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. HE 78-131-586

GOODYEAR TIRE AND RUBBER COMPANY
NIAGARA FALLS, NEW YORK

April 1979

I. TOXICITY DETERMINATION

It has been determined, based on medical evidence, that a hazard to the health of workers exposed to Kagarax A® (a rubber accelerator containing the sensitizer 2-mercaptobenzothiazole) existed at the Goodyear Tire and Rubber Company, Niagara Falls, New York, during the period of a Health Hazard Evaluation conducted by NIOSH on October 25-26, 1978.

Environmental sampling for morpholine and 2-mercaptobenzothiazole (MBT) indicated airborne concentrations which were less than or equal to, the lower limit of detection for the analytical methods used. However, the medical evaluation revealed wheal type lesions among the workers examined due to skin contact with Kagarax A.

Recommendations have been included to help improve the health and safety conditions in the employees' work area.

II. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report are currently available upon request from NIOSH, Division of Technical Services, Information Resources 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) Plant Manager, Goodyear Tire and Rubber Company, Niagara Falls, New York.
b) Safety Committee Chairman, Oil, Chemical, and Atomic Workers International Union - Local 8-277, Niagara Falls, New York.
c) Vice-President, Oil, Chemical and Atomic Workers International Union, Washington, D.C.
d) U.S. Department of Labor - Region II
e) NIOSH - Region II.

For the purpose of informing the 19 potentially exposed employees, the employer shall promptly "post" for a period of 30 calendar days the Determination Report in a prominent place(s) near where the affected 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 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 Safety Committee Chairman, Oil, Chemical, and Atomic Workers International Union - Local 8-277. As the authorized employee representative for the Goodyear Tire and Rubber Company, Niagara Falls, New York, the Safety Committee Chairman submitted the request on behalf of several employees who work in Department 245, the Kagarax® drying and bagging area. The requestor indicated that the affected employees are reportedly exposed to an irritating chemical substance in the form of a yellow dust. It was also noted that sixty-eight cases of dermatitis have been reported during the past five years among production workers and maintenance personnel.

Kagarax A is a trade name for 4-Morpholinyl-2-benzothiazole disulfide. This chemical compound is a rubber accelerator and is manufactured by the Goodyear Tire and Rubber Company by reacting morpholine with 2-mercaptobenzothiazole (MBT). The Material Safety Data Sheet reports that the physical appearance of Kagarax A varies from a cream to a light yellow powder and that its solubility in water is negligible. The Special Handling Precautions fact sheet indicates that Kagarax A is moderately hazardous by inhalation, is irritating to the eyes, and is a possible skin sensitizer.

In June 1978, the Occupational Safety and Health Administration (OSHA) conducted an environmental evaluation in the Kagarax A drying and bagging area. The OSHA inspection indicated that employees working in this area were exposed to a skin irritant in the form of a yellow dust. Excessive amounts of this dust were noted to cover the floor, bagging machine, dryer, and the railing and stairs. The work room conditions noted by the OSHA inspector resulted in the company being cited for poor housekeeping practices. (29 CFR 1910.22 [a][1]).

A NIOSH Interim - I Report, dated November 24, 1978, was distributed to representatives of both management and labor. Discussed in the Report were the observations and preliminary findings of the NIOSH investigators during the environmental and medical survey of October 25-26, 1978; recommendations to help improve the health and safety conditions in the employees' work environment were also included.

IV. HEALTH HAZARD EVALUATION

A. Process Description

The facility operated by the Goodyear Tire and Rubber Company in Niagara Falls, produces 3 chemical products: polyvinyl chloride; Nailax®, an anti-oxidant; and Kagarax A, a rubber accelerator. The plant has been in operation since 1946 and employs approximately 388 persons. Of the total work force, approximately 170 are administrative, 162 are production workers, and 56 are maintenance personnel; however, only 19 employees are directly affected by the alleged hazard (7 administrative and 12 production employees).

