

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. 73-156 -205

GOODYEAR TIRE & RUBBER COMPANY
ST. MARY'S, OHIO
JULY 1975

I. TOXICITY DETERMINATION

Based on the results of the National Institute for Occupational Safety and Health (NIOSH) medical evaluations conducted on January 2-3, 1974, July 23-26, 1974, and March 3-4, 1975 in Department 277 it may be definitely concluded that the compound 2,2' dithioaniline (Bis-2) is both a potent primary irritant and a cutaneous sensitizer. There appears to be no reasonable doubt that it was responsible for an extensive outbreak of dermatitis that developed in Department 277 in late summer of 1973. As used at that time this compound represented a definite health hazard. However, following extensive changes in production methods, including automated mixing and dispensing systems, the introduction of personal protective gear and ventilation improvements, this hazard has been essentially eliminated. At the present time the only possible contact with the compound occurs approximately once daily when a single employee manually pours a container of liquid Bis-2 into an elevated reservoir.

Based on the results of environmental evaluations conducted on July 24 and 25, 1974 it has been determined that the exposure to methylene bis-diisocyanate prepolymer (MDI) is not toxic at the concentrations measured in Department 277 during normal operating conditions. This determination is based on extensive environmental sampling and the absence of any significant pulmonary symptomatology.

II. DISTRIBUTION AND AVAILABILITY

Copies of this determination report are available upon request from the Hazard Evaluation Services Branch, NIOSH, U.S. Post Office Building, Room 508, 5th and Walnut Streets, Cincinnati, Ohio 45202. Copies have been sent to:

- a) Goodyear Tire & Rubber Company, St. Mary's, Ohio
- b) Authorized Representative of Employees
- c) U.S. Department of Labor - Region V
- d) NIOSH - Region V

For the purposes of informing the approximately 30 "affected employees" the employer will promptly "post" the Determination Report in a prominent place(s) near where exposed 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 received such a request from an authorized representative of employees regarding a severe dermatitis problem in Department 277. This department manufactures urethane products and the dermatitis problem appeared following the introduction of a new chemical agent, 2,2'-dithioaniline (Bis-2), into the technology employed by this department. Bis-2 was introduced in the summer of 1973 as a new urethane cross-linker to substitute for 4,4'-methylene-Bis (2-chloroaniline)(moca) which had recently been defined by the Department of Labor as a suspected carcinogen.

IV. HEALTH HAZARD EVALUATION

A. Description of Process - Condition of Use

This large industrial plant has been in production on this site since 1939. The entire complex of buildings covers several acres and is divided into numerous separate buildings each involved with widely varied-types of molded rubber and plastic products. Department 277 is housed in a building which was built in 1964. The building is approximately 100' x 120' and the products manufactured within are all made from various urethane plastics.

Department 277 has three major production areas: (1) the W.H. Minor pad area, (2) the urethane tire area, and (3) the saw blade area. The Minor pad area produces urethane rubber bumper pads which are used in the draft gears of railroad cars. The urethane tires produced in the area are used primarily on factory forklift and towmotor trucks. Production wise, the saw blade area is comparatively small. In this area small coping saw-type blades are incorporated into plastic discs which are ultimately used for rough rotary sanding operations. Urethane tire production is highly automated and employs a methylene bis-diisocyanate prepolymer. This prepolymer is nearly completely polymerized prior to the addition of the catalyst, and therefore, represents only a minor health hazard in terms of exposure. Bis-2 is utilized only in the production of Minor pads. The Minor pad resin system consists of three resins: Medic 013, Lolic 4050, and Udic 805. These three resins are now automatically mixed with a hardener (dimethylformamide) and the Bis-2 cross-linker before it is automatically dispensed into two-part separable steel molds. Once filled, the molds are conveyed into a 240° F. drying oven. After the initial curing period of approximately 40 minutes, they are transferred for a final 24-hour curing period to another low heat oven. The cured urethane Minor pad is then manually removed from the mold prior to final testing and inspection. Prior to reuse the interior mold surfaces are painted with a silicone mold release agent. When Bis-2 was first introduced into Department 277, late in the Summer of 1973, it was

utilized as a powder which was manually mixed with the foregoing resin mixture prior to being manually poured into the Minor mold. Within a few weeks after the introduction of Bis-2, some 12 to 14 cases of dermatitis appeared in Minor area employees within a two week period. Following this, the physical form of Bis-2 was changed from a powder to a cake form. In addition, ventilation improvements were made and protective clothing provided to the workers. Since Bis-2 is a solid at room temperatures, it is stored in a low temperature oven to liquefy it prior to useage.

