

HEALTH HAZARD EVALUATION REPORT 72-86-38  
HAZARD EVALUATION SERVICES BRANCH  
DIVISION OF TECHNICAL SERVICES

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Denver, Colorado

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

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GATES RUBBER COMPANY  
DENVER, COLORADO

APRIL 1973

I. SUMMARY DETERMINATION

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 to evaluate the potential hazards associated with the use of unknown chemical hazards in the braided hose department of the Gates Rubber Company, Denver, Colorado.

A NIOSH Industrial Hygienist conducted an observational survey on November 22, 1972. It was concluded, based upon information obtained at that time, that the potential hazards to which workers were exposed were numerous. Approximately 540 different formulations are used in this department, each composed of different chemicals. Chemicals that were used during the environmental phases of this investigation are listed below with their established health standards where such exist (Federal Register, Vol. 37, §1910.93, October 18, 1972).

<u>Substance</u>	<u>Standard Level or Concentration</u>
Styrene	100 ppm (TWA)
Toluene	200 ppm (TWA)
Toluene-2, 4-diisocyanate	C - 0.02
Formaldehyde	3 ppm (TWA)
Butadiene	1000 ppm (TWA)
Methyl chloroform	350 ppm (TWA)

ppm - parts of vapor or gas per million parts of contaminated air by volume

TWA - eight-hour time-weighted average

C - ceiling; this value shall at no time be exceeded

A medical evaluation was conducted on November 7, 1972. Nineteen (19) employees were interviewed. The following symptoms were reported by the stated number of employees: Sore throat, 7; burning or itching eyes, 12; cough, 7; tiredness, 8; runny nose, 7; numbness or tingling sensations, 7; and redness of eyes, 8.

Environmental surveys were conducted on November 22, 1972; January 10, 1973; and February 26, 1973. No exposures were found to exceed established health standards when expressed on an estimated eight-hour time-weighted basis.

The following chemicals were not toxic at the concentration found at the time of the environmental surveys: Styrene, toluene, toluene-2, 4-diisocyanate, vinyl pyridine, formaldehyde, butadiene, methyl chloroform, and resorcinol. Vinyl pyridine and resorcinol were not listed in the Summary Determination under standards, since there are no existing standards for these two substances. The potential of toxic conditions to exist in the future is possible, since at the time of the initial visit significant medical symptomatology was reported in employee interviews. Continued variation of formulations in use may require the submission of an additional hazard evaluation request.

Copies of this Summary Determination, as well as the full report of the evaluation, are available from the Hazard Evaluation Services Branch, NIOSH, Cincinnati, Ohio 45202. Copies of both have been sent to:

- a) Gates Rubber Company
- b) Authorized Representative of Employees
- c) U.S. Department of Labor - Region VIII

For purposes of informing the approximately 70 "affected employees," the employer will promptly "post" the Summary Determination in a prominent place near where affected employees work for a period of 30 calendar days.

II. 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.

This health hazard evaluation was received from the United Rubber Workers Union, Denver, Colorado. It concerns employees' exposure to numerous chemical hazards in the braided hose department, Gates Rubber Company, Denver, Colorado.

III. BACKGROUND HAZARD INFORMATION

A. Standards

The Occupational Health Standards as promulgated by the U.S. Department of Labor (Federal Register, Vol. 37, §1910.93, October 18, 1972) are given below for those potentially toxic substances identified in this hazard evaluation.

<u>Substance</u>	<u>Standard Level or Concentration</u>
Styrene	100 ppm (TWA)
Toluene	200 ppm (TWA)
Toluene-2, 4-diisocyanate	C - 0.02
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ppm - parts of vapor or gas per million parts of contaminated air by volume

TWA - eight-hour time-weighted average

C - ceiling; this value shall at no time be exceeded

Vinyl pyridine and resorcinol were also used during various phases of this investigation. However, there are no existing standards for these two substances.

According to plant management, many of the substances listed under the standards section were in use during the environmental phase of this investigation. Bulk samples of solutions supposedly containing these substances were collected in vials and sent to the Western Area Occupational Health Laboratory (WAOHL) for qualitative analyses.

## B. Toxic Effects

### 1. Styrene and Butadiene

Synthetic rubbers are complex organic mixtures to which a wide variety of pigments, antioxidants, accelerators, peptizers, and other chemicals are commonly added. While natural rubber latex is rarely a skin sensitizer, synthetic rubber and many of the additives frequently cause dermatitis even in the fully cured state. Styrene and butadiene, co-polymers of the GR-S latex group, are utilized to contribute hardness, strength, and chemical resistance to various cords and threads. These contain up to 55% styrene and require vulcanization to develop these useful properties. Unreacted styrene monomer currently has a standard of 100 ppm. When concentrations exceed 200 ppm, nasal and eye irritation occur. Burning or tingling sensations are also noted on skin surfaces. Higher concentrations have effects on the central nervous system, including abnormal reflexes, decreased dexterity and coordination, nausea, and headaches. The feeling of inebriation may also be experienced.