The plant's medical facilities included a first-aid station with several employees trained in first-aid who attend ill or injured employees. There is also a local doctor who has an agreement with the plant to care for minor medical problems and to take pre-employment medical histories and perform examinations. Workers with problems of a more severe nature are seen at a nearby hospital emergency room.

Kagarax A has been produced since 1970 and the present production rate is approximately 10 million pounds per year. Most of the product is used by the Company; however, a small percentage is sold under the trade name Morfax.

A slurry (approximately 75% liquid - 25% solid) consisting of isopropanol, water and Kagarax A is pumped from the reactor after quenching to the Kagarax A bagging area. Solid material is centrifuged out of the slurry and then continues on for further processing. The isopropanol is recovered and the remaining effluents are discharged to the sewer.

The solid material (Kagarax A) leaves the centrifuge and is gravity fed to a fluidized bed for air drying. The bed is equipped with hot-air jets to maintain fluidity throughout the drying cycle. Steam is used to heat the drying air which provides a maximum operating temperature of approximately 100°C.

After exiting the dryer, the product is conveyor-fed to a hopper which in turn feeds a hammer mill. The material then enters a series of seive-plates to reduce the particle size. A vacuum system operated at 10-15 in.Hg. draws the finished product into a bagging unit which operates automatically based on a weight of 50 pounds of product per bag. The final moisture content of the Kagarax A is between 1/2 - 1%.

Material too large to pass the seives, is recycled to the hammer mill. Material which is too wet is recycled to the dryer. Poor quality Kagarax A is slowly worked back into the operation. Material recovered through the dryer exhaust via a baghouse is also recycled.

Filled bags of Kagarax A are removed manually from the bagging unit and weighed. Differences are corrected by the operator who adds or removes material until the final weight of each bag is approximately 50 pounds. The bags are loaded on skids, 50 to each skid. Average time for the bagging operation from the start of the bag fill until the bag is placed on the skid is about 3 minutes. The area around the bagging operation is quite dusty due to the dryness of the Kagarax A. A vacuum line is positioned near the bagging unit and is used for cleaning.

Three (3) 8-hour work shifts are utilized for continuous Kagarax A production. A normal work shift will consist of a control operator and two production workers. The work routine for the production workers consists of 30 minutes on the line, then 30 minutes off. Off-time is spent in general utility, including loading and cleaning. Employees rotate jobs through the building every 2 weeks.

Periodically, the fluidized bed dryer must be shut down due to caking of the Kagarax A. When a blockage occurs, as it did during this survey on October 26th, the caked product must be chiseled and shoveled out by hand. Employees involved in this "raking" operation complain of a burning sensation on the skin, choking, and spitting-up phlegm.

Very little personal protective equipment is worn by the employees while on the line or during clean-up and raking. Of the 4 employees who were involved in removing the caked product from the dryer, only one employee was observed wearing an approved disposable dust mask; however, only one of the two head-straps was used. Personal protective equipment including respirators, goggles, gloves, paper hoods and coveralls, are available from the Company; however, usage is not mandatory.

B. Evaluation Design

In response to this request, an environmental and medical evaluation was conducted on October 25-26, 1978, in Department 245, the Kagarax A drying and bagging area. An opening conference was conducted and attended by representatives of both management and labor. Following the opening conference, a walk-through survey was performed in the Kagarax A production area. The employees' locker room, shower, and lunch room were also inspected.

Environmental sampling was conducted during the second (3:00 p.m. to 11:00 p.m.) and third (11:00 p.m. to 7:00 a.m.) shifts to evaluate employee exposures to airborne concentrations of morpholine and MBT in the Kagarax A production area. Multiple sampling media were utilized and included silica gel tubes for morpholine and glass fiber filters for MBT. Twenty-four area and personal breathing zone air samples were collected. A bulk sample of Kagarax A was also obtained for subsequent laboratory analysis.

During the medical evaluation, 18 employees working in Department 245 were privately interviewed, a physical examination was conducted, and photographs of employees with skin disorders were obtained.

At the conclusion of the survey, a closing conference was conducted to discuss preliminary findings and recommendations with representatives of management and labor.