When the study began early in 1974 there were approximately 2,100 production employees and 350 administrative personnel. Due to currently prevailing economic conditions, the production work force has been reduced by approximately 500 positions. Department 277 has 24 production workers, three supervisors and one maintenance man. Three shifts are worked per day for a five day work week. All the employees in this Department are men. The average age of the employees in this area was estimated by Management to be 27. Labor-management relations were judged to be average for a plant of this size. There have been no strikes or unusual labor problems in recent years.

There is a large dispensary located within the plant complex which is staffed by one nurse each shift. A plant physician is employed on a fee-for-services basis. Pre-employment physical examinations are required and these include back X-rays and audiometry. Annual or periodic examinations are not required by the company.

B. Evaluation Design

1. Preliminary Survey

A preliminary observational survey of Department 277 was made on January 2-3, 1974, to assess the alleged dermatitis problem which appeared following the introduction of a new chemical agent, 2,2'-dithioaniline (Bis-2).

Twenty-two employees in Area 277 were interviewed and received limited cutaneous examinations. Nine men worked the day shift, seven men worked the evening shift, and six men were employed on the night shift. While only twelve individuals spent a major portion of their time working in the Minor area, the remaining ten men were also interviewed since they often worked at least on an occasional basis with this product.

The average age of these 22 employees was 37 (range 19-55). The total duration of employment at Goodyear averaged 10 years with a range of 15 months to 32 years. The average length of employment in area 277 was 5 years.

Interviews quickly confirmed that there had been an extensive outbreak of dermatitis beginning in late August and early September of 1973. Of the twelve individuals who worked primarily in the Minor area, ten

related bouts of dermatitis during that time period. Five of these individuals related more than one episode of dermatitis and several individuals had between three and four separate bouts. Of the ten individuals who worked only occasionally, or in some instances only rarely in the Minor area, there were two definite cases of dermatitis during the critical time period. Typically, the dermatitis involved the arms, neck, face, trunk, and in several instances, legs, genitalia, and ankles. In most instances the dermatitis began two to three weeks after the introduction of Bis-2. In those individuals who experienced two or more bouts of dermatitis, the onset of secondary episodes was noticed to occur approximately two days following re-exposure to the area. From the time sequence of the dermatitis and especially the delay in onset following the introduction of the compound and the extensive nature of the dermatitis in many of the cases, it seemed quite likely that the offending agent was in all probability Bis-2 and that it was evoking an allergic contact dermatitis.

In order to confirm the etiologic role of Bis 2 in this outbreak and to rule out the possibility of sensitivity to other agents used in the work place, it was determined that patch testing should be carried out among a representative group of these workmen, and that personal and general area impinger samples be collected to determine the use of isocyanates MDI. At that time it was deemed necessary that a follow-up survey be conducted.

The medical interviews failed to elicit any significant symptomatology suggesting pulmonary sensitization to MDI or evidence of any medical problems other than dermatitis.

2. Follow-up Medical and Environmental Survey

On July 24, 25, and 26, 1974 a follow-up environmental-medical evaluation was conducted, operators were monitored on the first shift in Department 277. A total of 38 personal breathing zone samples and 8 general area samples were collected. Patch testing was carried out on nine volunteers who all gave histories compatible with allergic contact dermatitis during the initial phases of the investigation. In addition, two NIOSH volunteers were also patch tested.

C. Evaluation Methods

1. Environmental-Methylene Bis-Diisocyanate Prepolymer (MDI)

Employee exposures to MDI were measured via personal air sampling equipment. Both work area and breathing zone samples were obtained using midget impingers. Reagents and analytical procedures followed the "modified" Marcali method as reported by Grim and Linch. Samples were analyzed at NIOSH's Cincinnati laboratories.

2. Medical

The concentrations selected for patch testing (Table 1) were based upon rabbit skin irritation indices. To determine these indices six animals were tested with each of the compounds listed in Table 1. The skin irritation index is that concentration of the substance which produces no visible sign of skin irritation after a 48-hour application. The

rabbit is the test animal chosen for skin irritancy testing since its skin is generally considered to be somewhat more sensitive than human skin. To eliminate the possibility of any human hyper-reactors at the concentration determined by skin irritancy testing, the concentration determined in this test was reduced by 50 percent.

D. Evaluation Criteria

1. Environmental Criteria

MDI has a low oral toxicity for rats, repeated daily doses for five days in corn oil, produced only slight spleen enlargement in two of five rats. Isocyanates, in general, are irritating to skin, eyes and respiratory tract, causing damage to mucous membranes and are a common cause of allergic sensitization of the respiratory tract. Careful handling is demanded.

