U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
CENTER FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
CINCINNATI, OHIO 45202

HEALTH HAZARD EVALUATION DETERMINATION
REPORT NO. 74-120- 260

GOODYEAR TIRE & RUBBER COMPANY
GADSDEN, ALABAMA

JANUARY 1976

I. TOXICITY DETERMINATION

It has been determined that a significant number of the workers exposed to emissions from the manufacture of rubber sleeve stock experience moderate symptoms of irritation such as headaches, eye irritation, throat dryness and irritation, or nausea. These symptoms are generally short-lived and usually dissipate within several hours after removal from exposure. No toxic materials could be identified in concentrations considered to be harmful according to the most current hygienic guidelines on either of two days (February 11 and July 23, 1975) of normal operation when air samples were collected by NIOSH industrial hygienists. Both raw materials and thermal decomposition products were investigated in search of possible causative agents; substances evaluated included vinyl chloride, plasticizers, aldehydes, cyanide, butadiene, and acrylonitrile. Due to the brief time of exposure, the relative infrequency with which the operations are run, and the known toxicologic effects of those substances identified during this evaluation, it is believed it is unlikely that workers in the Banbury area (Building 2D) or the extrusion area (Building 9) will experience any long-term adverse health effects as a result of their work exposures. However, in the sleeve curing area (Building 8) where the operations are run continuously, it is not known what, if any, long-term consequences might result from daily and constant irritation. It is recommended that process modification or engineering controls be implemented in this area to reduce smoke and volatile emissions in order to eliminate the symptoms of irritation.

Recommendations have been offered in this report for better control of the smoke and volatile emissions and for minimizing the exposure time of employees to these materials.

II. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report are available upon request from the Hazard Evaluation Services Branch, NIOSH, U. S. Post Office Building, Room 508, Fifth and Walnut Streets, Cincinnati, Ohio 45202. Copies have been sent to:

A. Goodyear Tire and Rubber Company, Gadsden, Alabama
B. Authorized Representative of Employees
C. U. S. Department of Labor - Region IV
D. NIOSH Regional Consultant for OSH - Region IV

For the purposes of informing the approximately 25 "affected employees," the employer will promptly "post" the Determination Report in prominent places near where the affected employees work for a period of 30 calendar days.

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 any 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 an authorized representative of employees regarding the exposure of employees to polyvinyl chloride and plasticizers in the banbury mixing, milling, extrusion, and curing of rubber sleeve stock at the Goodyear Tire and Rubber Company plant at Gadsden, Alabama.

IV. HEALTH HAZARD EVALUATION

A. Plant Process - Conditions of Use

The Goodyear Tire and Rubber Company is engaged in the manufacture of rubber tires and tubes. Rubber sleeves are necessary for providing a surface upon which tires can be built.

The #15 Banbury mixer (located in the Tube Plant, Building 2D, Dept. 232) is the only such mixer used for the formulation and mixing of rubber sleeve stock. On the second floor of the building, three employees per shift (the Banbury operator, the batch builder, and the rubber opener) add the raw ingredients into the top of the Banbury. These raw ingredients include a vinyl chloride resin, three plasticizers, and a nitrile synthetic rubber. The materials are mixed and heated at temperatures up to 325 degrees F. When the batches of sleeve stock exit the bottom of the Banbury on the first floor of the building, large amounts of smoke are emitted. In spite of a local exhaust ventilation system, some of the smoke enters the workroom air. Each batch of sleeve stock is run through a series of rolling mills and then cut into 3x4 ft. sheets and stacked by the cutter man. The cutter man on the adjacent #13 Banbury line and a fork lift trucker in the area are also exposed to the smoke. Rubber sleeve stock is usually run in the Banbury area on only one shift per week, and may be done during either the day or evening shift.

Four employees per shift are exposed at the #13 mill line and 8-inch tuber, a milling and extrusion operation (located in the Flap Department, Building 9, Department 162 D). The mill man loads the sleeve stock which has come from the Banbury area onto a warm-up mill where the stock is heated slightly and milled. The stock is fed automatically in a continuous strip from the warm-up mill to the heating mill where the stock is heated considerably more and further milled. Local exhaust ventilation was installed over the heating mill after the Request for a Health Hazard Evaluation was submitted to NIOSH; a mill man said that the new ventilation had improved the situation considerably.

The stock is fed off the heating mill in a continuous strip to the tuber where it is extruded. One person operates the tuber. The stock is cut into lengths after extrusion, and two bookers lay off the slugs into trays. No chemicals are added in Building 9; the sleeve stock is simply heated and mechanically treated. Reportedly, milling of the sleeve stock is done for only about two hours at a time, but may be performed from one to several times per week.

