Applied Occupational and Environmental Hygiene

ISSN: 1047-322X (Print) 1521-0898 (Online) Journal homepage: https://www.tandfonline.com/loi/uaoh20

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To cite this article: Mark F. Boeniger (1991) Nonisocyanate Exposures in Three Flexible Polyurethane Manufacturing Facilities, Applied Occupational and Environmental Hygiene, 6:11, 945-952, DOI: 10.1080/1047322X.1991.10387996

To link to this article: https://doi.org/10.1080/1047322X.1991.10387996

Nonisocyanate Exposures in Three Flexible Polyurethane Manufacturing Facilities

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Although toluene diisocyanate (TDI) has been widely used for about 50 years, industrial hygiene characterizations of other chemical exposures used in conjunction with TDI have generally received much less attention. As part of a retrospective, cohort mortality study, industrial hygiene evaluations were performed in three facilities manufacturing flexible (TDI-based) foam. This report is concerned only with nonisocyanate exposures in that industry.

In each facility, the concentrations of several air contaminants, other than TDI, were assessed, including aliphatic amines, nitrosamines, nitrogen dioxide, thermal degradation products, organic solvents, polyurethane dust, and flame retardants. Air samples were also collected for subsequent assay of mutagenic activity using *Salmonella* bacterial tester strains TA98 and TA100.

Workers were found to have respiratory and probably dermal exposure to methylene chloride in each facility. Traces of nitrogen dioxide and some aliphatic amines were evident. However, *N*-nitrosamines were not found. Exposure to thermal degradation products, polyurethane dust, and to flame retardants does not appear to be a problem under reasonable hygienic conditions. However, evidence for the existence of acrolein and acrylonitrile was found in one facility due to the thermal degradation of finished foam. Mutagenic activity, appearing only in the particulate fraction, appeared highest when the total isocyanate group air concentrations (TRIG) were also high. In one facility, the mutagenic activity was up to 75 times higher than the mutagenic activity of the outside air. The methods used to characterize each of the exposures are provided and the results are discussed.

Boeniger, M.F.: Nonisocyanate Exposures in Three Flexible Polyurethane Manufacturing Facilities. Appl. Occup. Environ. Hyg. 6:945–952; 1991.

Introduction

In 1984, the Industrywide Studies Branch, National Institute for Occupational Safety and Health (NIOSH), initiated a retrospective, cohort mortality study of workers exposed to toluene diisocyanate (TDI). Workers in flexible foam manufacturing plants were selected to comprise the cohort since they generally had the fewest confounding exposures and they met the requirements of latency and record completeness. Although exposures in these plants were predominantly to TDI, other chemicals were sometimes used that might complicate the interpretation of the epidemiologic results. For this reason, other chemical exposures were also assessed which were suspected of having chronic or permanent effects on workers' health. This article presents the results of these assessments in three factories manufacturing TDI–polyol-based flexible foam. These same facilities were described more fully in a companion report on air concentrations of TDI and total reactive isocyanate group (TRIG).(1)

Two of the facilities, referred to as facilities A and B, manufacture molded, flexible foam parts for the automobile industry. The third facility, referred to as facility C, is a large slab foam facility that makes carpet cushioning, furniture, and bedding materials, as well as parts for the automobile industry. In facility C, all end products are fashioned by cutting and mechanically shaping the slab stock. At the time of this study, all of the facilities were large, employing between 150 and 450 production workers.

Survey Methods

Eight nonisocyanate chemical classes were identified as candidates for environmental assessment after a search of the process-related literature on the flexible polyurethane foam manufacturing industry. Selection of these chemicals was predominantly determined from a knowledge of the industry rather than finding reference to the chemicals in the occupational health literature. The agents chosen all shared the potential for being present and for possessing the potential to cause permanent adverse health effects. In some cases, the evidence for either the presence of the compound or its chronic toxicity was inconclusive or tenuous. Nevertheless, it was intended that all potential exposures which could lead to long-term impairment of health should be identified.

