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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 74-61-232  
GATES RUBBER COMPANY  
DENVER, COLORADO

NOVEMBER 1975

I. TOXICITY DETERMINATION

From the results of environmental and medical evaluations conducted by the National Institute for Occupational Safety and Health (NIOSH) on June 4 and 7, 1974; July 11, 1974; November 11, 1974; December 3, 1974; March 20, 1975; April 10, 1975; and May 5-7, 1975, it has been determined that a potential health hazard may exist from exposures to cyclohexanone in the Extruded Hose Department (Department 60) of the Gates Rubber Company, Denver, Colorado. This determination is based on airborne measurements of cyclohexanone which exceeded recommended hygienic standards for this substance. In addition several workers within this Department were found to have primary irritant contact dermatitis from repeated exposure to solvent containing solutions. All environmental measurements for toluene diisocyanate (TDI), trichlorethylene, and total dust were below NIOSH recommended standards and established OSHA Federal Standards. Only one of 38 vinyl chloride samples was found to exceed the Federal Standard action level of 0.5 ppm. It is NIOSH's policy to reject the concept of a threshold limit for vinyl chloride gas or any other carcinogen. NIOSH recommends that the employer reduce airborne concentrations of vinyl chloride to levels not detectable by the recommended analytical techniques. On three of four occasions when measured all vinyl chloride concentrations were below detection limits.

II. DISTRIBUTION AND AVAILABILITY

Copies of this hazard evaluation determination 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) Gates Rubber Company
- (b) United Rubber Workers, Local #154, Denver
- (c) U.S. Department of Labor - VIII
- (d) NIOSH - Region VIII

For the purpose of informing the approximately 60 "affected employees" this report should be posted in a prominent place accessible to the workers for a period of approximately 30 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 received such a request from the President of United Rubber Workers, Local #154, Denver, Colorado, to evaluate the hazards associated with various chemical substances used in the manufacture of extruded hose and dust generated by this manufacturing process.

### IV. HEALTH HAZARD EVALUATION

#### A. Plant Process

The Extruded Hose Department of Gates Rubber Company produces garden hose principally from the extrusion of polyvinylchloride (PVC). Other plastics are used infrequently in this process. Other chemicals used in preparing nylon cords for reinforcing the hose include cyclohexanone, TDI, trichloroethylene, Estane<sup>R</sup> thermoplastic polyurethane, methylene chloride, di-2-ethylhexyl phthalate (DOP oil), and nigrosine. Various combinations of these chemicals have been in use during the Health Hazard Evaluation study period. During the period of the medical evaluation two principal formulations were in use and designated numerically as compounds 10127 and 10139. While containing common ingredients the former compound also contains methylene chloride and DOP oil while the latter contains nigrosine. Only small quantities of compounds 10127 and 10139 are utilized. Nylon thread is passed through these mixtures, which serve as bonding agents, prior to entering knitting machines that produce a reinforcing matrix surrounding the hose core. Knitting machine operators, who for safety reasons cannot wear protective gloves, are the principal Department personnel exposed to these materials. Other major activities within the Department include plastic blending, extrusion, and hose finishing or coiling. Personnel per shift normally include two stockmen, one blender, four extruder operators, two knitting operators and seven or eight hose finishers.

#### B. Evaluation Design

The Extruded Hose Department normally works three shifts, with a 40-hour work week per shift. At the time of this evaluation

there were usually 17-18 employees per shift. Environmental evaluations were performed on all three shifts. Environmental samples were analyzed in both NIOSH Salt Lake City and Cincinnati laboratories. Employees from all shifts also participated in the medical evaluation which was principally conducted in the offices of Local Union No. 154, United Rubber, Cork, Linoleum and Plastic Workers of America - AFL-CIO.

### C. Evaluation Methods

Vinyl chloride, cyclohexanone, and trichloroethylene were collected on organic vapor sampling tubes and analyzed by gas chromatography. TDI samples were collected in all glass midjet impingers and analyzed by the Marcali method. Total dust samples were taken on pre-weighed filters and re-weighed in the laboratory.

Non-directed medical interviews and, when deemed advisable, limited physical examinations were carried out privately by a NIOSH physician. These examinations when indicated included cutaneous, eye, nose, throat, blood pressure, chest, heart, and hearing assessments.

