REPORT OF SURVEY
AIRBORNE DIISOCYANATE DURING SPRAY APPLICATION OF POLYURETHANE FOAM
MATHIES MINE, FINLEYVILLE, PENNSYLVANIA

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U. S. Department of Health, Education and Welfare
Public Health Service
Division of Occupational Health
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REPORT OF SURVEY OF AIRBORNE DIISOCYANATE DURING SPRAY APPLICATIONS OF POLYURETHANE FOAM MATHIES MINE, FINLEYVILLE, PENNSYLVANIA FEBRUARY 22, 1963

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SUMMARY

Representatives of the Division of Occupational Health and the U. S. Bureau of Mines collected air samples for diphenyl methane diisocyanate during spraying of polyurethane foam on air stoppages at the Mathies Mines, Mathies Coal Company, Finleyville, Pennsylvania. Twenty-eight samples, covering 73 minutes of operation, were taken and analyzed. Concentrations as high as 5 milligrams per cubic meter (equivalent to 0.5 parts per million in the vapor state) were determined near the spraying. It was found that most of this contamination (over 95% of the high samples) was particulate material larger than a nominal 12 microns diameter. No vapor concentrations greater than 0.02 parts per million were found. Fifty feet or more from the operation total concentrations greater than 0.4 milligrams per cubic meter (0.04 parts per million) were not observed.

It is recommended that during all spraying:

1. All personnel within 50 feet of the spraying operation wear Bureau of Mines approved organic vapor respirators with particulate prefilters.

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2. Work be scheduled or arranged so as to minimize the exposure time of personnel downwind. All unnecessary exposures to spray and vapor should be avoided.

3. Skin contact with the unmixed components be avoided.

INTRODUCTION

The Toxicology Section, Research and Technical Services Branch, Division of Occupational Health has been conducting toxicological experiments on toluene diisocyanate for more than two years. A related compound, 4,4 diphenyl methane diisocyanate (MDI) is also being used as a component of polyurethane foams in some applications. A relatively recent development by the Bureau of Mines is the formation of foam on surfaces by spraying an MDI - polyol mixture which reacts in place.

Potential uses, principles of equipment and application methods for this foam were explained and foam application demonstrated during a visit to the U. S. Bureau of Mines experimental mine at Bruceton, Pennsylvania on July 25 and 26, 1962 by L. D. Scheel and H. E. Ayer. Samples taken during the demonstration application showed that detectable amounts of isocyanate were released. It was also noted that particulate concentration in the mine air increased during the foam application.

From September 17 to 21, 1962 a survey of an application of polyurethane foam was carried out by personnel of the Branch

of Health Research, U. S. Bureau of Mines, and of the Division of Occupational Health, U. S. Public Health Service in the Steward Mine of the Anaconda Copper Company, Butte, Montana.(1) During this survey MDI concentrations up to 0.3 parts per million (ppm) were found near the spraying operation, but concentrations greater than 0.02 ppm were not encountered at distances greater than 110 feet from the operation. By companion filtered samples it was determined that the MDI contamination was principally in the particulate form.

Upon a request from Mr. Donald Mitchell, Chief, Mines Experiment Section, Branch of Dust Explosions, U. S. Bureau of Mines we agreed to conduct a similar survey in an operating coal mine using commercial spray equipment. Mr. Mitchell made arrangements to conduct the survey on February 22, 1963. We were met on this date by the rest of the survey team; Messrs. Edwin Murphy, Chemical Engineer, Mine Experiments Section, Branch of Dust Explosions, U. S. Bureau of Mines, Bruceton, Pennsylvania and Harold A. Watson, Chief, Gas Analysis and Research Section, Branch of Health Research, Pittsburgh, Pennsylvania and conducted to the Mathies Mine of the Mathies Coal Company.

OPERATIONS

The Mathies Mine is a highly mechanized coal mine, producing from 5,000 to 15,000 tons per day of cleaned metallurgical

grade coal as scheduled by demand. Coal is won by continuous miners, transported by shuttle car to a conveyor belt, by the belt to mine cars, and by the mine rail system to the cleaning plant. The mine has purchased MSA "Rigiseal" spray equipment for applying polyurethane foam, principally for the construction of air seals. The foam is sprayed onto brattice cloth and adjoining ribs, roof and bottom to form an airtight seal capable of withstanding considerable air pressure. Messrs. George L. Alston, Ronald Black and Paul Becker of the Mine Safety Appliances Company, Pittsburgh, Pennsylvania, were present to clean the equipment, place it in operating condition, and demonstrate its operation by the application of foam to a series of brattice cloth stoppings which had previously been erected. The system is advertised to cover 18 square feet per minute with a layer one inch thick; it was observed that a seven by eighteen foot brattice was actually covered and sealed at the edges in from eight to thirteen minutes of spraying time.