C. Evaluation Methods

1. Environmental

Employee exposures to MBT and morpholine were evaluated by drawing air through a 37 millimeter diameter type AE glass fiber filter connected in series with a two section 225 milligram silica gel tube. Vacuum sampling pumps were utilized to draw air through the sampling media at a flow rate of 1 liter per minute for both personal and area air samples. Personal air samples were collected in the breathing zone of the exposed employees, while area air samples were collected in locations adjacent to the fluidized bed dryer and the vacuum bagging unit in an effort to characterize the general work environment.

The silica gel tube samples for morpholine were transmitted to a NIOSH contract laboratory in Salt Lake City and were analyzed by a NIOSH gas chromatographic method.[1] The limit of detection was calculated to be 0.05 milligrams of morpholine per sample.

The glass fiber filter samples for MBT were transmitted to the NIOSH laboratory in Cincinnati for method development. Attempts to analyze for MBT without prior derivatization proved unsuccessful and the gas chromatographic analysis required preparation of a trimethylsilyl derivative. Since MBT is not very soluble in most organic solvents, a study to determine the most efficient solvent was required. Acetone was determined to be the solvent of choice and each filter was extracted with 10 milliliters of this solvent. The extraction solvent was evaporated and the residue redissolved in 1 milliliter of a 50:50 Acetone:BSTFA (silylating reagent) mixture. GC conditions were optimized using an authentic reference standard which was also used to establish minimum detection levels. The limit of detection was calculated to be 2.1 micrograms per sample.

2. Medical

The medical evaluation consisted of questionnaires administered to each worker, a physical examination, and photographs of employees with skin disorders. Medical releases were obtained from several employees and sent to their private physicians to obtain a medical summary of work-related illness. The employees' medical records were not reviewed due to the fact that they were not maintained at the plant.

The questionnaire attempted to define work history, other possible fume or dust exposures, general health problems and medications. Questions regarding past skin disorders and treatment received were asked. Information on work habits, such as eating or smoking at the plant, as well as the laundering of work clothing was also sought. Specific symptoms of skin and pulmonary disorders were sought, as well as more general symptoms such as fatigue or weight loss.

The physical examination included an inspection of the head, neck, chest, back, arms, hands, and legs for any skin disorders.

D. Evaluation Criteria

The concept that there are concentrations of air contaminants to which most employees may be exposed on a day-to-day basis, without discomfort or adverse health effects, is fundamental to the practice of industrial hygiene. Airborne exposure limits for many chemical substances encountered occupationally have been recommended or promulgated by several organizations. These limits are normally expressed as a time-weighted average (TWA) exposure for a normal 8 to 10-hour workday, or a 40-hour workweek, and are presumed to be valid through out a normal working lifetime. However, it should be noted, that due to a wide variation in individual susceptibility, a small percentage of employees may experience discomfort from exposure to some substances at concentrations at or below the recommended level; a smaller percentage may be affected more seriously by aggravation of a pre-existing condition or by development of an occupational illness.

For this investigation, environmental evaluation criteria were considered from the following sources: (1) American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs) with their supporting documentation, and (2) U.S. Department of Labor - Occupational Safety and Health Administration (OSHA) standards. For the chemical substances evaluated during this investigation, the primary environmental criteria selected were:

Chemical Substance	Environmental Criteria PPM**	Reference Source ***
Morpholine	20	(1,2)
MBT	NS*	---

* No standard has been recommended for 2-mercaptobenzothiazole.
** Parts of vapor per million parts of contaminated air by volume at 25°C and 760 mmHg.
*** Reference numbers in parenthesis refer to the source(s) from the above discussion from which the environmental standard was obtained.

The following discussion is provided so that the employees of Department 245 may better understand the potential health hazards associated with excessive occupational exposure to these chemical substances.

