, Ohio
b) Authorized Representative of United Rubber Workers, Local 7
c) United Rubber Workers International Union, Akron, Ohio
d) U.S. Department of Labor - Region V
e) NIOSH - Region V

For the purpose of informing the approximately 250 "affected employees" the employer shall promptly "post" for a period of 30 calendar days the Determination Report in a prominent place(s) near where exposed employees work.

III. INTRODUCTION

Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6), authorizes the Secretary of Health, Education, and Welfare, following a written request by an employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The National Institute for Occupational Safety and Health (NIOSH) received such a request from The United Rubber Workers to evaluate potential hazards to employees in the Firestone Synthetic Rubber Company plant located in Akron, Ohio, resulting from exposure to styrene, butadiene, acrylonitrile and other compounds used in the production of synthetic rubber. The requester stated that workers "have complained of eye injury including double vision, dizziness, nausea, and respiratory difficulty," and that workers were concerned about currently reported leukemia among styrene butadiene rubber (SBR) workers. A study had previously been undertaken by Spirtas, et. al.[5] regarding leukemia among SBR workers at this plant. In a report on that study, they state:

"A case-control study has been performed for deaths from neoplasms of lymphatic and hematopoietic tissues (NLHT; ICDA codes 200-209, 8th Revision) among persons whose work histories show some time of employment in synthetic rubber manufacturing from the Firestone-Akron 1964 cohort. Although the numbers involved are too small to make statements of statistical confidence levels, two findings are noteworthy.

(1) The relative risk estimate using the case-control design is 2.4. Although it is much lower than the relative risk factor of 6.2 yielded by the hybrid design study (Report F.8), this report does strengthen the hypothesis that experience in the synthetic plant may be associated with neoplasms of the lymphatic and hematopoietic tissues (NLHT).

(2) For the NHLT cases, two out of the three leukemia cases with SBR experience also had solvent exposure, while none of the three non-leukemia cases (ICDA codes 200-203) did. This would imply that the risk of SBR exposure, if any, is greater for the group of lymphomas rather than true leukemias."

In view of this previous work, no additional investigation was made on this subject in this survey. This Health Hazard Evaluation was involved primarily with the acute effects of exposure to synthetic rubber workers.

IV. HEALTH HAZARD EVALUATION

A. Process Description

This synthetic rubber plant produces primarily a copolymer of styrene and butadiene. These monomers, shipped into the plant by truck or rail, are pumped from closed storage containers into closed reaction vessels where they are combined with water, initiators, emulsifiers, and other agents. The nature of these minor reactants, as well as temperature, pressure, and reaction time, determines the composition of the resultant latex. The flow of materials as well as the parameters of the reaction are controlled and monitored remotely. When the reaction has reached the desired point, the material is pumped into a recovery tank where the unreacted substances are separated from the product. The unreacted styrene and butadiene are separated and recycled. Most of the product is shipped to consumers as latex in the liquid form so it is pumped to tank cars for shipment. During the entire process, from receipt of raw materials to shipment of finished product, production employees are exposed to styrene, butadiene and other major reactants primarily from leaks in the system. Some minor reactants are mixed in small lots in the solution area for subsequent addition to reaction vessels, and this is a potential exposure to the person handling these materials.

A small amount of the synthetic rubber produced at this plant is prepared for shipment in solid form. This involves coagulating, washing, and drying to obtain a clean solid rubber. These processes are in open vessels and are potential exposures, although there should be little unreacted monomers remaining at this point.

Periodically reaction, stripping, and storage vessels require removal of rubber buildup which accumulates on the inside of these tanks. This is generally accomplished by emptying, flushing and ventilating the container and then entering and physically cutting the caked material with a knife or high pressure water inside the vessel being cleaned. Several men are required to cut and remove the residue, and these men are potentially the highest exposures in the plant.

In addition to the potential exposures listed above, maintenance men are occasionally exposed to styrene and butadiene for short periods during repairs of leaks and routine maintenance, and to other materials when welding or doing these routine activities.

B. Evaluation Design

The initial visit to this plant on December 2, 1976 included a walk-through of all areas of interest conducted by representatives of labor and management. During this visit six high volume samples were taken in various areas using charcoal tubes to adsorb organic contaminants. These samples were subsequently analyzed qualitatively by gas chromatography/mass spectrometry.