Because there is no present information that would lead one to attribute a different type of toxicologic response, particularly sensitization of the respiratory tract, from that produced by TDI and, in view of the physical characteristics and industrial applications resulting in appreciable vapor and particulate concentration, a ceiling value of 0.02 ppm or 0.2 mg/M³ is recommended by the American Conference of Governmental Industrial Hygienists in its documentation of the threshold limit values for MDI in the workroom air.

The occupational health standard promulgated by the U. S. Department of Labor (Federal Register, June 27, 1974, Vol. 39, No. 125, Title 29, Chap. XVII, Part 1910, Subpart G, Table G-2) applicable to the substance of this evaluation is as follows:

Methylene Bis Diisocyanate (MDI)^C 0.02 ppm 0.2 mg/M³

^CCeiling value; this concentration shall not be exceeded for any period.
ppm - Parts of vapor or gas per million parts of contaminated air

by volume
mg/M³ - Milligrams of contaminant per cubic meter of air.

2. Medical

Bis-2 or 2,2'dithioaniline is a proprietary Goodyear product synthesized originally by their laboratories in Akron, Ohio. No human toxicological information is available regarding this compound. The small amount of animal toxicological data supplied by the company indicates the substance as having moderate oral toxicity for rats. It was not thought to be a primary irritant or have corrosive properties on animal testing although it was considered to be a probable sensitizing agent.

c. Evaluation Results and Discussion

1. Environmental

On July 24 and 25, 1974 a total of 38 personal samples and 8 work area samples were collected. These samples were taken in Department 277 where the MDI was being used. Sample results are presented in Table 2. The concentration of MDI ranged from 0.01 mg/M³ to 0.06 mg/M³ which are well below established federal standards.

2. Medical

Patch testing was carried out on nine volunteer employees who all gave histories compatible with allergic contact dermatitis during the initial phases of the investigation. In addition, two NIOSH volunteers were also patch tested. Since acetone was used as a solvent for the resins and other substances as listed in Table 1, it was also included for patch testing. Standard closed patch test methodology was employed and the mid-portion of the back was chosen as the test site. Patch test sites were initially examined at 48 hours, approximately 30 minutes after the occlusive tape was removed. This reading was confirmed approximately 12 to 24 hours subsequently.

Of all the substances tested, only Bis-2 was found to produce a reaction. Each exposed workman was found to have a reaction varying from 1 to 3+. Both control volunteers were also found to give reactive patch tests to this substance. The fact that the controls also reacted to Bis-2 indicated that despite its extremely low irritancy in test animals, it appeared to be a primary irritant in the human subject. In view of this very unusual finding, the animal studies to determine skin irritancy were repeated. Repeat animal testing with Bis-2 again confirmed that it was a non-irritant for rabbit skin at a 100% concentration.

Because of the demonstrated irritancy of this substance for human skin in the concentration tested, it was decided that human irritancy testing would be required to determine a proper patch test concentration to elicit sensitization. To determine the human irritancy index for Bis-2, five previously non-exposed NIOSH volunteers were utilized. Each individual was patch tested using one of five concentrations (0.01%, 0.1%, 1%, 5%, and 10%) using standard patch test methods as previously described. Four of the five volunteers had definite irritation with 1% and higher concentrations of Bis-2. One subject demonstrated irritancy only to the 10% concentration. Three of the five volunteers had minimal or questionable irritation at the .1% level. In all instances this minimal irritancy had disappeared within 24 hours after removal of the patch test although irritancy was clearly still demonstrable at all other patch test sites noted to be reactive when the tests were originally read. These data suggested that a concentration of 0.05% was probably suitable for use in testing persons with a suspected pre-existing cutaneous sensitivity to Bis-2. However, further observation of the patch test sites revealed that a secondary eruption occurred approximately eight to nine days after application of the various test concentrations. This secondary eruption was exzematous

in character and extended well beyond the confines of the original patch test sites. In three of the five volunteers it appeared in all five of the sites tested with varying concentrations of Bis-2 and in the other two subjects in all concentrations except for the 0.01% concentration. Thus, several sites showed secondary involvement even though no irritation was noted during the course of initial irritancy testing. These observations clearly indicated that the volunteers had become sensitized to the patch test material. These patch test results conclusively indicate that not only is Bis-2 a primary irritant for human skin, but that it is also an extremely potent cutaneous sensitizer. In fact, only a very few substances previously known have this degree of capacity for cutaneous sensitization. In view of these results, it was decided not to carry out subsequent patch testing upon the exposed workmen. While such patch testing could probably be carried out safely using a concentration of 0.01 to 0.05% Bis-2, such testing would not indicate whether the individual was sensitive as a result of previous occupational contact with the substance or from the preceding patch testing.

