Health Hazard Evaluation Report No. HHE-80-113-114, Mobay Chmeical Corporation, Plastics and Coatings Division, Pittsburgh, PA.

6. NA

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10. Project/Task/Work Unit No.
NA

11. Contract(C) or Grant(G) No.
(C)
(G)

12. Sponsoring Organization Name and Address

Same as Above

13. Type of Report & Period Covered
Health Hazard Evaluation
June 1980

14. NA

15. Supplementary Notes

NA

16. Abstract (Limit: 200 words)

Environmental and personal air samples from the Southern Ohio Coal Company's Meigs 1 mine (SIC-1211), near Longsville, Ohio, were collected and analyzed from July 7 to 9, 1980, to determine concentrations of isocyanates produced during injection of a polyurethane binder used in underground coal mine roof consolidation. The evaluation was requested by the management of the Mobay Chemical Corporation, Pittsburgh, Pennsylvania, who was seeking authorization for use of the system in the St. Clairsville Mine Safety and Health Administration Subdistrict. Seventy four samples were collected in a 2.5 hour period during which 2,800 pounds of the binder were injected. No measurable concentrations of diphenylmethane-diisocyanate (101688) (MDI) or phenyl-isocyanate (103719) were detected. The investigators note that standard for MDI is a time weighted average concentration of 0.005 parts per million (ppm), with a ceiling concentration of 0.02ppm. Standards for phenyl isocyanate have not been established. They conclude that the extremely low airborne concentrations of isocyanates are hazardous to the miners. They recommend that the guidelines in the NIOSH diisocyanate criteria document be followed when exposures to isocyanates in underground coal mines equal or exceed 50 percent of the proposed permissible concentrations, and suggest design and procedural changes in the injection process.

17. Document Analysis a. Descriptors

Health-surveys, Air-sampling, Coal-mining

b. Identifiers/Open-Ended Terms

c. COSATI Field/Group

18. Availability Statement

Available to Public

19. Security Class (This Report)
NA

21. No. of Pages
13

20. Security Class (This Page)

22. Price

ANSI-239.18) See Instructions on Reverse OPTIONAL FORM 272 (4-

U. S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Center for Disease Control
National Institute for Occupational Safety and Health

HEALTH HAZARD EVALUATION DETERMINATION
REPORT NO. 80-113-114
Mine I.D. No. 33-01172

Mobay Chemical Corporation
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I. SUMMARY

A health hazard evaluation was conducted by the National Institute for Occupational Safety and Health (NIOSH) on July 7-9, 1980 at the Southern Ohio Coal Company's Meigs #1 mine located near Longsville, Ohio. The survey was designed to determine if Baygal-Baymidur, a Mobay Chemical Company polyurethane binder marketed for use in roof strata consolidation in underground coal mines, was capable of producing hazardous concentrations of isocyanates during an actual mine application.

The injection time covered approximately 2-1/2 hours during which 2800 pounds of the binder were utilized. Over this period, seventy-four samples were collected and analyzed for diphenylmethane diisocyanate (MDI). Additionally, forty-eight of these samples were analyzed for phenyl isocyanate.

Analytical results of the NIOSH samples obtained during the injection indicated that the procedure, as conducted in this situation, did not produce detectable airborne concentrations of MDI or phenyl isocyanate in the mine environment. Similar results could be expected for similar applications in other mines, barring accidents, and provided environmental conditions such as temperature and ventilation rates were comparable.

II. INTRODUCTION

On June 23, 1980, NIOSH received a request from the Plastics and Coatings Division of Mobay Chemical Corporation in Pittsburgh, Pennsylvania, to conduct a health hazard evaluation of polyurethane binders injected to consolidate the roof of a coal mine. Mobay Chemical had obtained permission to use Meigs #1 mine of the Southern Ohio Coal Company, Athens, Ohio, for the evaluation. The Mine Safety and Health Administration (MSHA) also participated in this survey, and was fully involved in its execution.

III. BACKGROUND

On May 28, 1980, a meeting was held at Mobay Chemical Corporation, Pittsburgh, Pennsylvania, to discuss the injection process. Mobay Chemical was seeking MSHA authorization for the use of its Baygal-Baymidur polyurethane binding system for coal mine roof consolidation in the St. Clairsville MSHA Subdistrict.