A second visit on March 2-4, 1977 was made to collect personal breathing zone samples. As many samples as possible were taken on employees removing rubber buildup inside vessels since these were thought to be the highest exposures. Personal samples were also taken representative of the exposures of employees performing various jobs throughout the plant. Samples were obtained using battery powered personal sampling pumps operating at 100 or 200 ml/min, drawing air from the breathing zone of the employee across charcoal onto which the contaminants were adsorbed. The sampling period was as close to a full 8-hour work shift as possible. All samples were analyzed for six compounds identified by the previous qualitative testing - styrene, butadiene, vinyl cyclohexene, toluene, dimethylpyridine, cyclooctadiene - as well as benzene and vinyl pyridine. Quantitative analysis was by gas chromatography.

In addition to environmental sampling, workers were interviewed privately using non-directed questionnaires to obtain information on work and medical history, as well as medical and physical complaints.

C. Evaluation Criteria

It is the recommendation of NIOSH that occupational exposure to benzene be limited to 1 ppm[1], and occupational exposure to toluene be limited to 100 ppm[2]. Threshold Limit Values (TLV's) established by the American Conference of Governmental Industrial Hygienists (ACGIH)[3] recommended occupational exposure to styrene and butadiene be limited to 100 ppm and 1000 ppm respectively.

Two of the other compounds, vinylcyclohexene and cyclooctadiene, are butadiene dimers and as such might be expected to have similar toxicology, that is, a TLV on the order of 1000 ppm. Allowing even a hundred fold increase in toxicity over the monomer, this would lead to a recommended maximum concentration of 10 ppm.

The remaining two compounds, vinyl pyridine and dimethylpyridine, can be compared to the ACGIH TLV of 5 ppm for pyridine using acute animal toxicity data presented in Patty[4]. Oral LD_{50}'s for rats and mice to these compounds are:

	Oral LD_{50}, g/kg	
	Rats	Mice
Pyridine	0.8-1.6	0.8-1.6
Vinyl Pyridine	0.1-0.2	0.2-0.8
Dimethylpyridine	0.2-0.8	0.2-0.8

A second comparison, also presented in Patty, indicates that a pyridine concentration of 23,200 ppm caused death in 1.5 hours to 100% of the rats exposed, while a vinyl pyridine concentration of 2,000-5,500 ppm had the same effect. Since dimethylpyridine seems to be from 2 to 4 times as toxic as pyridine, an exposure limit of 2 ppm is recommended. Since vinyl pyridine seems to be up to 10 times as toxic as pyridine, an exposure limit of 0.5 ppm is recommended.

D. Evaluation Results

Tables I, II, and III show the results of three days of sampling with the exception of vinyl pyridine and dimethyl pyridine analysis. All samples analyzed for these two compounds were below the limits of detection of available technology. The limit of detection of dimethyl pyridine was approximately 0.5 ppm (compared with a recommended maximum of 2 ppm) and the limit of detection for vinyl pyridine was approximately 5 ppm (compared with a recommended maximum of 0.5 ppm). For this reason no conclusive statement can be made regarding exposure to vinyl pyridine. However, in view of the physical properties of vinyl pyridine, the process in which it is used, and the relative concentrations of other compounds, it is thought that vinyl pyridine exposure is below hazardous levels.

The average measurable styrene concentration was less than 1 ppm with several samples below the 0.05 ppm limit of detection. The average butadiene concentration was approximately 3 ppm with several samples below the 0.1 ppm limit of detection. The average toluene concentration was less than 1 ppm with several samples below the 0.05 ppm limit of detection. The average vinyl cyclohexene concentration was less than 0.5 ppm and approximately two out of every three samples were below the 0.05 ppm limit of detection. All but one benzene sample and five cyclooctadiene samples were below the limits of detection of 0.1 and 0.05 ppm, respectively.

Medical and physical complaints were elicited from workers during informal interviews. Of 65 employees questioned, 37 stated they had no illnesses either work related or non-work related. Ten workers listed illnesses felt not to be work related. Eighteen stated one or more symptom or illness they felt was work related. Among the most common in this group were nausea, irritation, high blood pressure and respiratory problems (two of the three workers stating respiratory problems were smokers) The complaints of nausea and irritation were possibly due to short term, acute exposure to some of the materials used in the workplace. There is no evidence to associate the other complaints with work exposure.