### 2. Toluene

Because of toluene's wide industrial use and chemical similarity to benzene, literature has recorded numerous investigations of the toxic effects of toluene. From the standpoint of chronic poisoning, toluene does not cause the severe injury to bone marrow characteristic of benzene poisoning. Some of the recorded investigations of toluene's toxic effect are apparently due to the benzene impurity in the toluene used. The most recent industrial experience does not provide evidence for a standard of safe exposure below 200 ppm (TWA).

### 3. Toluene-2, 4-diisocyanate (TDI)

This is best known for its ability to cause pulmonary sensitization resulting in an asthmatic syndrome. Studies in animals have shown that this isocyanate has a low oral toxicity (approximate lethal dose is 5.8g/kg). The capacity of TDI to produce allergic sensitization of the respiratory tract in man is its most serious toxicologic action and the one which determines the magnitude of the current standard. Respiratory involvement from repeated exposure to TDI has been demonstrated at 0.1 ppm. Respiratory effects should be minimum at levels of 0.01 to 0.03 ppm.<sup>1</sup>

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<sup>1</sup> American Conference of Governmental Industrial Hygienists, Documentation of the Threshold Limit Values for Substances in Workroom Air, 1971, page 260.

#### 4. Vinyl pyridine

Vinyl pyridines are reactive liquid pyridine derivatives with the vinyl group at the 2, 3, or 4 position. They may be condensed to form polyvinyl pyridine polymers and can combine with styrene-butadiene combinations to form terpolymer rubbers used in rubber textile bonding. The vinyl pyridines are absorbed by all routes. They can cause both skin burns and sensitization. Brief exposures to unknown concentrations have been reported to cause nasal, throat, and eye irritation in addition to headache, nausea, nervousness, and anorexia. No current Federal standard is in effect for vinyl pyridine.

#### 5. Formaldehyde

Formaldehyde is well known for its ability to cause irritation of the respiratory tract and mucosal membranes. Exposure to formaldehyde at concentrations of 5 ppm may produce itching eyes, dry and sore throat, disturbed sleep, and an unusual thirst on awakening. The standard of 3 ppm should prevent any adverse effects, except to those people who are hypersensitive to formaldehyde.

#### 6. Methyl chloroform

Methyl chloroform is a widely used solvent. Exposure to this substance produces a functional depression of the central nervous system typical for anesthetic agents. The earliest symptoms are dizziness and lassitude, which rapidly progress to unconsciousness. Chronic exposure has a minimal potential for producing liver or kidney injury. The most recent health standard of 350 ppm (TWA) should be tolerated without any serious ill effects. The apparent low toxicity of methyl chloroform is due to its inertness in the body.

#### 7. Resorcinol

Resorcinol is readily absorbed from the gastro intestinal tract and through the skin. The compound is excreted in the urine as other phenols in a free state and conjugated with hexuronic, sulfuric, and other acids. Resorcinol causes direct local damage by irritation of the mucosal membranes and may also cause systemic effects. It is doubtful that this compound was being used during the environmental phases of this investigation.

#### IV. HEALTH HAZARD EVALUATION

##### A. Observational Survey

An initial hazard evaluation survey of the braided hose department, Gates Rubber Company, Denver, Colorado, was made on November 22, 1972, by Industrial Hygienists Bobby J. Gunter, Ph.D., and David J. Burton. The function of NIOSH and its relation to Section 20(a)(6) of the Occupational Safety and Health Act of 1970 and the purpose of the visit were explained to Union Representative, and Management Representative. A walk-through survey was made of the braided hose department, and bulk samples were collected. These bulk samples were solutions of chemicals used to treat fibers that are used in the manufacture of braided hose.

##### Plant Process: Conditions of Use

The braided hose department employing approximately 70 people occupies three floors of a brick building with wooden floors. Identical solutions are used on each floor, with frequent changes in the formulations. The process consists of applying a braided polyester thread reinforcement to various types of unvulcanized rubber hose. Braiding machines weave the thread around the hose and most of the work force are engaged in operating these machines. The threads are passed through dip tanks containing the previously-mentioned chemicals prior to winding on spools and utilization by the braider. The composition of these dips is varied depending upon the characteristics desired in the finished hose.