Bulk samples of compounds 10127 and 10139 along with the individual ingredients of each mixture were obtained and concentrations suitable for patch testing prepared. The following concentrations and vehicles were utilized:

#### Patch Test Materials

1. Estane<sup>R</sup>, 1% in acetone
2. Nigrosine, 1% in petroleum
3. DOP oil, 1% in petroleum
4. Mixture 10127, 5% in acetone
5. Mixture 10139, 5% in acetone

These concentrations are known to be sufficiently low to preclude irritant reactions.

Standard patch test procedures were followed in testing four worker volunteers, each of whom gave histories compatible with repeated episodes of irritant or allergic contact dermatitis. Appropriate acetone and petroleum control patches were also applied. Cyclohexanone and methylene chloride were not tested individually since they have never been reported to cause allergic sensitization and were already present in formulas 10127 and 10139. In addition, a reactive patch test to either or both these formulas plus the reaction pattern to the other materials tested would permit the identification of either of these solvents in the

unlikely event that they were causing sensitization. Patch test sites were carefully examined 48 hours after application and volunteers were urged to report promptly any reactions which might appear subsequently.

#### D. Evaluation Criteria

Vinyl chloride is considered a carcinogenic agent. It is suspected of being an etiologic agent in the development of angiosarcoma of the liver (a rare form of liver cancer). As stated in NIOSH's Recommended Standard for Occupational Exposure to Vinyl Chloride, "there is probably no threshold for carcinogenesis although it is possible that with very low concentrations, the latency period might be extended beyond the life expectancy." In view of these considerations and NIOSH's inability to define a safe exposure level the concept of a threshold limit for vinyl chloride gas in the atmosphere is rejected. As a result, the NIOSH Recommended Standard for Occupational Exposure to Vinyl Chloride states that exposure to vinyl chloride monomer should not exceed levels that are detectable by the recommended methods of sampling and analysis. These views are not universally held and as will be subsequently presented the OSHA Federal Standard for vinyl chloride has been set at 1.0 ppm.

Cyclohexanone is commonly used as a solvent and chemical intermediate. It is considered to be low in degree of hazard to health under the usual conditions of use. While capable of causing narcosis and even death at very high levels its low volatility at room temperatures renders this possibility negligible. Definite eye, nose, and throat irritation have been reported at levels of 75 ppm. Since cyclohexanone is an excellent lipid solvent it is very likely that repeated contact will result in skin irritation. It has a TLV of 50 ppm.

Trichloroethylene is commonly used as an industrial solvent particularly in degreasing metal parts. It has narcotic effects in high concentrations and was fairly widely used as a surgical anesthetic in the past. Chronic exposure has been reported to cause abnormal fatigue, increased need for sleep, irritability, headache, and decreased tolerance to alcohol. Ventricular fibrillation resulting in death has been related to trichloroethylene exposure in several reports. Adverse kidney and liver effects were noted in the older literature, but are thought to be due to other chlorinated hydrocarbons present as contaminants. Very recently it has been reported that large amounts of trichloroethylene when fed to rats resulted in cancer development in high percentage of animals. The relevance of such

experiments to the usual types of human exposure remains to be determined. To date there are no studies suggesting that trichlorethylene is a human carcinogen.

TDI is the most commonly used isocyanate and is widely used in the manufacture of "polyurethanes" or "polyurethane plastics." In higher concentrations it is a potent pulmonary tract irritant. It is also capable of inducing an allergic pulmonary sensitization which results in an asthma-like syndrome. This sensitization occurs in only a small proportion of exposed individuals, but once developed precludes any further contact with the unreacted substance. The current standard is thought to be sufficiently low to prevent the occurrence of sensitization.

Estane<sup>R</sup> is a trade mark of the B.F. Goodrich Co. for a group of theroplastic polyurethanes. Presumably any toxic properties would be due to any unreacted isocyanate present and might, in general, be expected to resemble those of TDI.

Nigrosine is a widely used black dye. While uncommonly a cause of dermatitis it is a known skin sensitizer. Most cases have been reported from handling "carbon paper."

Methylene chloride is another widely used industrial solvent and is widely used in de-greasing metal parts. Since it is non-flamable its use appears to be growing. In high concentrations it has anesthetic action manifest by headache, giddiness, stupor, irritability, sensations of "drunkenness", and loss of coordination. It is moderately irritating to the skin upon repeated contact.

Di-2-ethylhexyl phthalate (dioctyl phthalate) is one of the most widely used plasticizers and as such as received fairly extensive toxicologic investigation. Based on these studies it may be concluded that the hazard to workers under the usual conditions of use would be extremely low. Patch tests with undiluted material do not cause irritation nor has it been reported to cause sensitization.