One welder, when asked if he had any medical problems which he felt might be job related, stated that he usually felt nauseated when burning galvanized metal, and "shivered" three or four hours afterward. He further stated that this work was done in a small room with insufficient ventilation. While no atmospheric sampling was done to determine exposure to welding fumes, the conclusion based on symptomology and observation is that this welder suffers from metal fume fever (sometimes called zinc chills) due to acute exposure to the zinc oxide fume produced in this operation.

V. CONCLUSIONS AND RECOMMENDATIONS

With the exception of vinyl pyridine, for which a sensitive analytical method is not available, concentrations of all compounds were shown to be generally far below recommended levels. While a few employees

stated symptoms which might be related to the compounds under study, environmental levels do not lead to this conclusion. One employee, however, did express symptoms which are felt to be due to occupational exposure to zinc oxide.

Adequate exhaust ventilation should be installed in welding areas. The large fans currently in those areas should be removed since they only serve to stir up the welding fumes and dust and contaminate a larger area.

Continued attention should be given to leaks in the production system, and also monitoring for contaminants. Accurate measurements of vinyl pyridine exposure should be made when an analytical method is available.

VI. REFERENCES

1. Revised recommendation for an Occupational Exposure Standard for Benzene, NIOSH, August 1976.

2. Criteria for a Recommended Standard, Occupational Exposure to Toluene, NIOSH, 1973.

3. Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1976, American Conference of Governmental Industrial Hygienists.

4. Patty, F.A., Ed., Industrial Hygiene and Toxicology, Vol. 2, Interscience Pub., 1963.

5. Toxicologic, Industrial Hygiene and Epidemiological Considerations in the Possible Association Between SBR Manufacturing and Neoplasms of Lymphatic and Hematopoietic Tissues, Spirtas, R., Mark Van Ert, John Gamble, Pamela Wolf, Anthony McMichael, Proceedings of NIOSH Styrene Butadiene Briefing, 1976.

VII. AUTHORSHIP AND ACKNOWLEDGMENTS

Report Prepared By:

G. E. Burroughs
Industrial Hygienist
Industrial Hygiene Section
Hazard Evaluations and
Technical Assistance Branch
Cincinnati, Ohio

Acknowledgments

Study Participants:

Kenneth Kronoveter
Industrial Hygienist
Industrial Hygiene Section
Hazard Evaluations and
Technical Assistance Branch
Cincinnati, Ohio

Clifford Moseley
Industrial Hygienist
Industrial Hygiene Section
Hazard Evaluations and
Technical Assistance Branch
Cincinnati, Ohio

Originating Office:

Jerome P. Flesch, Acting Chief
Hazard Evaluations and
Technical Assistance Branch
Cincinnati, Ohio

Report Typed By:

Marie Holthaus, Clerk Typist
Industrial Hygiene Section
Hazard Evaluations and
Technical Assistance Branch
Cincinnati, Ohio

Table I

Results of Full Shift Personal Breathing Zone Samples

Firestone Synthetic Rubber Company
Akron, Ohio

March 2, 1977

Employee Description or Location	Contaminant Concentration (ppm)					
	Styrene	Butadiene	Toluene	Vinyl Cyclohexane	Benzene	Cyclo-Octadiene
2S & 3S control room	*	*	*	*	*	*
Janitor - all areas	*	*	*	*	*	*
In tank 632	0.3	0.4	*	*	*	*
Hauling from tank 526	0.08	0.9	*	*	*	*
In tank 526	0.6	*	*	*	*	*
In tank 632	0.1	0.4	0.1	*	*	*
Oiler-all plant	*	0.5	1.1	*	*	*
In tank 526	0.6	*	*	*	*	*
In tank 526	0.7	0.2	0.06	*	*	*
In tank 632	0.4	0.5	0.2	*	*	*
Pres. relief man	0.4	0.5	0.1	*	*	*
1S control room	0.4	0.5	2.0	0.05	*	*
1S control room	0.5	0.3	2.7	0.06	*	*
1S compressor house	2.3	$\geq$26	0.5	0.2	*	*
Pump house	2.8	$\geq$46	0.4	0.2	*	*
2S compressor house	2.9	18	2.2	1.2	*	*
Packager in drying room	*	*	*	*	*	*
Coalgulator operator	0.06	*	*	*	*	*
Drying room utility man	0.06	0.06	0.03	*	*	*
Drying room checker/fork lift	*	*	*	*	*	*
Coagulator	0.06	*	*	*	*	*