The eight selected classes of compounds and the sampling and analytical methods used for their determination are provided in Table I. In summary, air samples for organic solvents, especially methylene chloride, were collected due to the recent evidence of its carcinogenicity in rodents and the long-term use of this solvent in this industry. Samples for aliphatic amines were collected since

TABLE I. Sampling and Analytical Methods Used in Study of Flexible Polyurethane Manufacturing Facilities

Compound	Sampling/Analysis	Reference
Solvents	Charcoal/GC	45
Aliphatic amines	Acid Impinger/GC	24, 25
N-Nitrosamines	Thermosorb/N/GC-TEA	3
Nitrogen dioxide	Passive Reactive Collection/Spectroscopy	45
Toluenediamine	Reagent Impinger/HPLC	26
Flame retardant compounds		
2,3-Dibromopropanol	Carbotrap/GC	27
1,3-Dichloroisopropyl	Filter + Tenax/GC	28
Respirable dust	Filter + Cyclone/Weighing	47
Thermal decomposition products		
Acrylonitrile	Charcoal/GC	48, 49
Pyridine	Charcoal/GC	50
Acrolein	Special XAD-2/GC	51
Vinyl chloride	Charcoal/GC	52

at least one has been experimentally associated with carcinogenic or mutagenic effects.(2) In addition, amines may react in the factory air with nitrogen dioxide, if present, to form potentially carcinogenic nitrosamines.(3) Nitrogen dioxide could result from in-plant space heating, gas curing ovens, or thermally degraded foam. To evaluate the occurrence of nitrosamines and their precursors, all three of the above possible air contaminants were evaluated during the surveys.

Several references were found in the literature suggesting the hydrolysis of TDI to its corresponding amine, toluenediamine.(4–6) Since toluenediamine has been indicated to be a carcinogen in rodents, air and bulk dust samples were collected to determine the presence or absence of the chemical in these facilities.(7) Many of the flame retardant compounds have been found to be mutagenic or carcinogenic.(8–11) Therefore, where they were in use, air samples were taken. There is evidence (although inconclusive) that respirable foam dust may cause permanent lung damage over extended time.(12–14) Therefore, the personal air concentrations in the dustiest jobs were evaluated.

There was further concern that the foam might undergo thermal decomposition while in hot curing ovens or when cut with electric inductively heated tools.(15–19) After searching the literature, it was decided that air samples for acrylonitrile, pyridine, acrolein, and vinyl chloride would be collected.

Finally, the mutagenic activity of air was assessed using the Ames assay since it may detect potentially carcinogenic products that standard industrial hygiene chemical determinations might overlook. Studies on the combustion toxicity of various common materials have discovered that flexible polyurethane foam thermally decomposes to mutagenic products.(20) In addition, TDI monomer may be mutagenic in certain test assays.(21)

Most of the sampling and analytical procedures used in this evaluation are established methods. A summary of the sampling and analytical methods is provided below only for those compounds which required method development or the modification of published methods.

Aliphatic Amines

General air samples for aliphatic amines were initially collected in the center of all major work departments. The air samples were collected using Thermosorb/A® tubes (Thermedic, Inc.) and large silica gel sampling tubes (SKC, Inc.). Air was drawn at a flow rate of up to 3 L/min and 1 L/min, respectively, for 5 to 10 hours. The sample media in the Thermosorb/A tube consists of a proprietary dry absorbent.(22) Analysis was performed by extracting the sorbent with methanolic potassium hydroxide and injecting an aliquot into a gas chromatograph with a thermal energy analyzer (TEA) set in the nitrogen mode (unpublished). This analytical method is suitable for quantitation of aliphatic amines in air at the parts-per-billion level.