Three sources of criteria were considered in assessing the workroom concentrations of air contaminants encountered in evaluation. These are: (1) Recommended and proposed threshold limit values (TLV's) and their supporting documentation as set forth by the American Conference of Governmental Industrial Hygienists (ACGIH) (1974); (2) Occupational health standards as promulgated by the U.S. Department of Labor (Federal Register, June 27, 1974, Title 29, Chapter XVII, Subpart G); and (3) NIOSH recommended criteria for occupational exposures.

In the following tabulation criteria, the most appropriate value in the opinion of the authors is presented with its reference footnoted.

| <u>Substance</u>                     | <u>Permissible Exposures<br/>8-Hour Time-Weighted<br/>Exposure Basis</u> |
|--------------------------------------|--|
| <sup>1</sup> Vinyl Chloride .....    | 1 ppm (a)  |
| <sup>2</sup> Cyclohexanone .....     | 50 ppm   |
| <sup>3</sup> TDI .....               | C--0.12 mg/M <sup>3</sup> (b)  |
| <sup>4</sup> Trichloroethylene ..... | 100 ppm  |
| <sup>5</sup> Total Dust .....        | 10 mg/M <sup>3</sup> (c)   |

(a) ppm = parts of vapor or gas per million parts of contaminated air

(b) C = ceiling value; this concentration shall not be exceeded for any period

(c) mg/M<sup>3</sup> = approximate milligrams of substance per cubic meter of air

<sup>1</sup>Reference: current OSHA standard. As previous discussed NIOSH has recommended that exposure to VC should not exceed levels that are detectable by recommended methods of sampling and analysis.

<sup>2</sup>Reference: 1974 ACGIH TLV and current OSHA standard.

<sup>3</sup>Reference: 1974 ACGIH TLV and current OSHA standard.

<sup>4</sup>Reference: 1974 ACGIH TLV and current OSHA standard.

<sup>5</sup>Reference: 1974 ACGIH TLV

Occupational health standards are established at levels designed to protect individuals occupationally exposed to individual toxic substances on an 8-hour per day, 40-hour per week basis over a normal working lifetime.

#### E. Evaluation Results and Discussion

The environmental measurements are presented in Tables I-IV. Only one vinyl chloride sample exceeded 0.5 ppm out of 38 samples submitted for analysis and all values are within the current Federal Standard (OSHA) for this substance (Table I).

Nuisance dust levels obtained by personal breathing zone collection and general area sampling methods were found to be well under the hygienic standard (Table II). The blender operator was felt to be the only individual potentially exposed to excessive dust based on a careful walk through assessment of the Department.

Cyclohexanone levels were found to exceed the recommended standard for three of the four samples analyzed for this substance (Table III). In view of the restricted usage of this solvent to the knitter operation sampling was limited to those employees working in immediate proximity to that process.

All samples for trichloroethylene (Table III) were reported as being less than 0.05 mg/M<sup>3</sup>, the limit of sensitivity for the method employed. TDI sample results (Table IV) were also less than the sensitivity of the current analytic procedure.

A total of 18 Department 60 employees (4 women and 14 men) participated in the medical portion of the evaluation. The average age was 42 (range 28-60 years). The average duration of employment by Gates was 14 years (range 3-29) and most had spent a majority of this employment (average 10 years) in Department 60. It should be pointed out that these employees were not randomly selected for participation in the study, but rather represent a group who voluntarily came forth on learning that a medical evaluation was planned. It is probably valid to conclude that such a group would contain those employees who are the most likely to have symptoms or complaints which they attribute to their work or who have other health problems and concerns. This sample represents about 30-35% of the total Department work force.

As might be anticipated from the age and size of this group a wide range of symptoms, chronic illnesses, and physical complaints were identified. The most common symptom elicited was headache with five employees mentioning this as a problem. In most instances the headaches were occasional in incidence and not related to any particular department process. One individual did attribute his headaches to the process of purging the tubing extruder.

Four cases of dermatitis were identified and characterized as ezematous in type. The hands were the most common site involved and in several workers the problem had been intermittently present for several years. While the limited distribution to the hands, wrists, and arms suggested primary irritant dermatitis, allergic contact dermatitis could not be excluded on clinical grounds. These four individuals were therefore patch tested as outlined in Section C. The results of these tests were entirely negative confirming the probable irritant nature of the dermatitis. Three of the four employees with dermatitis work as knitter operators in which some exposure to cyclohexanone and methylene chloride, agents easily capable of defatting the skin, is essentially unavoidable since safety considerations preclude the use of gloves.