Mobay pointed out that their injection process did not involve spraying and emphasized that adverse publicity on the hazards of polyurethane utilization in mining was related to spraying operations. They also provided industrial hygiene data from previous injections showing that levels of isocyanates from the injection process were below the MSHA standards and NIOSH recommended limits for MDI. Their data further indicated phenyl isocyanate, a contaminant, was present in concentrations less than 0.01 ppm(6).

NIOSH, MSHA AND Mobay conducted a joint evaluation of the injection process on July 7-9, 1980 at the Meigs #1 mine, Athens, Ohio.

IV. PROCESS DESCRIPTION

The injection site chosen was an extensively fractured roof requiring a method of control beyond the capabilities of roof bolting alone. Two-thousand eight hundred pounds of the binder was injected into a one-hundred foot section of the mine roof in order to join the fragments and thereby render the roof bolting more effective in reducing the potential for a roof fall. "The two components of the binder are blended together at the work site in a 1:1 ratio by volume, by the use of a portable, air operated injection machine that pumps the two components under pressure through a mixer tube (which blends them). With continuous pumping, the blended chemicals are injected through "packers" which have been inserted and anchored into 1 3/4" holes drilled into the strata"(10).

"The pattern of drill hole (spacing and depth) depends upon the nature of the fractured strata. The blended chemicals react as they penetrate the cracks and fissures, producing an expanded, rigid polyurethane binder that consolidates the strata"(10). The method used in Meigs Mine #1 was to drill seven 1-3/4" holes 6 feet deep and 14 feet apart starting 35 feet outby the number 3 entry, second longwall panel off the west main. After the first hole was drilled, the packer inserted and the roof supported; the injection commenced.

The Baymidur A-2 component is polymethylene polyphenylisocyanate containing approximately 50% diphenylmethane diisocyanate (MDI). Phenyl isocyanate may be present as a contaminant. The Baygal B-3 part of the system contains a hydroxylterminated poly (oxy-alkylene) polyether resin (1). These components collectively form the polyurethane binder.

All components of the system are shipped and handled in sealed 5 gallon containers, and when needed, are transferred into the covered pump containers. This transfer process is a potential exposure point, both operationally and in the event of spillage. Miners involved in transporting the chemicals to the injection site may also be exposed should a container(s) rupture.

Roof movement and leaks from the fissures in the strata are monitored at all times. If excessive movement or leaks appear, the injection is stopped. Individuals placing roof supports or dial indicators and the injection operators are potentially exposed. Drillers are upstream from the injections and thus should not be exposed.

Ventilation at the time of injection averaged 121 feet per minute through an approximate cross-sectional area of 89 square feet resulting in an estimated total air flow of 10,769 CFM.

V. METHODS AND MATERIALS

As the injection process started at the first hole inby, drilling continued upstream. Subsequent injections were performed in each of the other holes working upstream to insure that the air flow would carry any vapors or aerosols away from the drillers. The sampling schedule included two personal samples; one on the injector operator and one on the pump operator. Additionally, one breathing zone sample was collected for the pump operator. A total of thirteen duplicate area samples were collected upstream in order to estimate exposures for the drill crew, while a total of eighteen duplicate area samples were collected downstream to assess the potential for exposures to any personnel working inby. The downstream sampling points were rotated upstream in sequence with the changes in location of the injection points. The duplicate area samples were collected for analysis by the Marcali method and the NIOSH method MR 240 (2). Ten twenty minute samples were also collected at various locations in order to assess excursions.

The sampling train for both methods utilized an MSA pump adjusted to 1.8 lpm with a single impinger in-line. Sample air was not required to pass through any apparatus prior to entering the impinger. When necessary, sample volumes were adjusted for temperature and pressure.

VI. EVALUATION CRITERIA

NIOSH evaluation criteria are used in assessing worker exposure to potentially hazardous agents except in cases where more current and stringent Federal or consensus standards exist or where sufficient health research information is available and can be applied.