One operator (cure man) per shift works in the sleeve curing area(Bldg.8). His duties include (1) cutting slugs of previously extruded sleeve stock to the proper length and weight, (2) curling the slugs into a circular shape, (3) placing the slugs into a pre-heating oven at 125 degrees F, (4) inserting the pre-heated slugs into the mold presses and removing the molded sleeves, and (5) inspecting the sleeves. There are about 5 presses in the area which mold the slugs into sleeves. The slugs are molded and compressed by a hydraulic press. The sleeves are cured in the press mold under pressure at 300-400 degrees F for 15 minutes each. The operator removes the sleeves manually from the presses and throws them onto metal tables to cool. No local ventilation is present either at the press or the cooling table. The sleeves smoke for quite some time after removal from the press. This process operates continuously for three shifts per day.

B. Evaluation Design

During the initial plant visit by the NIOSH investigators, it was determined that the adverse symptoms occurred only when sleeve stock, and not any of the other rubber formulations, was processed. The materials which were unique to the sleeve stock were identified as polyvinyl chloride resins, three plasticizers, and a nitrile synthetic rubber. Personal, breathing-zone samples for vinyl chloride monomer and the plasticizers were collected from employees in the Banbury and extrusion areas. Virtually all employees in these two areas on both the day and evening shifts were interviewed privately to determine any symptoms which the employees experience when working with sleeve stock.

Since the environmental samples detected no significant concentrations of vinyl chloride or any of the plasticizers, and since the initial employee interviews revealed that a majority of the employees experienced one or more irritant symptoms, it was decided to investigate thermal decomposition products of the raw materials as well as those of the sleeve stock itself. A sample of the sleeve stock sheets from the Banbury area, a slug from the extrusion area, and a piece of the pure nitrile synthetic rubber were heated to process temperatures by the NIOSH Physical and Chemical Analysis Branch in Cincinnati, Ohio in order to determine the major components of the thermal emissions. A follow-up visit to the plant by NIOSH industrial hygienists was then made to measure airborne concentrations of these emissions in the work environment. A more detailed explanation of these procedures is provided in the Evaluation Methods and Discussion sections of this report.

C. Evaluation Methods

1. Initial Survey Sampling (February 11, 1975)

Prior to the initial NIOSH visit to the plant, the chemical composition of the rubber sleeve stock was obtained from the plant management. The toxicity of each of the components was reviewed, and it was decided to concentrate on those materials which were unique to the sleeve stock. Thus on the initial plant visit, the NIOSH industrial hygienists sampled for vinyl chloride and the three plasticizers used in the sleeve stock. Vinyl chloride and plasticizer vapors were sampled using charcoal air sampling tubes and were analyzed by a gas chromatographic method patterned after that of White et al. 1,2,3. A miniature battery-powered pump was clipped to an employee's belt and drew air at a pre-set rate through a small glass tube containing activated charcoal which was clipped to the employee's shirt as near as possible to the breathing zone. The vinyl chloride and plasticizer vapors were collected by the activated charcoal and later desorbed in a laboratory with carbon disulfide. The desorbed materials were then analyzed using a gas chromatograph equipped with a flame ionization detector.

Aerosols of the plasticizers were collected on cellulose membrane filters having a mean pore diameter of 0.8 micrometer held in a three-piece plastic cassette having a closed face. Air was drawn through the filter at a measured rate by means of a battery operated pump attached to the employee's belt. The collected particulates of the plasticizers were dissolved from the filter with carbon disulfide and analyzed by the same method used for the charcoal tubes.[3]

No vinyl chloride was detected on any of the charcoal tube samples; the limit of analytical detection is 0.2 microgram of vinyl chloride per sample(approximately 0.1ppm . None of the three plasticizers were detected on any of the charcoal tubes. Dibutyl phthalate was the only plasticizer detected on the filters. None of the filters showed more than 0.1 mg of dibutyl phthalate, except for one filter which had approximately 0.2 mg.(approximately 0.4 mg/cu.m.). Those quantities are not thought to be of hygienic significance.

2. Laboratory Tests of Sleeve Stock Emissions

Because no hygienically significant contaminant concentrations could be identified from the samples of the initial survey, laboratory tests were proposed for samples of the raw nitrile rubber and samples of the rubber sleeve stock taken from processing in the banbury area and in the extrusion area. The Physical and Chemical Analysis Branch of NIOSH in Cincinnati, Ohio conducted laboratory tests in which the rubber samples were heated to the same temperatures as in the actual plant process in order to drive off and identify the volatile substances, whether raw materials or thermal decomposition products, which could be causing the irritancy symptoms among the workers.