Other signs, symptoms, and conditions encountered were: asthma-1; allergic rhinitis-2; deafness-1; nose bleeds-1; eye irritation-2; shortness of breath-1; cough-1; arthritis-1; cataract-1; sub-cutaneous lipomatosis-1; prostatitis-2; cystitis-1; high blood pressure-1; hypercholesterolemia-1; diabetes-1; seizure disorder-1; and post operative status (lipoma excision). The diversity and low frequency of these, not uncommon medical problems, make it quite unlikely that they are related to current occupational exposure.

#### G. Recommendations

1. Adequate ventilation should be provided during hose extrusion.
2. Exhaust ventiation should be provided above the hopper where powdered and chipped PVC is hand poured and mixed.
3. Adequate ventilation should be installed in the vicinity of the knitter machines to control cyclohexanone exposure.
4. Knitter machine operators should be supplied with barrier creams formulated to resist organic solvents. Examples of such products are:
  - (1) PLY 9 (Milburn Co., 3246 E. Woodbridge, Detroit, Michigan 48207)
  - (2) West No. 411 (West Chemical Products, 42-16 West St., Long Island City, New York)
  - (3) FEND S-2 (Mine Safety Appliances Co., Pittsburgh, Pa.)
  - (4) Kerodex 51 (Ayerst Laboratories, 685 Third Ave., New York, N.Y. 10017)
  - (5) MAN-0 (MAN-0 Products, 3710 Floral Ave., Cincinnati, Ohio 45207)

V. AUTHORSHIP AND ACKNOWLEDGMENT

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TABLE I  
Breathing Zone and General Room Concentrations of  
Vinyl Chloride (VC)

Gates Rubber Company  
Denver, Colorado

June and July 1974

| <u>Date</u>  | <u>Job</u>       | <u>Sample<br/>Vol(cc)</u> | <u>Sample<br/>Number</u> | <u>Vinyl Chloride (VC)<br/>ppm</u> |
|--------------|------------------|---------------------------|--------------------------|------------------------------------|
| June 4, 1974 | Blender Operator | 377                       | 1                        | None Detected                      |
| "            | Tuber Operator   | 599                       | 2                        | "                                  |
| "            | Hose Finisher    | 494                       | 3                        | "                                  |
| "            | Knitter Operator | 794                       | 4                        | "                                  |
| "            | Blender Operator | 479                       | 5                        | "                                  |
| "            | Tuber Operator   | 590                       | 6                        | "                                  |
| "            | Hose Finisher    | 611                       | 7                        | "                                  |
| "            | Knitter Operator | 874                       | 8                        | "                                  |
| "            | Blender Operator | 426                       | 9                        | "                                  |
| "            | Tuber Operator   | 1306                      | 10                       | "                                  |
| "            | Hose Finisher    | 1155                      | 11                       | "                                  |
| "            | Knitter Operator | 1520                      | 12                       | "                                  |
| June 7, 1974 | Knitter Operator | 1958                      | 13                       | < 0.2                              |
| "            | Insulator        | 927                       | 14                       | < 0.2                              |
| "            | Hose Finisher    | 1015                      | 15                       | < 0.2                              |
| "            | Insulator        | 1166                      | 16                       | < 0.2                              |
| "            | BLANK            |                           | 17                       | < 0.2                              |
| "            | BLANK            |                           | 18                       | < 0.2                              |

(continued)

TABLE I  
(continued)