The foam applications were made to both sides of each of the framed brattice cloth walls which formed an airlock, and to one side of each of six brattice cloth air stoppages between two parallel airways. Each stoppage was in a cross-section of approximately seven by eighteen feet. At the airlock, a total of 12,000 cubic feet per minute (cfm) of air was flowing through the

space above the belt and the open doors with a velocity of 500 feet per minute (fpm). The air stoppages were 15 to 42 feet from the main passageway through which air flow was maintained. Air velocity in the section in which the first series of samples was taken was 60 fpm (airflow = 5,800 cfm); it was 120 fpm (airflow = 11,000 cfm) in the section in which the second series was taken. Air velocities in the sections being closed were not measurable. Air temperatures were 56 - 58 °F.

All operations were conducted under the supervision of Mr. Bob Lauder, General Superintendent and Mr. Bill Kabblish, Underground Superintendent, Mathies Mine. Mr. C. William Parisi, Safety Director, Pittsburgh Coal Company also cooperated and assigned Mr. William Blacka to assist with the sampling. Airflow measurements and temperatures were furnished by Mr. Blacka.

SAMPLING METHODS

Because the metal mine application had demonstrated that a major portion of the airborne MDI was in a particulate form, sampling was designed to measure both total and vapor phase MDI, thus determining the particulate MDI by difference. Midget impinger pumps, adjusted for eight inches of water vacuum were used as the sources of suction, each for two midget impingers in parallel. A Millipore aerosol field monitor (37 mm type AA Millipore filter in a plastic holder) was used as the pre-filter for one impinger. Another field monitor was used between the

other impinger of the pair and the pump to balance the flow at approximately 1.1 liters per minute per midget impinger.

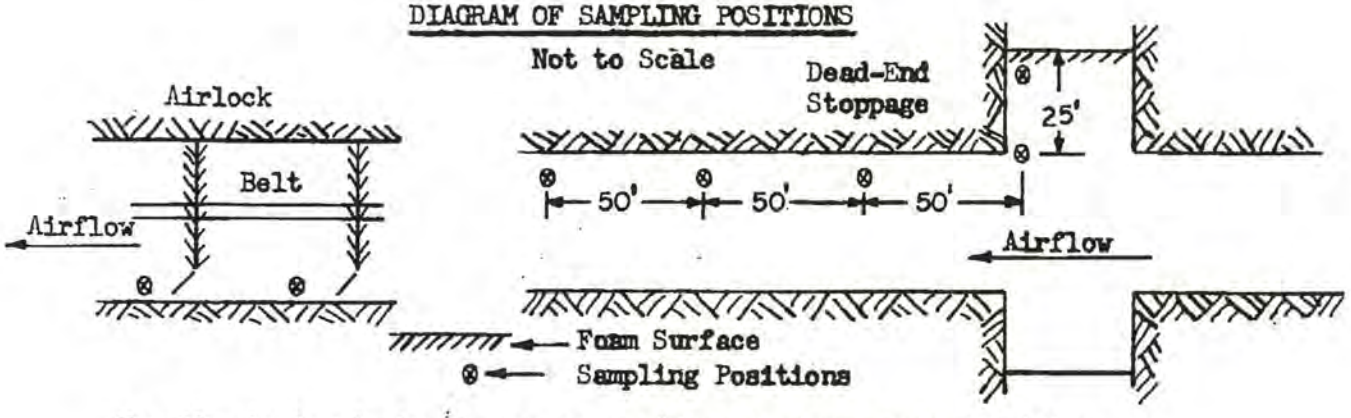
Additional information on particulates was obtained by preceding a Greenberg-Smith impinger with a two-stage cascade impactor for one sample, and preceding an impinger with a 4-stage cascade impactor for another sample. The suction source for each of these trains was a Roberts hand-cranked pump operated at 36 revolutions per minute. Flow was 21 liters per minute (lpm) through the Greenberg-Smith impinger alone, 20 lpm through the first two stages of a Laskin impactor(2) followed by an impinger, and 12 lpm through the four stages of a Unico cascade impactor followed by an impinger. Assuming unit density for the particulate, May's data(3) gives a stage particle diameter at 20 lpm of approximately 12 microns for stage two, while Lippmann's(4) calibration of the Unico cascade impactor gives a stage mass median diameter of 3.3 for stage four at 12 lpm. Each cascade impactor - impinger sample was taken adjacent to and simultaneous with a filtered-unfiltered midget impinger pair so that the particulates retained on the impactor could be determined by difference. To check the relative efficiency of the samplers, a third Greenberg-Smith impinger sample at 21 lpm was taken adjacent to a midget impinger pair. A 0.4 M acetic acid - 0.4 M hydrochloric acid solution was used as the sampling reagent in all cases, using 15 ml in the midget impingers and 100 ml in the Greenberg-Smith

impingers. Analyses were made by the Marcali method.(5) Color intensity was ready by a Bausch and Lomb Spectronic 20 colorimeter at 550 mμ in matched test tubes. The calibrations, which were furnished by H. A. Watson, had been against pure MDI.

SAMPLING PROGRAM

During foam applications to the airlock, a 25 minute Greenberg-Smith impinger sample was taken about 15 feet downwind from the air lock door. This sample was taken during part of the application to the first surface and the entire application to the other three as illustrated below (spraying proceeded from the upwind side of the upwind airlock barrier to the downwind side of the downwind barrier). A midget impinger sample was taken during the final 17 minutes of the above operation.