Medical interviews with a high percentage of the total employees in Department 277 confirmed that an extensive outbreak of dermatitis had occurred during August and September of 1973. Patch testing to various resins and other chemical substances utilized in this Department yielded reactive results only with the compound Bis-2. Unexpectedly, this initial patch testing indicated that Bis-2 was an irritant for human skin as well as probably a contact sensitizer. Subsequent patch testing on a group of NIOSH volunteers confirmed the irritant nature of Bis-2 and also demonstrated that it is an extremely potent cutaneous sensitizer.

F. Conclusion

It may be definitely concluded that the compound 2,2'dithioaniline (Bis-2) is both a potent primary irritant and a cutaneous sensitizer. There appears to be no reasonable doubt that it was responsible for an extensive outbreak of dermatitis that developed in Department 277 in late Summer of 1973. As used at that time this compound represented a definite health hazard. However, following extensive changes in production methods, including automated mixing and dispensing systems, the introduction of personal protective gear and ventilation improvements, this hazard has been essentially eliminated. At the present time the only possible contact with the compound occurs approximately once daily when a single employee manually pours a container of liquid Bis-2 into an elevated reservoir. This brief operation requires not more than a few minutes daily.

V. RECOMMENDATIONS

It is recommended that the operation of manually pouring a container of liquid Bis-2 into an elevated reservoir be carried out at the end of the shift so that the employee, immediately upon finishing, can then proceed to shower and remove any possible airborne contamination from his skin. He should also be provided with disposable gloves and a disposable smock to prevent accidental contamination of his skin.

VI. REFERENCES

1. Grim, K.E. and A.L. Linch. Recent Isocyanate-in-air Analysis Studies. Am. Ind. Hyg. Assoc. J., Vol. 25, May-June, 1964.

VII. AUTHORSHIP AND ACKNOWLEDGMENTS

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TABLE 1

Substance and Concentrations Used in Patch Testing

<u>Substance Trade Name</u>	<u>Chemical Nature</u>	<u>Concentration</u>
Isonate 136T	Isocyanate (TDI)	25%
Paratax (Ashland)	Accelerator	50%
Hardener Mixture	Catalyst	10%
Sawblade Mixture	Isocyanate Type Resin	10%
Meplic 013	Resin	50%
Lolic 4050	Resin	25%
Udic 805	Resin	25%
Bis-2	Cross-linker	50%
Mold Release 1XF-92	Silicone	50%
Acetone	Solvent for Patch Test Substances	100%

Table II (cont'd)

July 25, 1974 Field Number	Job and/or Location	Type	Sample Period	Sample Volume Liters	MDI* mg/M ³
25	Casting Machine	BZ	8:40 - 11:06	146	<0.01
26	Tire Line Operator	BZ	8:41 - 11:03	142	<0.01
27	Testing and Inspecting	BZ	8:43 - 10:15	92	<0.01
28	Cementing Metal	BZ	8:44 - 10:40	116	<0.01
29	Trim and Pack Products	BZ	8:50 - 10:42	112	<0.01
30	Mold Operator	BZ	8:48 - 11:05	137	0.01
31	Mold Operator	BZ	8:51 - 10:15	84	<0.01
32	Mold Operator	BZ	8:54 - 11:01	127	<0.01
33	Outside of Shipping Dock	GA	9:03 - 11:10	127	<0.01
34	Tire Pouring Operation	GA	8:54 - 11:08	134	<0.01
35	General Area Dept. 277	GA	9:05 - 11:12	128	<0.01
36	General Area Dept. 277	GA	9:07 - 11:13	127	<0.01
37	Tire Line Operator	BZ	12:49 - 2:08	79	0.01
38	Tire Line Operator	BZ	12:51 - 2:10	79	<0.01
39	Casting Machine	BZ	12:55 - 2:12	77	<0.01
40	Tire Line Operator	BZ	12:52 - 2:09	77	<0.01
41	Cementing Metal	BZ	1:01 - 2:00	59	<0.01
42	Trim and Pack Products	BZ	1:05 - 1:52	47	<0.01
43	General Area Dept. 277	GA	12:53 - 2:11	78	<0.01
44	Mold Operator	BZ	12:57 - 2:15	78	0.05
45	Mold Operator	BZ	12:59 - 2:01	62	<0.01
46	Tire Pouring Operation	GA	1:08 - 2:30	82	<0.01

Detection Limits for these samples are 0.01 Mg MDI/M³

*Milligrams of contaminant per cubic meter of air

BZ - Personal breathing zone air samples

GA - General Area