Substance	NIOSH Evaluation Criteria*	Current MSHA Standard
Diphenylmethane Diisocyanate (MDI)	0.005 ppm** TWA 0.02 ppm Ceiling	0.02 ppm Ceiling
Phenyl isocyanate	Not Established	Not Established

* NIOSH Recommended Occupational Health Standard (2)
**Parts Per Million

Diphenylmethane Diisocyanate (MDI)

The toxicity of MDI is similar to that of toluene diisocyanate (TDI). In the absence of data indicating that any of the diisocyanates are substantially less toxic than TDI, the exposure recommendations for TDI should be extended to all diisocyanates(2). The biological effects include irritation of the eyes and mucous membranes and sensitization of the respiratory tract. Symptoms of the former include increased secretions, cough and pain on respiration. Symptoms of the latter include asthmatic manifestations (3).

Phenyl Isocyanate

Phenyl isocyanate appears in the activator as a contaminant imparted during the manufacture of the MDI. Little information is available on phenyl isocyanate inhalation toxicity; however, it should be considered to have the same toxicological actions as TDI, but potentially more hazardous because of its higher vapor pressure (4,5).

VII. RESULTS AND DISCUSSION

Diphenylmethane Diisocyanate (MDI)

The results of the sampling yielded undetectable concentrations of MDI when analyzed by both the Marcali Method (Table I) and the Nitro Reagent Method (Table 2).

Phenyl Isocyanate

The results of the sampling yielded undetectable concentrations of phenyl isocyanate (Table 2) as analyzed by the Nitro Reagent Method.

It should be noted that at one point during the injection the connection between the mixer and the packer separated allowing polyurethane to spurt out. Additionally, the fractured condition of the roof allowed many leaks. Thus, conditions were less than ideal and could have been expected to result in measurable concentrations of isocyanates if in fact significant amounts of the unreacted material were released.

VIII. CONCLUSIONS

No measurable airborne concentrations of MDI or phenyl isocyanate were found in the mine environment by NIOSH.

Two of the twenty-six samples collected by Mobay detected isocyanates. One sample by the #6 drill hole indicated 0.005 ppm phenyl isocyanate and one sample six feet downstream from drill hole #2 indicated 0.002 ppm total isocyanate (7). In all but these two instances NIOSH results agree with those obtained by Mobay. Additionally, this evaluation is in agreement with results obtained from the sampling of previous injections by Mobay (6).

Based upon the results of this and other trial injections, it appears that the airborne concentrations of isocyanates are quite low and that the irritative effects associated with concentrations of about 0.5 ppm would not be expected to occur. It is reasonable to expect that the skin of operators may come into direct contact with the binder during its application, an exposure which may result in irritation of the contacted body parts. Skin sensitization may also occur (2).

Previous studies indicate that a time weighted average concentration of 0.005 ppm with a ceiling concentration of 0.02 ppm will provide adequate protection for unsensitized workers. However, it is known that individuals who have previous respiratory sensitization to isocyanates may develop bronchospasm upon exposure to minute airborne concentrations of the same or other isocyanates (2, 3). The lowest published exposure causing an allergic systemic reaction by a previously sensitized individual was 0.13 ppm MDI for thirty minutes (8).

No definite conclusions can be drawn about the ability of this operation to produce initial sensitization, as the minimum exposures and times required to initiate this particular response are not known. Several authors have noted that workers often become sensitized during brief exposures to high concentrations resulting from spills or leaks. However, sensitization has been reported in workers with no known history of exposures to spills or leaks (2). One NIOSH survey found no TDI sensitization in 9 workers where their exposures averaged less than 0.01 ppm and did not exceed 0.02 ppm indicating that sensitization may be rare or nonexistant at such low concentrations (9). Our sampling results indicate that the level of 0.01 ppm was not approached. From Figure II it can be shown that had an excursion of 0.02 ppm occurred for any length of time in excess of one minute, the sampling and analytical method would have been capable of detecting it.

IX. RECOMMENDATIONS

A. Where applications of isocyanates in underground operations have produced exposures which equal or exceed 0.0025ppm as a time weighted average or 0.01ppm as a fifteen minute ceiling (one-half

the proposed permissable exposure level), the guidelines in the diisocyanate criteria document should be followed. As a minimum the precautions should include provisions for: (1) eye protection; (2) respiratory protection; (3) instruction in proper application techniques; (4) obtaining work histories of applicators specific for previous utilization and/or prior sensitization responses to isocyanates; (5) informing employees of the hazards associated with exposures to isocyanates including special emphasis on the increased risks for previously sensitized individuals; (6) other safeguards as appropriate.