A large component of the volatile emissions appeared to be aldehydes; these were suspected to be largely those of low molecular weight. It was suspected that some butadiene and acrylonitrile might be liberated from the nitrile rubber; a thermal decomposition product, HCN, which might result from the acrylonitrile component was also suspected. Color changes were produced when the emissions were sampled with colorimetric gas detector tubes for formaldehyde, butadiene, acrylonitrile, and HCN. However, since the specificity of the detector tubes was questionable, the test did not conclusively prove the presence of these substances.

3. Follow-up Survey Sampling (July 23, 1975)

During the follow-up survey, the NIOSH industrial hygienists sampled for thermal break-down products - aldehydes, HCN, butadiene, and acrylonitrile.

Aldehydes in the air were collected by both personal samplers worn by employees in all three plant areas and by a fixed sampler located in the Banbury area. The aldehydes were collected by bubbling the air through a midget impinger containing a chromotropic acid-sulfuric acid absorbing solution. Formaldehyde was measured colorimetrically using a spectrophotometer[4]; other aldehydes were isolated and measured by gas chromatography.

Cyanide was collected by fixed samplers located in the general area of the process machinery in all three affected plant areas. The cyanide was collected by bubbling the air through a midget impinger containing 0.1 M sodium hydroxide absorbing solution. The collected cyanide was quantitated by means of a cyanide ion-specific electrode.[5]

Acrylonitrile and butadiene were collected on charcoal tubes and analyzed by gas chromatography as previously described.[6]

4. Private Employee Interviews

During the initial survey of February 10 and 11, 1975, employees in the Banbury area (Building 2D) and the extrusion area (Building 9) on the day and evening shifts who sometimes work with or in the vicinity of the rubber sleeve stock production were administered a questionnaire privately by NIOSH industrial hygienists to find out if the employees felt that they might have health problems related to their work. Employees were also asked whether they had experienced symptoms in the past when working with sleeve stock, and if so, what the symptoms were, when they occurred, and when they went away.

During the follow-up visit of July 22 and 23, the employees in the Banbury area (Bldg. 2D) and the curing area (Bldg. 8) who wore personal samplers were given a short questionnaire before and after the work shift to evaluate what symptoms might have developed during the shift as a result of exposure to sleeve stock emissions.

D. Evaluation Criteria

The following discussion describes the toxicologic effects that may occur in workers exposed to the chemical substances evaluated during this study. The effects are described so that workers may know the symptoms and potential health consequences of excessive exposure. The effects described here depend upon a number of factors such as airborne concentrations, length of exposure, individual susceptibility and possibly additive or synergistic effects of two or more substances in combination. If the airborne concentrations of these substances are maintained below the levels indicated below, it is believed that long-term adverse health effects will not occur.

Vinyl Chloride

Vinyl chloride is a colorless, odorless gas at low concentrations in air. It is used as a basic chemical raw material in the production of polyvinyl chloride plastic resin which has many commercial uses. The resin itself is not thought to be toxic; rather it is the unreacted vinyl chloride gas which is of concern. Vinyl chloride has been identified as a causative agent in the development of angiosarcoma, a rare and fatal form of liver cancer. NIOSH recommends that no worker be exposed to measurable amounts of vinyl chloride gas, since no safe level is known.[7] The current OSHA standard for vinyl chloride is 1 ppm.[8]

Dibutyl Phthalate

Dibutyl phthalate is a common plasticizer used in the rubber industry. It is considered to be of a low order of toxicity. Phthalate esters closely related to dibutyl can be somewhat irritating to the eyes and nose.[9] The American Conference of Governmental Industrial Hygienists (ACGIH) recommends that no worker be exposed in excess of 5 mg/m^3 as an 8-hour-average airborne exposure.[10] The OSHA standard is the same.

Acrylonitrile

Acrylonitrile is an ingredient in the production of synthetic nitrile rubber. Exposure to very high concentrations of acrylonitrile has been known to cause such symptoms as weakness, light-headedness, headache, and nausea.[11] Nitriles also act as primary irritants on the skin and eyes. The ACGIH recommends a TLV of 20 ppm.[10] The OSHA standard is the same.[12]

Butadiene

Butadiene is an ingredient in the production of synthetic nitrile rubber. It may be irritating to skin and mucous membrane and narcotic in very high concentrations.[11] However, it is generally considered to be only slightly toxic.[9] The ACGIH recommendation[10] and the OSHA standard[12] are 1,000 ppm.