Approximately 2,200 different types of hose are produced and usually in relatively small lots. This makes the task of identifying the exact composition of an individual dip very difficult, since hose lots are identified by serial number; and these are seldom remembered by employees.

Exposure to the employees would result from vaporization of chemicals coming from the fibers that have been pre-treated. The chemical containers, where the fibers pass through and are coated with the numerous formulations, are closed and are located on the floor. Any exposure coming from the tanks or from the treated fibers would have been collected on the breathing zone samples of the workers involved, since these workers have to replenish the supply of solutions in the chemical containers.

##### B. Environmental Evaluation

On November 22, 1972, environmental samples were collected during a typical work situation. All three floors of the braided hose department were in full operation. Breathing zone samples were collected, using charcoal tubes and MSA Model G personal pumps. Samples were collected for approximately ten minutes on each worker, and in most cases several samples were collected on each worker. Plant management provided a list of chemicals used during this sampling. The chemicals in use at this time were styrene, vinyl pyridine, and butadiene. All charcoal tubes were forwarded to the Salt Lake City laboratory for analyses by gas chromatographic techniques. All results were negative.

A second series of samples was collected on January 10, 1973. These samples were analyzed for 1, 3-butadiene, styrene, isocyanates, caustic soda, formaldehyde, resorcinol, and vinyl pyridine. Management stated that these were the chemicals that were in use during this sampling period. These samples were also forwarded to Salt Lake City for analyses. Laboratory results were all negative.

A third series of samples was collected on February 26, 1973. These samples were analyzed for styrene, toluene-2, 4-diisocyanate, vinyl pyridine, methyl chloroform, resorcinol, formaldehyde, and butadiene. The only chemical found in these samples was methyl chloroform. Concentrations ranged from 17.5 ppm to 179 ppm. None of these concentrations were over the eight-hour time-weighted average health standard of 350 ppm.

During all phases of the environmental investigation, windows were open on the second and third floors of the braided hose department, allowing air to circulate throughout the area. This was the only apparent ventilation in any of the three floors.

In this section when laboratory results are referred to as negative, this means that samples were below the sensitivity as given below. This may also be referred to in various sections as none-detected (N/D).

<u>Substance</u>	<u>Sensitivity</u>
Styrene	2 mg/sample
Toluene	2 mg/sample
Toluene-2, 4-diisocyanate	0.2 mg/sample
Formaldehyde	0.2 mg/sample
Butadiene	5 mg/sample
Methyl chloroform	12 mg/sample

All environmental samples had concentrations well below the established health standards as promulgated by the U.S. Department of Labor (Federal Register, Vol. 37, §1910.93, October 18, 1972).

A total of 26 samples were taken during three different environmental evaluations, with a total of approximately 100 analyses performed on these samples. Results of these evaluations are given in Table I. The large number of samples with none-detected concentrations is valid, since several of these samples were run for over thirty minutes.

It is the Industrial Hygienist's opinion that during all three environmental evaluations, there was not a hazardous chemical exposure to any of the employees that were monitored.

Additional environmental evaluation in this department could possibly show that a health hazard exists, since approximately 540 different chemicals are used. It would always be possible for these to be used in concentrations that could prove to be a potential hazard. During the environmental evaluations, the Industrial Hygienist did not receive any complaints from workers that were monitored. During this evaluation, controls were adequate, since no hazardous concentration was found.

### C. Medical Evaluation

A medical evaluation was conducted on November 7, 1972 by James B. Lucas, M.D., NIOSH physician. Nineteen employees were interviewed and, in a number of instances, examined. Seventeen women representing a cross section of those working on both the first and second shifts completed a medical screening questionnaire (copy in Appendix). This was necessitated by a very brief interview time available to obtain histories. Conversation was completely impossible in the actual work area because of noise. Workers were reluctant to leave the area during the shift, since they are paid on a piece work basis. Therefore, workers were asked to complete the questionnaire and then to elaborate on symptoms in the interval between shifts.

Two persons were interviewed in the Union facility, and these case histories follow in detail because they differ somewhat from the questionnaire data.

1. Case 1 ( ) This 56-year old woman has over twenty years of service with the company. Her problem began in 1967 following a change in the process in which new dip mixtures were introduced as substitutes for benzene. Initially, she noted a foreign body sensation in her left eye. This was subsequently diagnosed as a corneal ulceration. Since then, five other bouts of corneal ulceration have occurred as documented by her medical records. The same eye is not always involved, and the ophthalmologist's records do not suggest a cause. She very definitely relates the onset to the use of certain "new" dips which are periodically tried on an experimental basis. She relates the onset of burning and other symptoms of impending ulceration to exposure times as short as five minutes. The accuracy of these observations is difficult to judge.