B. For the Mobay injection process, consideration should be given to the development of design and procedural changes aimed at eliminating the necessity for transferring the components from the supply containers to the injection machine reservoirs. It may also be advisable to provide a removable shield around the connection between the mixer and the packer capable of deflecting or containing the chemicals in the event the connection separates as occurred at the trial injection.

X. AUTHORSHIP AND ACKNOWLEDGEMENTS

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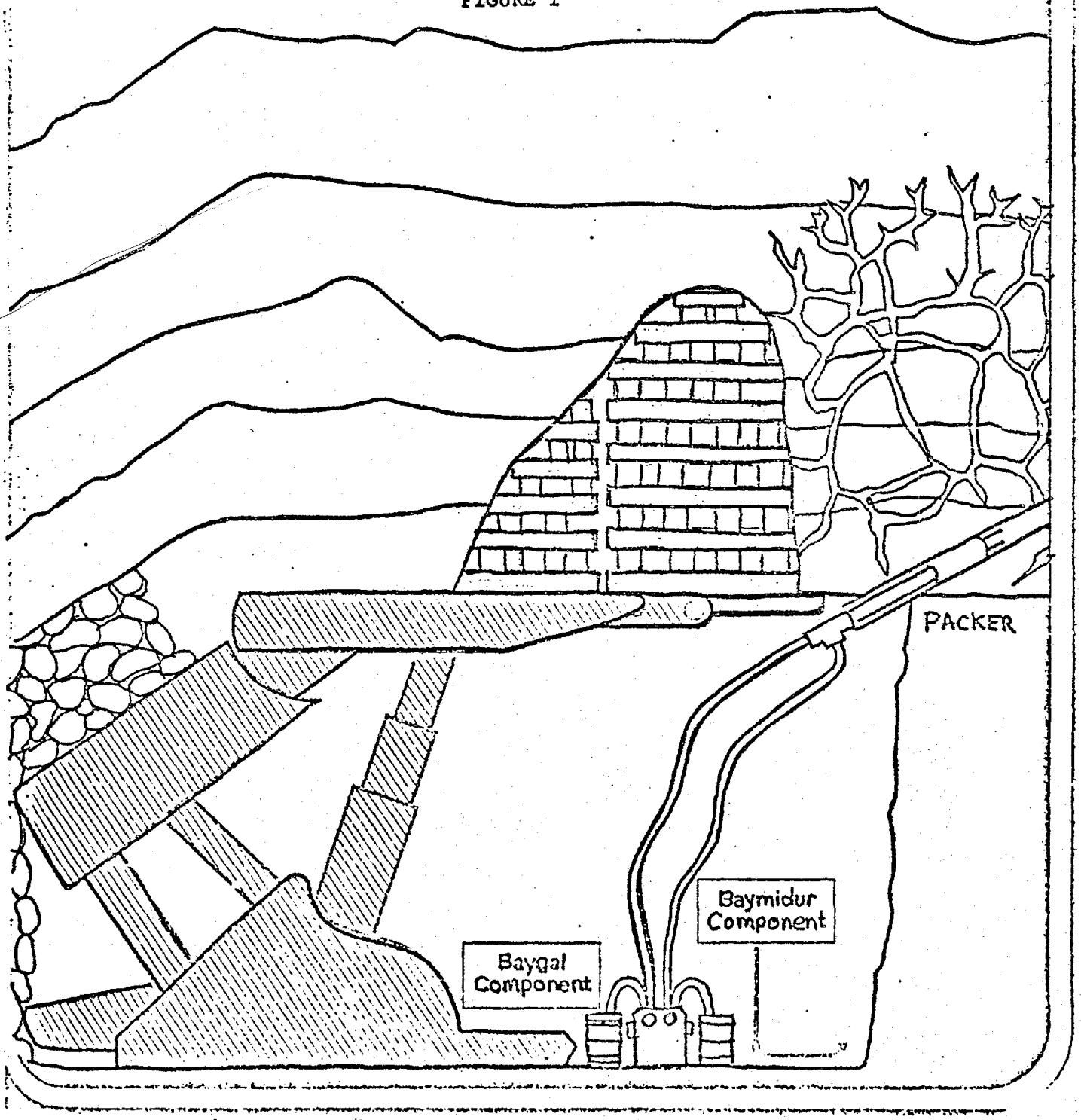
Binder B-3