Cyanides

Cyanides may be produced by the breakdown of acrylonitrile or nitrile rubber. Very high concentrations, when inhaled, can cause immediate collapse, cessation of respiration, and death. Lower concentrations may produce early symptoms such as weakness, headaches, confusion, and occasional nausea and vomiting.[13] The ACGIH recommended limit[10] and OSHA standard[12] are 5 mg/m^3.

Formaldehyde

Formaldehyde may be produced by thermal breakdown of many organic substances. It is irritating to the eyes, respiratory tract, and skin.[9] The ACGIH recommends a ceiling value of 2 ppm[10]; the OSHA 8-hour-average standard is 3 ppm.[12]

E. Evaluation Results and Discussion

1. Employee Interviews

The results of the employee interviews during the initial plant visit on February 11, 1975, are summarized in Table 1. This table reports symptoms which employees experienced on February 11 or any prior day when working with the rubber sleeve stock production. Of particular interest is that 6 out of 10 employees in the Banbury area had experienced headaches during sleeve stock production; all eight employees in the extrusion area associated burning or irritated eyes with sleeve stock production.

Three employees were given pre- and post-shift questionnaires on July 23, 1975. Results of these questionnaires indicated that during the workshift, one employee developed dry throat, burning eyes, running nose, and headache. Another employee experienced burning and tearing of the eyes. The third employee showed no change in pre- and post-shift symptoms.

2. Results of Environmental Sampling

Sampling results from the initial plant survey revealed no detectable levels (less than 0.2 microgram per sample) of vinyl chloride gas and only trace quantities of dibutyl phthalate on a couple of filter samples.

Aldehyde samples were collected on the follow-up survey. No low molecular weight aldehydes of the C2 through C5 group of compounds were detected. Formaldehyde was measured in 3 of 5 samples (Table 2), but the the highest measured concentration was only about 25% of the ACGIH 8 hr.- TLV. This level is believed to be sufficiently low to prevent respiratory injury, but may not prevent symptoms of irritation in all workers. A fabrics industry study reported irritation of mucous membranes among workers exposed to concentrations generally ranging from 0.3 to 2.7 ppm with an average of 0.68 ppm.[9]

Results of the cyanide samples are given in Table 3. The levels appear to be insignificant. Table 4 shows the levels of free acrylonitrile

and butadiene measured on July 23; these levels also appear insignificant in comparison with hygienic standards.

F. Conclusions

Due to the brief time of exposure, the relative frequency with which the operations are run, and the known toxicologic effects of those substances identified during this evaluation, it is believed it is unlikely that the workers in the Banbury area (Bldg. 2D) or the extrusion area (Bldg. 9) will experience any long-term adverse health effects as a result of their work exposures. However, due to the prevalence of symptoms of irritation among the workers, and especially in the sleeve curing area (Bldg. 8) where the operations are continuous and exposure is chronic, additional efforts should be made to reduce thermal emissions from sleeve stock production in the workroom air.

G. Recommendations

1. The local exhaust system at the bottom of the #15 Banbury mixer was judged to be insufficient in its efficiency of collection of volatile material from the rubber sleeve stock. This was indicated by the drift of visible smoke across the room in the general direction of the #13 Banbury. The inlet of the hood is too far from the point of generation of the smoke to provide sufficient capture velocity at the point of smoke generation. The cross current in the room aggrevates the situation. An attempt should be made to relocate the exhaust hood slot closer to the point of smoke generation and shield or partially enclose the bottom of the Banbury to improve smoke and fume capture.

2. The NIOSH industrial hygienists discovered from private interviews with employees that due to the coding system which Goodyear uses to conceal the identity of its chemical formulations, the employees who work at the top of the Banbury do not know the chemicals to which they are exposed or the potential consequences of excessive exposure to their health. NIOSH recommends that workers be informed of all toxic substances to which they are exposed, the possible toxic effects of overexposure, and the methods of engineering control, protective equipment, and work practices used to minimize such exposure.

3. A system of administrative controls is recommended for the employees in the Banbury and extrusion areas. The sleeve stock production should be scheduled in such a way as to regularly alternate between work shift groupings so that the exposure to sleeve stock emissions is distributed to a larger population of workers but the length and frequency of exposure in each group is minimized.

4. Due to the continuous nature of the process of sleeve production in the curing area, the company is encouraged to consider the installation of additional local exhaust hoods to remove smoke at the locations where newly molded sleeves are cooled to provide relief from daily and continous eye irritation of the cure man.