* Indicates concentration below limit of detection

Table II

Results of Full Shift Personal Breathing Zone Samples

Firestone Synthetic Rubber Company
Akron, Ohio

March 3, 1977

Employee Description or Location	Contaminant Concentration (ppm)					
	Styrene	Butadiene	Toluene	Vinyl Cyclohexane	Benzene	Cyclo-Octadiene
In tank 632	0.5	0.4	0.1	0.05	*	*
In tank, #12 stripper	0.6	1.6	0.8	0.07	*	*
In tank, #12 stripper	0.6	2.6	0.8	0.09	*	*
In tank, #12 stripper	0.6	1.7	1.0	0.09	*	*
In tank 526	1.5	*	0.09	0.1	*	*
In tank 526	1.3	*	0.1	0.1	*	*
In tank 632	0.3	0.4	0.2	0.04	*	*
3S janitor	1.2	1.1	0.3	0.09	*	*
1S & 2S janitor	0.4	0.1	0.03	0.02	*	*
In tank 526	0.7	*	*	*	*	*
1S janitor	0.8	0.5	0.08	0.2	*	*
Dryer room janitor	0.2	0.09	0.03	*	*	*
1S & 2S scraper	0.5	0.3	*	*	*	*
1S lab	0.2	0.2	0.06	*	*	*
Rubber hauler-all plant	0.3	0.2	0.08	*	*	*
Rubber hauler-all plant	0.3	0.2	0.09	*	*	*
1S & 2S dish room	0.6	0.09	*	*	*	*
1S control room	0.5	0.7	0.2	*	*	*
#3 & 4 stripper	0.9	0.7	0.4	0.07	*	*
Pressure man-all plant	0.4	0.4	0.2	0.05	*	*
1S compressor	7.1	$\geq$19	0.8	0.5	*	*
Pump house	1.6	$\geq$39	0.1	0.06	*	*
2S compressor	10	5.5	$\geq$12	5.8	*	*
#9 & 10 stripper	0.6	0.3	0.2	0.1	0.7	*
3S latex bldg, loader	0.3	0.2	0.04	*	*	*
1S latex bldg, soln. blender	1.2	1.0	0.1	0.3	*	*
2S control room	0.8	1.0	0.03	*	*	*
3S latex bldg, soln. blender	0.5	0.6	0.1	0.03	*	*
1S soln. area, blender	0.2	*	*	*	*	*

* Indicates concentration below limit of detection

Table III

Results of Full Shift Personal Breathing Zone Samples

Firestone Synthetic Rubber Company
Akron, Ohio

March 4, 1977

Employee Description or Location	Contaminant Concentration (ppm)					
	Styrene	Butadiene	Toluene	Vinyl Cyclohexane	Benzene	Cyclo-Octadiene
Instrument man, All Plant	0.2	0.2	0.05	*	*	*
1S Soln. Area, Painter	0.5	0.1	0.8	*	*	0.2
Electrician, All Plant	0.08	0.2	*	*	*	0.02
Oiler, All Plant	0.3	0.6	*	*	*	*
Pipe Coverer, All Plant	0.06	0.3	*	*	*	*
1S Pipe Fitter	0.1	0.4	0.1	*	*	*
1S Maint. Shop Welder	*	*	*	*	*	*
1S Electrician	0.1	*	*	*	*	*
1S Pipe Fitter	0.4	1.3	0.1	*	*	*
2S & 3S Pipe Fitter	*	*	*	*	*	*
Pipe Coverer, All Plant	0.06	0.2	*	*	*	*
Laborer, All Plant	1.9	0.4	0.3	0.1	*	*
3S Mechanic	0.09	0.06	0.1	*	*	*
Mechanic, All Plant	0.3	*	*	*	*	*
2S Instrument Man	0.1	0.3	*	*	*	*
Mechanic, All Plant	0.2	*	*	*	*	0.05
2S & 3S Pipe Fitter	0.6	0.07	0.3	*	*	0.1
Shipper, All Plant	0.05	0.2	*	*	*	*
1S Pep Area	0.9	0.2	0.03	*	*	0.07
Trackmobile Engineer	0.06	*	*	*	*	*

* Indicates concentration below limit of detection