for Consolidating Strata in Coal Mines

FIGURE I



General Information

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TABLE I

DIPHENYLMETHANE DIISOCYANATE (MDI) CONCENTRATIONS
AS DETERMINED BY THE MARCALI METHOD

Location	Sampling Time in Min. at 1.8 Liter Per Min.	Number of Samples At This Location	MDI Parts Per Million Parts of Air (ppm)
5 Feet Downstream From Hole #5, 5 Minutes Prior to Moving to Hole #6	58	1	ND*
20 Minute Ceiling 10 Feet From Hole #7, Downstream	21	1	ND
Area Near the Compressor Operator Breathing Zone. A 20 Minute Ceiling Downstream	20	3	ND
30 Feet Downstream From Hole #5 Started After All Injection is Completed	40	1	ND
50 Feet Downstream From Last Injection Point at Hole #5	40	2	ND
By Pump Man Clean-up Operation	25	2	ND

FIGURE II

DETECTABLE MDI CONCENTRATIONS FOR

VARIOUS TIMES

(Lower Limit Of Quantitation 0.0005 PPM)

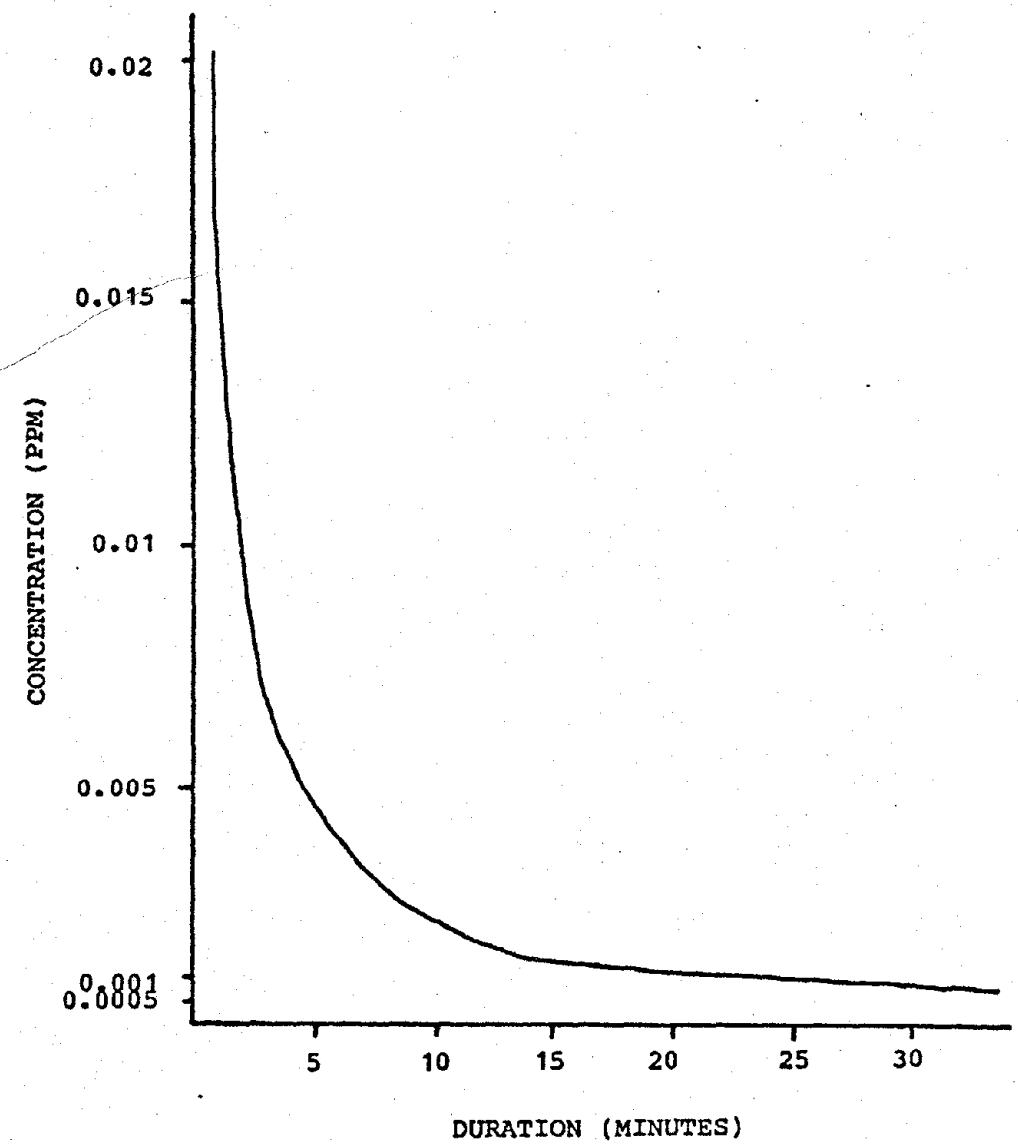

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TABLE I (con't.)

Location	Sampling Time in Min. at 1.8 Liters Per Min.	Number of Samples at This Location	ppm
80 Feet Upstream of Injection	60	5	ND
Upstream Approximately 60 Feet Away From Injection	60	5	ND
Approximately 4 Feet Upstream of Injection	62	3	ND
Approximately 15 Feet Downstream from Injection. Injection Process Stopped 45 Minutes Into the Sampling Period.	60	3	ND

MINIMUM DETECTION LIMIT	0.002 ppm
NIOSH RECOMMENDED LIMIT	0.005 ppm (50 ug/m)

* - Non-Detectable Concentrations

TABLE II

DIPHENYLMETHANE DIISOCYANATE (MDI) CONCENTRATIONS
AND PHENYL ISOCYANATE CONCENTRATIONS AS
DETERMINED BY THE NITRO REAGENT METHOD