In a follow-up survey in factory A, aliphatic amines were sampled simultaneously from air in pairs of samples consisting of a midget impinger containing 15 ml of Marcali solution and a Thermosorb/A tube.(23) Eight sample pairs were run at a flow rate of about 1 L/min for equal lengths of time. The impinger sampling method and a gas chromatographic analytical method used to analyze the impinger solutions were adapted from previously reported studies.(24,25)

N-Nitrosamine Compounds

Air samples for *N*-nitrosamine compounds were obtained using Thermosorb/N® tubes (Thermedics, Inc.). The samples were analyzed by desorption with methylene chloride and methyl alcohol (1:4) and the eluent injected into a gas–liquid chromatograph with a TEA detector.(3) This method is very specific and sensitive for determining volatile *N*-nitrosamine compounds. Nonvolatile *N*-nitrosamine bulk dust samples were analyzed using a high-performance liquid chromatograph (HPLC) with an ultraviolet detector (unpublished). The bulk dust samples were extracted three times with 5 ml of dichloromethane (DCM). The extracts were combined and dried over anhydrous sodium sulfate, filtered, and the sodium sulfate washed two times with fresh DCM. The combined extracts were concentrated on a Kuderna–Danish evaporator using isooctane as a keeper, to a volume of 1 ml. All bulk samples were submitted for mass spectrometric analysis. Recovery of spiked dimethylnitrosamine into the bulk dust samples over the range 25–500 mg per sample was better than 95 percent.

Toluenediamine

Area air samples for toluenediamine (TDA) were collected in a midget impinger containing 1-(2-methoxyphenyl)piperazine in toluene. Because TDI might hydrolyze in the sample to TDA, this solution was used to stabilize any TDI that might also be present in the air. The samples were analyzed using a HPLC and any suspect peaks were submitted to mass spectrometric analysis.(26)

Bulk settled dust samples were also collected in glass vials. The bulk samples were extracted with methanol, centrifuged, and any amines present were derivatized with acetic anhydride. The HPLC procedure used above was used for the preliminary determination of both the 2,4- and 2,6-isomers of TDA. Confirmation of chromatograph peaks corresponding to TDA was performed by mass spectral analysis.

Flame Retardant Compounds

Area air samples were collected to determine two flame retardant chemicals in two of the three factories. Facility A uses 2,3-dibromopropanol at their hot cure foam line. Sampling and analysis of 2,3-dibromopropanol was performed using a Carbotrap sorbent tube through which air was drawn at 200 cc/minute for 5 hours and analyzed on a gas chromatograph. The analytical limit of detection for these samples was 4 μg per sample.(27) At facility C, tris (dichloroisopropyl) phosphate ("Tris") is added to the foam during formulation. "Tris" was sampled using Stauffer Company Method 230.(28) The sampling medium consisted of a mixed cellulose ester fiber filter followed by a Tenax sorbent tube. Analysis was performed on a gas chromatograph with a flame-ionization detector.

Mutagenic Activity

Particulate air samples for mutagenic assays were collected on 4-inch, type A/E, High-Vol filters. Vapors and gases for mutagenic assay were collected by a sorbent cartridge containing 5 cc each of charcoal, Tenax-GC, XAD-2, and magnesium silicate. Both indoor and outdoor samples were collected at each plant site so that the degree of in-plant activity could be differentiated from ambient pollution. The standard plate incorporation test (Ames assay) was used with bacterial tester strains TA98 and TA100 of *Salmonella typhimurium*, with and without metabolic activation.(29) Four concentrations of each extract were tested and two plates were used for each concentration. Additional details of these tests are described elsewhere.(30)

Chemicals for which there are NIOSH recommended exposure limits (RELs), American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit values (TLVs), or U.S. Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs) are provided in Table II. These evaluation criteria are provided solely for comparison to this study's results. Evaluation criteria have not been established for all the compounds that were measured in this study. It should also be recognized that such criteria may not always incorporate the most recent and significant data.