Morpholine - is a colorless, alkaline liquid with an amine like odor. Because its aqueous solutions are highly alkaline, morpholine is very irritating to the eyes, skin, and mucus membranes. Concentrated morpholine will readily permeate the skin and some reports of skin and respiratory tract irritation have been noted from industrial usage; however, no chronic effects have been reported.[2,3]

The environmental criteria recommended by the ACGIH (1978) is a TLV-Skin of 20 ppm as determined by an 8-hour TWA exposure, and a Short Term Exposure Limit (STEL) of 30 ppm. The STEL is a maximum allowable concentration, or ceiling value, which may not be exceeded during a 15-minute excursion period. The "Skin" notation refers to the potential contribution to the overall exposure by cutaneous absorption. The present Federal Standard, as promulgated by OSHA, is 20 ppm as an 8-hour TWA exposure.[5]

2-Mercaptobenzothiazole - is a rubber accelerator which varies from a cream color to a light yellow powder. This compound is irritating to the eyes, skin, and is a known contact allergen (skin sensitizer).[6,7]

Dermatitis is the most common industrial disease. Most occupational dermititis is caused by primary irritant chemicals; however, approximately 20 percent of occupational contact dermititis is caused by allergenic materials. Almost any chemical can act as a skin sensitizer, but certain ones are more conspicuous because of this capacity. Some examples are: poison ivy, poison oak, formaldehyde, and mercaptobenzothiazole. It should be noted that many skin sensitizers do not produce adverse skin changes on the initial contact or perhaps for many days or weeks. However, a sensitizer induces certain cellular changes in the skin so that after a short incubation period, further contact with the sensitizer on the same or other parts of the body results in an acute dermatitic reaction.[8] Only total removal or isolation of the affected employee from exposure to the sensitizer will prevent further occurance of adverse health effects.

No occupational exposure criteria have been recommended or promulgated for 2-mercaptobenzothiazole.

E. Evaluation Results and Discussion

1. Environmental

Results from personal and area air samples for morpholine are reported in Table I. The results indicate airborne concentrations of approximately 2.0 percent of the environmental criteria and are thus, not considered to constitute a health hazard during the period of this evaluation. During the Kagarax A bagging operation, most environmental exposures were below the analytical limit of detection; however, one worker was exposed to a concentration of 0.4 ppm while removing a blockage on the fluidized bed dryers.

Results from personal and area air samples for 2-mercaptobenzothiazole are reported in Table II. The results indicate that environmental exposures during the Kagarax A bagging and dryer clean out operations were below the analytical limit of detection. Based on a 60 liter air sample, the lower limit of detection was calculated to be approximately 0.035 mg/M^3.

A bulk sample of Kagarax A was transmitted to the NIOSH laboratory for analysis. The bulk sample was shown to contain approximately 38 percent morpholine and 62 percent MBT as the volatile components when analyzed by gas chromatography.

2. Medical

The total number of workers participating in the medical evaluation was 18, which represents approximately 94 percent of the work force assigned to the Kagarax A drying and bagging area. All workers were males, ages ranging from 19 to 63 years, with a mean age of 38.1 years. The mean length of employment at the plant is 6.7 years.

Skin reactions of mild to moderate degree associated with exposure to Kagarax A were described by 6 out of the 18 interviewed. Five workers had evidence of localized reaction on exposed sites on examination. Medical reports received from private physicians of two of the five with skin disorders indicated that they had been, or were being, treated for Kagarax induced dermatitis and had been advised not to work with Kagarax A until the rash was cleared up.

Ten (10) of the workers stated that they very rarely use the personal protective equipment provided by the company because they were uncomfortable to work in. They did not use the barrier cream supplied, either. They stated that they had experienced some degree of skin disorder in the past, but had failed to report it to their supervisor.

All employees interviewed stated it was unnecessary for employees to shower after each shift and it was common practice for them to take their work clothes home for laundering.

A review of OSHA Form 102 revealed that; one employee in 1976, two employees in 1977, and five employees as of October 24, 1978, had reported a work related skin rash.

Housekeeping could be greatly improved. The working areas, showers, locker room and lunch room were found to be in a poor state of cleanliness.