Location	Sampling Time In Min. At 1.8 Liters Per Min.	Number of Samples At This Location	PPM MDI	PPM Phenyl Isocyanate
4 feet from injection of Hole At Room Height. 80 LBS. of Urethane Foam Injected. A Leak Did Develop. These Samples Are Downstream.	71	7	ND	ND*
Same Location As Above But Grouped On The Floor of the Mine.	64	3	ND	ND
20 Minute Ceiling At The Above Location.	20	1	ND	ND
Downstream of Hole #3, 20 Minute Ceiling With Much Urethane Leakage.	20	1	ND	ND
14 Feet Downstream of Hole #4.	60	3	ND	ND
20 Minute Ceiling Downstream From Hole #5. A Leak Developed Around Roof Cracks.	20	1	ND	ND
5 Feet Downstream From Hole #5, 5 Minutes Prior To Moving To Hole #6.	58	4	ND	ND
20 Minute Ceiling 10 Feet Downstream from Hole #7.	21	1	ND	ND

TABLE II (con't.)

Location	Sampling Time In Min. At 1.8 Liters Per Min.	Number Of Samples At This Location	PPM MDI	PPM Phenyl Isocyanate
20 Minute Breathing Zone Sample Downstream For Compressor.	20	1	ND	ND
30 Feet Downstream From Last Injection Point, At Hole #5.	60	1	ND	ND
50 Feet Downstream Of Last Injection Point At Hole #5.	60	2	ND	ND
By Pump Man, Personal Sample.	30	1	ND	ND
Area By Pump Man.	60	5	ND	ND
Injection Man Personal Sample.	60	1	ND	ND
Approximately 80 Feet Upstream of Injection.	60	5	ND	ND
Approximately 60 Feet Upstream of Injection.	60	5	ND	ND
Approximately 4 Feet In Front Of Injection Point.	62	3	ND	ND
Approximately 15 Feet Downstream From Injection Point, 45 minutes After Injection Process Had Stopped.	60	3	ND	ND

MINIMUM DETECTABLE LIMIT MDI = 0.0005 PPM PHENYL + 0.001 PPM

* - Non-Detectable Concentrations