TABLE II. Exposure Evaluation Criteria for Possible Exposures in the Polyurethane Foam Manufacturing Industry

Compound	ACGIH TLV[A] (mg/m³)	OSHA PEL[B] (mg/m³)	NIOSH[C] (mg/m³)
2,4-Toluene diisocyanate	0.04 (8-hr) 0.14 (15-min)	0.04 (8-hr) 0.15 (15-min)	LFL[D]
Acrylonitrile	4.3 (8-hr)	4.3 (8-hr) 21.7 (15-min)	2.2 (8-hr) 21.7 (15-min)
Methylene chloride	103 (8-hr) 207 (15-min)	1740 (8-hr) 3476 (15-min)	LFL[E]
Vinyl chloride	13 (8-hr)	2.6	LFL
Pyridine	16 (8-hr)	15	
Acrolein	0.23 (8-hr) 0.69 (15-min)	0.25 (8-hr) 0.8 (15-min)	
Nitrogen dioxide	5.6 (8-hr) 9.4 (15-min)	1.8 (15-min)	1.8 (15-min)
Diethanolamine	13 (8-hr)	15 (8-hr)	

[A] 1990–1991 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. American Conference of Governmental Industrial Hygienists, Cincinnati, OH (1990).

[B] Occupational Safety and Health Standards. 29 CFR V. Sec. 1910.1000, Air Contaminants. Revised by 54 FR 2920, January 19, 1989.

[C] NIOSH Pocket Guide to Chemical Hazards. DHEW (NIOSH) Pub. No. 78-210. NIOSH, Cincinnati, OH (September 1985).

[D] NIOSH Current Intelligence Bulletin 53, Toluene Diisocyanate (TDI) and Toluenediamine (TDA). DHHS (NIOSH) Pub. No. 90-101. NIOSH, Cincinnati, OH (1990).

[E] NIOSH Current Intelligence Bulletin 46, Methylene Chloride, DHHS (NIOSH) Pub. No. 86-114. NIOSH, Cincinnati, OH (1986).

LFL = Lowest Feasible Limit, Regard as Suspected Human Carcinogen.

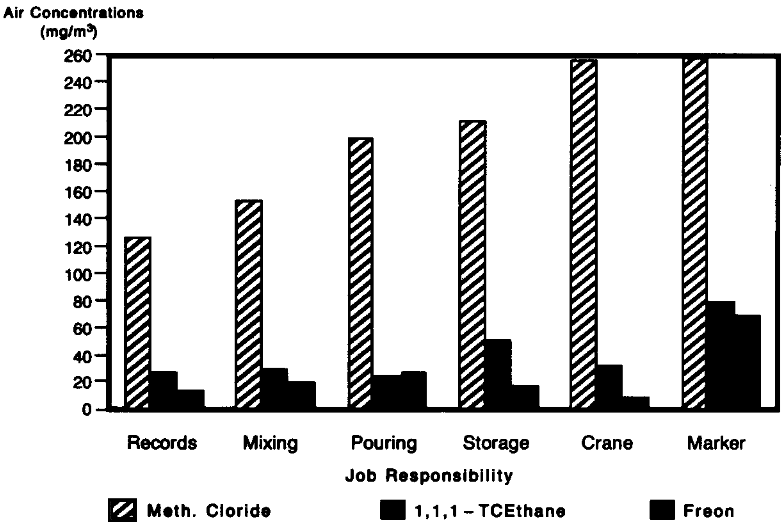

FIGURE 1. Air concentrations of solvent vapors among pouring line workers in facility C.

Survey Results

Organic Solvents

At the time of the surveys, methylene chloride was used in facility A on two pouring lines as a nozzle flush, glue solvent, and mold release solvent. Facility C used methylene chloride as a foaming agent in making slab foam and as a nozzle flush and general cleaning solvent. Methylene chloride was also found as a contaminant in the solvent of the glue used to repair many finished products in facility C.