F. Conclusion and Recommendations

Based on medical information obtained and the low levels of environmental contamination found, it is the opinion of the authors, that some of the workers in the Kagarax A production area may have become sensitized from

exposure to Kagarax A. Based upon laboratory analysis of this product, it is theorized that the allergenic material is 2-mercaptobenzothiazole, a known skin sensitizer. Particular medical recommendations should be followed to remedy the present hazard.

The following recommendations, based on employee work practices and other observations during the initial survey are presented in the interest of minimizing the employee's exposure to Kagarax A and preventing adverse health effects.

1. Employee Education - An educational program should be developed to inform the employees of the hazards associated with the chemical substances encountered in the work environment. The employees should be apprised of any toxic or irritant materials that they are likely to encounter and must understand the importance of avoiding contact with them. Specific work practices and hygienic measures must be developed and discussed with each worker to assure minimal skin contact and reduce contamination of the work area.

2. Personal Hygiene - Personal cleanliness is one of the most effective preventive measures for eliminating skin irritation. Direct contact with Kagarax A powder should be avoided; however, if skin contact occurs, the employee should wash the comtaminated area or shower and change clothing if necessary. At the end of each work shift, all production and maintenance workers should shower and exchange their soiled work clothing for clean garments. To ensure maximum skin protection, only long sleeve garmets (coveralls or work shirts) should be utilized.

3. Láundry Facilities - When employees are exposed to toxic or irritant substances, management should provide the necessary protective work clothing and laundry facilities. The employees should not be permitted to launder their own work clothing as this practice may contaminate the employees' home.

4. Personal Protective Equipment - As previously stated, all production and maintenance workers should wear long sleeve work shirts or coveralls. Additionally, cotton gloves, chemical safety goggles, and a NIOSH approved dust respirator should be worn by all employees during bagging, routine maintenance, and cleanup operations. However, when exposure to the Kagarax A feed slurry or wet product is likely, as during maintenance operations on the centrifuge of fluidized bed dryer, impervious gloves should be substituted for the cotton gloves.

5. Eyewash Facilities - Because Kagarax A is irritating to the eyes, emergency eyewash fountains should be provided near the centrifuge, fluidized bed dryer, and the vacuum bagger.

6. Protective Creams - When exposure to contact allergens or "sensitizers" is likely, the use of barrier creams is contraindicated.

7. Housekeeping - A regular cleanup schedule should be developed using vacuum cleaners or lines to remove Kagarax A dust which has accumulated in the workplace. Particular attention should be given to overhead ledges, around machinery, and on the floor.

8. Physical Examinations - A preplacement physical examination should be administered to all prospective employees to help identify those people who may be especially susceptible to skin irritations. The physician administering the examination should be provided with detailed information concerning the position for which the applicant is being considered. If exposure to skin irritants and/or allergenic materials is likely, the physician should determine whether or not the applicant possesses deficiencies or characteristics that are likely to predispose him to dermatitis.

9. Employee Participation - All cases of dermatitis, regardless of the severity, should be reported to the employee's supervisor and the plant medical department.

The NIOSH staff would like to thank both management and labor for their cooperation and assistance during this evaluation.

V. REFERENCES

1. S150 - Morpholine, NIOSH Manual of Analytical Methods, Second Edition - Volume III, U.S. Department of Health, Education, and Welfare, PHS, CDC, NIOSH, April 1977. DHEW (NIOSH) Publication No. 77-157-C.

2. Patty, F., Industrial Hygiene and Toxicology, Second Revised Edition - Volume II, Interscience Publishers, New York, New York, 1963.

3. American Conference of Governmental Industrial Hygienists: Documentation of the Threshold Limit Values for Substances in the Workroom Air, Third Edition, Cincinnati, Ohio, 1971.

4. American Conference of Governmental Industrial Hygienists: Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1978, Cincinnati, Ohio 1978.