DIAGRAM OF SAMPLING POSITIONS



For the dead-end air stoppages, a midget impinger pair was taken at about six feet from the stoppage, others were at 25 feet, 75 feet, 125 feet and 175 feet downwind from the stoppage as diagrammed

on the preceding page. Two series of samples were taken. The first series included two successive samples at the six foot position during which one continuous sample was taken at each of the other positions, that is; 25, 75, 125 and 175 feet downwind. The second series included one sample at the six foot position, accompanied by two simultaneous samples at the 25 foot position and one each at the 75 and 125 foot positions. Sampling was conducted only while spraying was taking place, and the sampling positions were moved to similar relative positions when the spraying system was moved to successive stoppages. The first sample at the 6 foot position in the first series was accompanied by a 2-stage cascade impactor-impinger sample, the second sample at the six foot position of the first series was accompanied by a 4-stage cascade impactor-impinger sample, and the sample at the 6 foot position in the second series was accompanied by a Greenberg-Smith impinger sample.

RESULTS

Sample results are presented in the table on the following page.

DISCUSSION OF RESULTS

None of the samples taken would represent exactly the exposure of a particular miner under normal application conditions. The samples at the airlock would, however, approximate the exposure of men a short distance downwind; the man using the spray

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SAMPLE RESULTS

Location	Sample Type	Total MDI Concentration	
		mg/m^3(1)	ppm(2)
Airlock Door	Greenberg-Smith Impinger	0.1	0.01
	Midget Impinger(3)	0.3	0.03
	Filtered Midget Impinger(3)	0.1	0.01
Dead-End Stoppages	First Series		
6 feet away	Midget Impinger	3.1	0.3
	2 stage Cascade Impactor + Greenberg-Smith Impinger	0.06	0.006
	Filter + Midget Impinger	0.1	0.01
	Midget Impinger	4.9	0.47
	4 stage Impactor + Greenberg-Smith Impinger	0.03	0.003
	Filter + Midget Impinger	0.1	0.01
25 feet away	Midget Impinger	1.0	0.1
	Filter + Midget Impinger	0.07	0.007
75 feet away	Midget Impinger	0.4	0.04
	Filter + Midget Impinger	0.05	0.005
125 feet away	Midget Impinger	0.20	0.02
	Filter + Midget Impinger	0.04	0.004
175 feet away	Midget Impinger	0.30	0.03
	Filter + Midget Impinger	0.00	0.00
	Second Series		
6 feet away	Midget Impinger	3.2	0.30
	Greenberg-Smith Impinger	4.2	0.40
	Filter + Midget Impinger	0.2	0.02
25 feet away	Midget Impinger	0.5	0.05
	Midget Impinger	0.4	0.04
	Filter + Midget Impinger	0.1	0.01
	Filter + Midget Impinger	0.01	0.001
75 feet away	Midget Impinger	0.3	0.03
	Filter + Midget Impinger	0.06	0.006
125 feet away	Midget Impinger	0.05	0.005
	Filter + Midget Impinger	0.05	0.005

(1) Milligrams MDI per cubic meter of air
(2) Parts per million by volume calculated as if all MDI were vapor
(3) Vacuum gauge failed during sample; sample volume uncertain

gun would have a considerably larger potential exposure, and exposures upwind would be negligible. At the dead-end stoppages, the potential exposure of the gun operator would be at least as high, perhaps higher than those indicated by the six foot samples. The 25 foot results might be typical of a man tending the spray equipment, and the downwind samples indicate the dilution and reaction of the MDI. Although the number of samples are too limited to draw definite conclusions, the data suggest that the airborne MDI decreases with a half-period of 0.7 minute; this rate would reduce the particulate concentration to 10% of the original amount in less than 2-1/2 minutes. Whatever contamination occurs as vapor would persist for longer periods of time. With the concentrations, temperature, reaction mix, and airflows observed in this survey, one would not expect the concentration to exceed 0.2 mg/m^3 (0.02 ppm) more than 350 feet from the spraying site. If spraying is done at lower temperatures, distance of contamination would be increased; at higher temperatures the distance would be lessened.

The companion unfiltered, cascade-impactor-preceded, and filter-preceded samples demonstrated not only that the greatest amount of contamination occurs in the particulate form, but that over 95%, by weight, of the MDI is present in particles larger than the nominal stage 2 diameter of 12 microns. (It might be noted that the low quantities of MDI in the filtered samples were near the limit of sensitivity of the colorimetric method, so that

precision was low in these samples; larger sample volumes gave greater precision to the Greenberg-Smith impinger sample results.)

RECOMMENDATIONS

Because high concentrations were encountered at dead-ends, it is recommended that all those applying foam or working within 50 feet of the application wear Bureau of Mines approved organic vapor respirators, with particulate prefilters, during all spray operations. Further precautions may become necessary if any of those working with the material develop reactions or symptoms of intoxication.

Operations should be arranged so that work progresses in an upwind direction, potential exposures downwind should be minimized by appropriate scheduling of operations.

Skin contact with the components, particularly the isocyanate component, should be avoided, as should any unnecessary exposure to spray or vapor.

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