In facility A, workers' exposures resulting from using methylene chloride as a nozzle flush were below 13 mg/m^3. However, repair workers using glues had exposures ranging from 20 to 455 mg/m^3, while a worker spraying the mold release agent was exposed to 46 mg/m^3. In facility C, methylene chloride, 1,1,1-trichloroethane, and trichlorofluoromethane were used in the pouring department as blowing agents and cleaning solvents. The mean exposures to these solvents for workers on the pouring line and slab storage room are depicted in Figure 1. One mixing head operator had measured exposures of 576, 214, and 212 mg/m^3, respectively, for each of the three solvents during a 72-minute period. In the slab storage rooms, levels exceeded 370 mg/m^3 in some areas. Finishing workers using glues had exposures of 12–15 mg/m^3 methylene chloride, 11–44 mg/m^3 of 1,1,1-trichloroethane, and 16–18 mg/m^3 of fluorotrichloromethane (two samples taken). A portion of this exposure may result from the gradual release of the volatile residual foaming agent that was used in manufacturing the foam. In some jobs, skin exposure to methylene chloride probably occurred.

Aliphatic Amines

Aliphatic amines were not detected in any of the facilities using the Thermosorb/A sampling tubes or large silica gel sampling tubes. However, acid-filled impingers used in facility A in conjunction with the Thermosorb/A tubes found two amines, 1,4-diazabicyclo(2,2,2)octane (DABCO or triethylenediamine) and 2,2-oxybis(N,N-dimethyl)ethyl amine. Both amines were detected in appreciable amounts. DABCO concentrations in facility A ranged from 40 to 616 μg/m^3. The highest air concentrations were near the foam crusher units where corneal opacity and halovision was most often reported. 2,2-Oxybis(N,N-dimethyl)ethyl amine concentrations ranged from nondetectable to 1374 μg/m^3. Again, the highest concentration was found near the foam crusher units. The reason for the inability of the Thermosorb/A sampling method to detect amines during these surveys has not been established. Repeat surveys in facilities B and C using acid-filled impingers were not performed. Therefore, the comparison of methods raises concern about the collection efficiency of the Thermosorb/A method and the results obtained with this method.(23)

N-Nitrosamines

A total of nine air samples and five bulk scraped dust samples were collected and analyzed for volatile and nonvolatile *N*-nitrosamines, respectively. The limits of detection of *N*-nitrosamine compounds in air and in the bulk samples were 10 ng per sample and 10 ng per ml of extract, respectively. *N*-Nitrosamine compounds were not detected in any of the samples. Since most air sample volumes exceeded 1 m^3, the corresponding limit of detection in air was less than 10 ng/m^3. Two additional air samples and two bulk samples were also submitted to a private laboratory to determine *N*-nitrosourea compounds.(31) These samples were collected in facility B. The analysis (using an unpublished method) did not detect the presence of nitrosoureas or other nitroso compounds. The analysis did detect an unknown nitrogen-containing compound in the bulk samples that accounted for about 10 percent (by weight) of the samples.

Nitrogen Dioxide

The sampling results concerning nitrogen dioxide (NO_2) are summarized in Table III. The extended period air con-

TABLE III. Summary of Nitrogen Dioxide Air Concentrations for Three Facilities (mg/m^3)

Facility	Number Samples	Mean	Range	Standard Deviation
A	9	0.7	0.4–1.1	0.2
B	5	ND*	—	—
C	13	0.5	0.4–0.6	0.1

*The limit of detection for this set of samples was approximately 0.75 mg/m^3.

centrations of NO_2 in all operations were consistently lower than the former OSHA permissible exposure limit of 25 mg/m^3 (OSHA has since revised the PEL to 1.8 mg/m^3 for 15 minutes). The highest extended period air sample results for NO_2 were collected in facility A and revealed concentrations that ranged from 0.4 to 1.1 mg/m^3. These exposures may be related to the use of natural gas direct-heating units throughout the facility and to gas-heated curing ovens.