5. U.S. Department of Labor, Occupational Safety and Health Administration, 29 CFR 1910.1000, January 1, 1978.

6. Fisher, A., Contact Dermatitis, Second Edition, Lee and Febiger, Philadelphia, Pennsylvania, 1973.

7. Hamilton, A. and H. Hardy, Industrial Toxicology, Third Edition, Publishing Sciences Group, Inc., Acton, Massachusetts, 1974.

8. Occupational Diseases. . . A Guide to Their Recognition, Revised Edition, U.S. Department of Health, Education, and Welfare, PHS, CDC, NIOSH, June 1977. DHEW (NIOSH) Publication No. 77-181.

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TABLE I

Results of Personal and Area Air Sampling for Exposure to Morpholine

Goodyear Tire and Rubber Company

Department 245 - Kagarax A Process
5408 Baker Street
Niagara Falls, New York
October 25-26, 1978
HE 78-131

Time Weighted Average Exposure in PPM[1]

Sample Number	Description/Location	Time	Volume (Liters)	Morpholine
S-1	Personal - production operator, vacuum bagging	1550-1623	33	ND[2]
S-2	Personal - control operator	1554-1648	54	ND
S-3	Area - top of vacuum tank	1557-1657	60	ND
S-4	Area - desk near control panel	1558-1658	60	ND
S-5	Area - near vacuum bagger	1628-1700	32	ND
S-6	Personal - production operator, vacuum bagging	1623-1655	32	ND
S-7	Personal - production operator, fluidized bed clean out	0605-0640	35	0.4
S-8	Personal - production operator, fluidized bed clean out	0607-0640	33	ND
S-9	Personal - production operator, fluidized bed clean out	0608-0640	32	ND
S-10	Personal - production operator, fluidized bed clean out	0611-0642	31	ND
S-11	Area - fluidized bed, middle cleaning vent	0610-0710	60	ND
S-12	Area - fluidized bed, R.H. access door	0613-0713	60	ND
S-13	Blank Silica Gel Tube	-----	--	ND
S-14	Blank Silica Gel Tube	-----	--	ND
	Environmental Criteria			20.0 (Skin)[3]

1. PPM - Parts of vapor per million parts of contaminated air by volume at 25° C and 760 monthly.

2. ND - None detected, less than the lower limit of detection for this gas chromatographic method of 0.05 milligrams per sample.

3. Skin - adsorption by cutaneous routes must also be considered.

TABLE II

Results of Personal and Area Air Sampling for Exposure to 2-Mercaptobenzothiazole (MBT)

Goodyear Tire and Rubber Company

Department 245 - Kagarax A Process
5408 Baker Street
Niagara Falls, New York
October 25-26, 1978
HE 78-131-586

Time Weighted Average Exposure in mg/M^3

Sample Number	Description/Location	Time	Volume (Liters)	MBT
1	Personal - production operator, vacuum bagging	1550-1623	33	ND[2]
2	Personal - control operator	1554-1648	54	ND
3	Area - top of vacuum tank	1557-1657	60	ND
4	Area - desk near control panel	1558-1658	60	ND
5	Area - near vacuum bagger	1628-1700	32	ND
6	Personal - production operator, vacuum bagging	1623-1655	32	ND
7	Personal - production operator, fluidized bed clean out	0605-0640	35	ND
8	Personal - production operator, fluidized bed clean out	0607-0640	33	ND
9	Personal - production operator, fluidized bed clean out	0608-0640	32	ND
10	Personal - production operator, fluidized bed clean out	0611-0642	31	ND
	Area - fluidized bed, middle cleaning vent	0610-0710	60	ND
12	Area - fluidized bed, R.H. access door	0613-0713	60	ND
13	Blank Glass Fiber Filter	-----	--	ND
14	Blank Glass Fiber Filter	-----	--	ND
	Environmental Criteria			NA[3]

1. mg/M^3 - milligrams of substance per cubic meter of air.

2. ND - None detected, less than the lower limit of detection for this gas chromatographic method of 2.1 micrograms per sample.

3. NA - None applicable, no occupational exposure criteria have been recommended or promulgated for this substance.