Corneal ulcer is a condition of diverse causation. The most common primary causes are bacterial infections following mechanical trauma or complicating foreign bodies lodging on the cornea. They may also accompany various other ocular diseases; for example, trachoma,

dacryocystitis, or other acute infectious diseases. In addition, disturbances in corneal nutrition secondary to keratomalacia, glaucoma, and corneal drying due to defective closure of the lids are occasionally responsible. While chemical exposure might induce sufficient trauma to predispose a person to corneal ulceration, it is difficult to explain effects to only one eye at a time or to only one individual so exposed.

2. Case 2 ( ) This 30-year old woman worked for only five months prior to termination as unsuitable for the job. She was asymptomatic during her first three months of employment. In early July she developed an inflammatory eye condition diagnosed as "viral or allergic conjunctivitis" on July 5. On July 24 edema of the lids developed which spread to her face and neck. The diagnosis of urticaria, possibly due to previously prescribed medication (sulfacetamide), was made. Appropriate drugs were prescribed which largely controlled the symptoms. On July 29 subcutaneous nodules developed on the left arm and sole. These were also felt to be an allergic reaction. Medications were discontinued. Two days later the urticaria returned. On August 10 a change in work area was prescribed; and during the next week, symptoms disappeared and medications were tapered off. On August 18 eyelid swelling promptly returned (within four hours) when she was reassigned to the braided hose area. Following this, she was discharged by the company. This patient has no previous episodes of urticaria and has no history of other allergic manifestations.

Urticaria can be related to an extremely wide variety of causes. Foods, drugs, chemicals, pollens, fungi, parasites, systemic illnesses, psychogenic problems, genetic predisposition, and even physical factors such as light and pressure have all been implicated in individual cases. Proof of causation can only be established by history and the repeated reoccurrence of symptoms on re-exposure to the suspected agent. In practice, the etiology is never discovered in some 70% of the cases. As previously mentioned, formaldehyde is known to be a cause, and it is entirely possible that any of the other substances in this work environment could be responsible.

As a result of the questionnaire, it was learned that two other women also have urticaria. Three cases occurring in such a small population is surely far more than would be expected on the basis of chance, and it is probable that one or more of the substances in use are responsible.

#### Summary of Results:

Of the seventeen persons completing the questionnaire, all indicated one or more symptoms felt to be related to the job. Significant responses were obtained to the following symptoms: Sore throat (7), burning or itching eyes (12), cough (7), tiredness (8), "runny nose" (7), numbness or tingling sensations (7), and redness of eyes (8). The number of responses to the other symptoms listed were

probably too few to be meaningful, except for hives (urticaria) as previously discussed. Interestingly, two women also mentioned sensations of intoxication, described as "being on a cheap drunk" when interviewed.

From these histories, it was also learned that only certain lots of chemicals used to treat fibers that are used in the production of braided hose were responsible for the symptomatology. Thus, the symptoms were basically sporadic and not continual. The difficulty in identifying the lots in question has already been mentioned. One employee was able to identify several lots which produced irritation. These contained unusually high concentrations of vinyl pyridine and resorcinol, each approximating 15%. These lots were apparently experimental and are said to be no longer used.

One case of subsiding dermatitis was also mentioned, and nearly half the employees relate similar problems in the past. These cases have no particular time sequence and represent either allergic or primary irritant reactions apparently due to a variety of causative compounds. All have responded to appropriate therapy and protective measures.

There is sufficient evidence to conclude that a hazard responsible for upper respiratory tract and eye irritation exists. This hazard is, however, sporadic and associated only with dips of certain composition. The substances most likely implicated are styrene, butadiene, vinyl pyridine, and possibly resorcinol. It also seems entirely possible that a single irritating substance may not be responsible but, rather, that an additive or even potentiative effect among several of the agents in use may be causal.

#### D. Conclusions

From the environmental sampling, it is well documented that levels of exposure were well below those known to affect the health of the workers in the braided hose department. Since environmental samples were taken during three different time periods and no exposure documented, it is concluded that a health hazard does not exist under work situations that were evaluated during the environmental survey.

The potential of toxic conditions to exist in the future is possible, since at the time of the initial visit significant medical symptomatology was reported in employee interviews. Continued variation of formulations in use may require the submission of an additional hazard evaluation request.