Toluenediamine

Twenty air samples and two bulk settled dust samples were collected during the three surveys for the determination of the two isomers of toluenediamine (TDA). The level of detection (LOD) for TDA in the air samples was 0.2 μg/m^3. In the bulk dust samples, as little as 0.6 μg of 2,4-TDA and 0.4 μg of 2,6-TDA per gram of sample could have been detected.

Although other unidentified compounds were seen in the chromatogram, TDA was not present in either the air or bulk scrape samples.

Flame Retardants

Spiking and recovery evaluations of the methods used to collect both flame retardant compounds indicated a recovery efficiency of about 100 percent. The LOD in air under the conditions used was 0.1 mg/m^3 (0.02 ppm) for 2,3-dibromopropanol and 0.25–1 mg/m^3 (0.1–0.06 ppm) for tris(dichloroisopropyl) phosphate. Detectable levels of the flame retardants were not found in any of the samples.

Respirable Dust

Respirable dust exposures in even the dustiest operations, e.g., buffing and mechanical sanding, were all substantially less than the current nuisance dust exposure criteria allow. In facility A, the respirable dust concentrations determined for seven finishing operators ranged from 0.19 to 0.72 mg/m^3 (mean = 0.45). In facility B, the respirable dust exposures to six workers ranged from 0.05 to 0.66 mg/m^3 (mean = 0.21). Personal respirable dust exposures among six finishing workers in facility C ranged from 0.14 to 0.57 mg/m^3 (mean = 0.34).

Thermal Decomposition Products

The minimal air detection limits for the compounds sampled were as follows: acrolein, 0.01 mg/m^3; acrylonitrile, 0.2–0.7 mg/m^3; vinyl chloride, 0.01–0.6 mg/m^3; and pyridine, 0.08–0.1 mg/m^3. None of the four possible decomposition products sought in facility A were found in any of the area air samples. In facility B, where the hot iron tool was used, only elevated TDI air concentrations were detected.(1) In facility C, trace amounts of acrolein and acrylonitrile were detected in the exhaust stack that contained the smoke removed from several hot wire cutting tools. These manually guided cutting tools utilize a resistance-heated wire that burns a clean cut through the foam. Each cutting unit is locally exhaust ventilated to the roof through rigid ductwork. The exhaust air was found to contain concentrations of 0.3 mg/m^3 for acrylonitrile and 0.02 mg/m^3 for acrolein. Since the exhaust air probably contained most of the thermal decomposition product emissions, personal exposures were expected to be extremely low to nondetectable.

Mutagenic Activity

The mutagenic activity of the extracts from the particulate collected within each facility was greater than the samples collected outside. This finding remains valid whether the sample results were compared by equal air volumes (revertants/m^3) or by equal particulate masses (revertants/g). Mutagenic activity was not found in any of the sorbent extracts, indicating that the mutagenic activity was limited to particulates. In addition, the mutagenic activity seen was only in the TA98 tester strain, indicating (DNA) frame-shift mutations. Mutagenic activity, although seen without enzyme activation with S9, was enhanced when S9 was added. Summary data on the mutagenic activity in each facility are presented in Table IV.

A positive mutagenic response was recognized when the test extract produced at least twice the number of revertants as the negative test agent or a blank filter (whichever was greater) and also an increase in the number of revertants with increasing concentration. In calculating the number of revertants observed per unit particulate mass or unit air volume, a rather stringent process was used. First, the number of spontaneous revertants in the negative control agent or blank filter test was subtracted from the field sample results. Next, the mutagenic response from several dilutions of each sample collected in each facility were plotted against dose on graph paper. Because toxicity in the bacterial test assay may diminish the mutagenic response and because the toxicity increases with concentration, a single unit mass or volume was selected where toxicity was not observed and most sample responses produced a linear dose-related response. This procedure was

TABLE IV. Mutagenic Activity of Air Inside and Outside Polyurethane Foam Factories

Facility	Number of Indoor Sample Sites	Outside Air		Inside Air	
		r/mg[A]	r/m^3[B]	r/mg	r/m^3
A	9	30	0.6	154	45
B	2	12	1.3	43	8
C	5	21	3	240	39

[A] Average revertants per milligram of particulate.
[B] Average revertants per cubic meter of air.

felt to minimize the response bias introduced by bacterial toxicity. This procedure should result in improving the validity of making comparisons between samples and sample locations; therefore, it was used within this article to express the mutagenicity results.