5. The company should be encouraged to continue to seek substitutes for vinyl chloride resins and perhaps nitrile synthetic rubber as well which would result in less toxic and irritating emissions from the manufacture of sleeves.

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Table 1

Historical Symptomatology in Exposed Employees

	Work Area			
	Tube Plant, Banbury Area	Bldg. 9, Milling & Extrusion	Bldg. 8 Sleeve Curing	Total
No. of Employees Questioned	10	8	1	19
No. of Employees who associated sleeve stock with these symptoms:				
(1) Headache	6	1	0	7
(2) Nausea	3	1	0	4
(3) Burning or irritated eyes	4	8	1	13
(4) Burning Throat	3	2	0	5
(5) Dry Throat	2	1	0	3
(6) Burning Nose	2	0	0	2
7) Cough	1	0	0	1
(8) Lightheadedness	1	0	0	1
(9) Drowsiness	1	0	0	1

Table 2

Results of Environmental Sampling for Formaldehyde

Goodyear Tire and Rubber Co.
Gadsden, Alabama
July 23, 1975

Sample No.	Operator/Location	Sample Volume (Liters)	Sampling Period	Formaldehyde Concentration (PPM)	Type of Sample
I-1	Curing Man/Bldg. 8	425	7:20 am - 2:25 pm	*N.D.	BZ
I-3	Mill Man/Bldg. 9	121	12:32 pm - 2:33 pm	0.55	BZ
I-4	Tuber Operator/Bldg. 9	120	12:35 pm - 2:35 pm	0.15	BZ
I-5	Banbury Opr./Banbury Area	108	7:37 am - 9:25 am	N.D.	BZ
I-7	Area Sample At Top of Banbury	221	9:47 am - 1:28 pm	0.01	GA

PPM = Parts of vapor or gas per million parts of contaminated air by volume.

BZ indicates that the measured concentration represents an average contaminant concentration for the sampling period obtained by a personal, breathing-zone sampler worn by the employee.

GA indicates that the measured concentration represents an average contaminant concentration for the sampling period obtained by a fixed sampler located in the general area of a machine or operation.

*N.D. means "none detected".
For formaldehyde, the lower limit of detection by the analytical method was 1.2 microgram per sample.

Environmental Criterion: 2 ppm of formaldehyde as an 8-hour-average limit recommended by the American Conference of Government Industrial Hygienists (ACGIH) as a TLV for 1974.

Table

Results of Environmental Sampling for Cyanide
(General Area Samples)

Goodyear Tire and Rubber Co.
Gadsden, Alabama
July 23, 1975

Sample No.	Operation/Location	Sample Volume (Liters)	Sampling Period	Cyanide Concentration (Mg/m^3)
I-2	Area sample, beside mill, Bldg. 9	161	11:51 am - 2:32 pm	<0.02
I-8	Area sample, bottom of banbury	339	7:55 am - 1:34 pm	<0.01
I-9	Area sample, Curing Press #4, Bldg. 8	420	7:25 am - 2:25 pm	<0.01
I-10	Area sample, top of banbury	345	7:43 am - 1:28 pm	<0.01
I-11	Area sample, beside extruder, Bldg. 9	162	11:55 am - 2:37 pm	<0.02

Mg/m^3 means milligrams of cyanide per cubic meter of air sampled.

< means "less than".

Environmental criterion: 5 mg/m^3 of cyanide as an 8-hour-average limit recommended by ACGIH as a TLV for 1974.

Table 4

Results of Environmental Sampling for Butadiene and Acrylonitrile

Goodyear Tire and Rubber Co.
Gadsden, Alabama

July 23, 1975

Sample No.	Operation/Location	Contaminant	Sample Volume (Liters)	Sampling Period	Contaminant Concentration (PPM)
CT-1	Area Sample, Bottom of banbury	Butadiene	61.2	7:55 am - 12:53 pm	1.8
		Acrylonitrile			0.15
CT-2	Personal Sample, Cutter Man Bottom of Banbury	Butadiene	19.6	7:51 am - 1:37 pm	2.1
		Acrylonitrile			*N.D.

PPM means parts of vapor or gas per million parts of contaminated air by volume.

*N.D. means "none detected".
For acrylonitrile the lower limit of detection by the method used was 0.005 mg per sample.

Environmental Criteria: Guideline Limits for Airborne Exposures		
Substance	Source of Criterion	8-Hr. Avg. Limit
Butadiene	ACGIH TLV, 1974	1,000 ppm
Acrylonitrile	ACGIH TLV, 1974	20 ppm