V. RECOMMENDATIONS

1. A record of all formulations used in the braided hose department should be readily available to employees. Employees should be informed if a hazardous chemical is being used in the dip tanks, and proper protective equipment should be provided.
2. An additional Request for Health Hazard Evaluation should be filled out if outbreaks of complaints occur resulting from an occupational exposure to chemicals used in this department so that immediate steps can be taken to measure and identify suspected substances.
3. Employees should be encouraged to report immediately to the Gates Clinic when they have been overexposed to a hazardous chemical or physical agent.
4. A thorough industrial hygiene evaluation of all chemicals used in this department should be made by the Gates Rubber Company, either by their staff people or by consultants, so that when hazardous formulations are used, proper protective procedures may be put into effect.

TABLE I

LABORATORY RESULTS OF ALL ENVIRONMENTAL SAMPLING  
Gates Rubber Company -- Braided Hose Department

Sample No.	Date	Styrene	Toluene	Toluene-2, 4-diiso-cyanate	Vinyl Pyridine	Formaldehyde	Butadiene	Methyl Chloroform	Resorcinol
1	11/22/72	N/D			N/D	N/D	N/D		N/D
2	"	N/D			N/D	N/D	N/D		N/D
3	"	N/D			N/D	N/D	N/D		N/D
4	"	N/D			N/D	N/D	N/D		N/D
5	1/10/73	N/D			N/D	N/D	N/D		N/D
6	"	N/D			N/D	N/D	N/D		N/D
7	"	N/D			N/D	N/D	N/D		N/D
8	"	N/D			N/D	N/D	N/D		N/D
9	"	N/D			N/D	N/D	N/D		N/D
10	"	N/D			N/D	N/D	N/D		N/D
11	"	N/D			N/D	N/D	N/D		N/D
12	"	N/D			N/D	N/D	N/D		N/D
13	"	N/D			N/D	N/D	N/D		N/D
14	"	N/D			N/D	N/D	N/D		N/D
15 (blank)	"	N/D			N/D	N/D	N/D		N/D
16 (blank)	"	N/D			N/D	N/D	N/D		N/D

TABLE I

LABORATORY RESULTS OF ALL ENVIRONMENTAL SAMPLING  
Gates Rubber Company -- Braided Hose Department

Sample No.	Date	Styrene	Toluene	Toluene-2, 4-diisocyanate	Vinyl Pyridine	Formaldehyde	Butadiene	Methyl Chloroform	Resorcinol
17 (blank)	1/10/73	N/D			N/D	N/D	N/D		N/D
18	2/26/73	N/D	N/D	N/D	N/D			58.0 ppm	N/D
19	"	N/D	N/D	N/D	N/D			179.0 ppm	N/D
20	"	N/D	N/D	N/D	N/D			52.0 ppm	N/D
21	"	N/D	N/D	N/D	N/D			18.0 ppm	N/D
22	"	N/D	N/D	N/D	N/D			46.0 ppm	N/D
23	"	N/D	N/D	N/D	N/D			<17.5 ppm	N/D
24	"	N/D	N/D	N/D	N/D			N/D	N/D
25 (blank)	"	N/D	N/D	N/D	N/D			N/D	N/D
26 (blank)	"	N/D	N/D	N/D	N/D			N/D	N/D

N/D - none detected (at sensitivity of laboratory analytical instruments)

## NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH

Confidential Health Questionnaire

Name \_\_\_\_\_ Age \_\_\_\_\_

Home Address \_\_\_\_\_ (Street) \_\_\_\_\_ (City) \_\_\_\_\_ (ZIP) \_\_\_\_\_

Duration of employment at Gates? \_\_\_\_\_ years

How long have you worked in area 21? \_\_\_\_\_ years

Which floor do you work on? \_\_\_\_\_

Which shift do you work? \_\_\_\_\_

Job Title \_\_\_\_\_

Please check any of the following problems which you have had during the past year and that you feel may be related to your job:

Sore throat  
 Wheezing  
 Nervousness  
 Burning or itching eyes  
 Chest pain  
 Tearing  
 Cough  
 Frequent headaches  
 Tiredness  
 Rashes  
 Swelling of eyelids  
 Weight loss  
 Sneezing  
 Insomnia  
 "runny nose"

Numbness or tingling sensations  
 Hoarseness  
 Nasal stuffiness  
 Shortness of breath  
 Skin sores  
 Upset stomach  
 Redness of eyes  
 Hives  
 Diarrhea  
 Excessive thirst on arising  
 Loss of appetite  
 Changes in skin color  
 Vomiting  
 Other (please list)

Have you been treated in the clinic for any of these problems within the past year?  Yes  No

Have you ever had (check):  Hay fever  
 Allergy to any medicine  
 Allergy to jewelry or metals  
 Asthma  
 Infantile eczema  
 Food allergies