At facility A, the outside air was found to have virtually no mutagenic activity. At facility B, the outside air was found to be slightly mutagenic since the number of revertants in the largest air sample was exactly twice the negative control value. At facility C, the outside air, collected on separate days, had 2.3 and 4.0 times more mutagenic activity than the negative control values. Facilities A, B, and C were located in a rural farming area, an industrial area, and an urban industrial area, respectively.

Inside facility A, the mutagenic activity of an indoor unit-mass of particulates (i.e., revertants/g) was clearly higher than an equivalent mass of outside particulates. Furthermore, an equivalent volume of indoor air was about 75 times more mutagenic (Tables IV and V). Thus, in the above case, both the greater quantity of particulate plus the higher inherent mutagenic activity per unit-mass of particulate found within the factory contributed to the higher mutagenic activity than was found in outside air. Similar results were found in factories B and C. The highest mutagenic activity in facility C was found near the hot wire cutting operation in a finishing department. Mutagenic activity was found to be lower elsewhere in the facility.

Since mutagenic activity was limited to the particulate samples, it was considered whether the particulate could be identified based on a correlation with any of the industrial hygiene data. However, only the total reactive isocyanate group (TRIG) samples could be capable of collecting particulates. Biologically, it would seem plausible that reactive isocyanate groups attached to high molecular weight molecules might be at least partly responsible for the frame-shift mutations seen in the mutagenic assays. Unfortunately, at the time of the surveys, few TRIG samples were collected next to the samples collected for mutagenic assay. Because of the small number of paired samples for TRIG and mutagenic activity and a lack of reliance on the TRIG data, it was felt that determination of a correlation was not presently appropriate. Thus, additional sample data will be needed to determine the relationship between TRIG particulates and mutagenic activity.

Discussion

NIOSH researchers have recently reviewed the animal bioassay data on methylene chloride. As a result, NIOSH has recommended that methylene chloride be treated as a potential human carcinogen and that worker exposure be controlled to the lowest feasible level.(32) Methylene chloride was found to be carcinogenic in rats and mice when exposed via inhalation.(33) Methylene chloride has multiple uses as a nozzle flush, glue solvent, and foaming agent. Methylene chloride was detected in each of the three facilities surveyed. In facility B, methylene chloride had been replaced with 2,2,4-trimethyl-1,3-pentanediol diisobutyrate as a nozzle flush. In facilities B and C, methylene chloride was detected in the air near the glue patching operations where none was believed to be used. In such situations, when the exact identity of solvents in a product are not known, it is prudent to check either by taking air samples or by analyzing the bulk material.

TABLE V. Mutagenic Ratio of Indoor to Outdoor Air

Facility	r/mg[A]	r/m³[B]
A	5:1	75:1
B	3.5:1	6:1
C	11:1	13:1

[A] Average revertants per milligram of particulate.

[B] Average revertants per cubic meter of air.

Other solvents encountered in this study include trichlorofluoromethane, which was used as a blowing agent and in cold-patch resin formulations, and 1,1,1-trichloroethane, which was used as a solvent in glue. Although presently these solvents appear relatively safe, particularly regarding chronic effects, substantial exposures could have narcotic effects on workers and can both impair work performance and increase employees' risk of accidents.(34)