Gates Rubber Company  
Denver, Colorado

| <u>Date</u>       | <u>Job</u>           | <u>Sample<br/>Vol(cc)</u> | <u>Sample<br/>Number</u> | <u>Vinyl Chloride (VC)<br/>ppm</u> |
|-------------------|----------------------|---------------------------|--------------------------|------------------------------------|
| July 11, 1974     | Tuber Operator       | 4100                      | 1                        | < 0.2                              |
| "                 | Tuber Helper         | 390                       | 2                        | < 0.2                              |
| "                 | Tuber Operator       | 4000                      | 3                        | < 0.2                              |
| "                 | Blender Operator     | 9500                      | 4                        | 0.25                               |
| "                 | Tuber Operator       | 2300                      | 5                        | 0.25                               |
| "                 | Hose Manager         | 6500                      | 6                        | < 0.2                              |
| "                 | Knitter Operator     | 4400                      | 7                        | 0.21                               |
| "                 | General Blender Area | 3200                      | 8                        | 0.25                               |
| "                 | BLANK                |                           | 13                       | < 0.2                              |
| "                 | Tuber Operator       | 7100                      | 18                       | < 0.2                              |
| "                 | Tuber Helper         | 10100                     | 17                       | < 0.2                              |
| "                 | Tuber Operator       | 7100                      | 20                       | < 0.2                              |
| "                 | Blender Operator     | 9500                      | 16                       | < 0.2                              |
| "                 | Tuber Operator       | 4000                      | 23                       | 0.29                               |
| "                 | Hose Manager         | 2000                      | 22                       | 0.46                               |
| "                 | Knitter Operator     | 9300                      | 19                       | < 0.2                              |
| "                 | General Blender Area | 2300                      | 21                       | 0.52                               |
| Nov. 11, 1974     | Tuber Operator       | 8953                      | 1                        | < 0.2                              |
| "                 | Tuber Operator       | 4239                      | 2                        | < 0.2                              |
| "                 | Tuber Operator       | 9826                      | 3                        | < 0.2                              |
| "                 | Tuber Operator       | 4483                      | 4                        | < 0.2                              |
| "                 | Tuber Operator       | 3686                      | 5                        | < 0.2                              |
| "                 | BLANK                |                           | 6                        | None Detected                      |
| "                 | BLANK                |                           | 7                        | None Detected                      |
| "                 | Tuber Helper         | 1922                      | 8                        | < 0.2                              |
| HYGIENIC STANDARD |                      |                           |                          | 1.0                                |

The lower limit of detection of vinyl chloride in the NIOSH Salt Lake City laboratory is 0.2 ppm.

TABLE II  
Breathing Zone Concentrations of  
Nuisance Dust

Gates Rubber Company  
Denver, Colorado

June 7, 1974

| <u>Job</u>           | <u>Sample<br/>Vol(Liters)</u> | <u>Sample<br/>Number</u> | <u>Nuisance Dust<br/>mg/M<sup>3</sup></u> |
|----------------------|-------------------------------|--------------------------|---|
| Blender Operator     | 180                           | E-24                     | 2.2                                       |
| Blender Operator     | 456                           | 31                       | 5.2                                       |
| General Blender Area | 456                           | 38                       | 2.1                                       |
| HYGIENIC STANDARD    |                               |                          | 10.0                                      |

TABLE III  
Breathing Zone Concentrations of  
Cyclohexanone and Trichloroethylene

Gates Rubber Company  
Denver, Colorado

July 11, 1974

| <u>Job</u>         | <u>Sample<br/>Vol(Liters)</u> | <u>Sample<br/>Number</u> | <u>Cyclohexanone<br/>mg/M<sup>3</sup></u> | <u>Trichloroethylene<br/>mg/M<sup>3</sup></u> |
|--------------------|-------------------------------|--------------------------|---|---|
| Knitter Operator   | 10.5                          | 9                        | 86.0                                      | < 0.05  |
| Knitter Operator   | 9.5                           | 10                       | 68.0                                      | < 0.05  |
| Knitter Operator   | 20.0                          | 14                       | 68.0                                      | < 0.05  |
| Knitter Operator   | 39.0                          | 15                       | 8.0                                       | < 0.05  |
| HYGIENIC STANDARDS |                               |                          | 50.0                                      | 100.0   |

TABLE IV

Breathing Zone and General Room Concentrations of  
TDI

April 10, 1975

| <u>Location</u>   | <u>Sample<br/>Vol(Liters)</u> | <u>Sample<br/>Number</u> | <u>TDI,<br/>mg/M<sup>3</sup></u> |
|-------------------|-------------------------------|--------------------------|----------------------------------|
| Knitter Operator  | 68                            | 1                        | < 0.02                           |
| General Room      | 61                            | 2                        | < 0.02                           |
| Knitter Operator  | 66                            | 3                        | < 0.02                           |
| General Room      | 63                            | 4                        | < 0.02                           |
| BLANK             |                               | 5                        |                                  |
| HYGIENIC STANDARD |                               |                          | 0.12                             |

The lower limit of detection of TDI by current NIOSH analytical methods is 0.02 mg/M<sup>3</sup>.