With respect to the findings reported here, it is suggested that not all aliphatic amines may be efficiently collected from air using silica gel or Thermosorb/A tube sorbents. It appears that sampling with an impinger containing an acid may more efficiently collect the analytes.(35) Visual disturbances had been intermittently reported in facilities A and B prior to our surveys. In facility A, workers reported vision problems in the areas where the highest air concentrations of aliphatic amines were measured. Although the visual disturbances appear to be transient; the condition may lead to serious injury from accidents. The complaints of visual disturbances due to aliphatic amine exposure are supported elsewhere in the literature.(36–38)

The inability to detect *N*-nitroso-containing compounds in any of the three facilities suggests that the necessary intermediates, or the conditions for nitrosamine formation, were not present. While traces of NO_2 would likely be found in each facility, especially during the winter months, most aliphatic amines used at the facilities were tertiary compounds. Such amines provide poor intermediates for nitrosation.(3) However, if secondary or primary aliphatic amines were used in the foam formulation, formation of nitroso compounds might occur.

The failure to detect TDA in air and in bulk settled dust is in general agreement with the findings of others.(4,5) No evidence was found which would indicate that TDI appreciably hydrolyzes to its corresponding amine in air. TDA has been reported to occur, however, in finished foam and foam that is pyrolyzed.(6,39) TDA could be absorbed through the skin of workers if it were present on foam; however, this aspect was not assessed during the surveys.

Results from many studies indicate that polyurethane foam dusts are not carcinogenic.(12) However, little attention has been given in the literature towards specifying the nature of the foam and the differences between flexible and rigid foams made from different isocyanates. Polyurethane dust, in general, is viewed as a potential health hazard in that it may irritate the eyes, nose, and throat and may affect the lungs.(12) Chronic exposure could possibly result in an emphysematous condition.(13,14) However, our data indicate that respirable dust exposure is quite low and would not likely be of concern, especially if dust respirators are worn by the workers when performing dusty operations.

The Ames mutagenicity assay has received much attention as a screening test for detecting both frame-shift and base-pair substitution mutations.(40) The correlation between selected classes of known carcinogens and subsequent positive mutation results in this system is about 90 percent.(41–43) However, there are false positives among some compounds when compared with animal bioassay data. At present, insufficient data exist to permit a quantitative analysis of the mutagenic assay data for determining human risk.(44) Therefore, until additional information is available, mutagenic activity results should be considered in light of their uncertainty in establishing human mutagen and carcinogen potential.

Overall, worker exposures to most of the agents that were monitored in this study were low compared with the established evaluation criteria or were nondetectable. Based on that criteria, it would appear, but not proven, that workers in this industry would be at low risk from workplace exposures. However, it is because wide variations in exposures to these individual agents are expected within the industry, resulting in a real risk to workers in some cases, that the information from this study was provided.

Recommendations

The facilities described here were not necessarily chosen based upon their being representative of the industry, but rather were chosen primarily due to epidemiological considerations. If the three facilities are representative of the flexible polyurethane foam manufacturing industry, then clearly TDI is only one of several chemicals to which workers may be potentially exposed. Other potential chemical hazards, notably exposure to methylene chloride, aliphatic amines, nitrosamines, thermal decomposition products, and heating gases, should be monitored. The procedures and results described here can be used as a guide in those determinations.

Specific concerns and recommendations are delineated below:

1. Worker exposure to aliphatic amines should be routinely monitored with the intention of preventing visual impairment and potentially serious safety problems.
2. Air samples should be taken and/or bulk material analyzed to ascertain worker exposure to methylene chloride. Appropriate controls should be implemented to reduce exposure as much as possible. Substitution of methylene chloride with less hazardous solvents should be considered.
3. A continued effort should be made to use amines that are derived from tertiary-type compounds (e.g., nitrogen that is occupied in all three bonding sites) so that the probability for nitrosamine formation is minimized. Monitoring for nitrosamines should be conducted periodically to ensure that *N*-nitroso-containing compounds do not occur.
4. Although air concentrations of both TDA and flame retardant compounds were below the limits of detection, it may be possible for workers to have dermal contact with these substances. Additional research to determine the extent of surface contamination with these compounds might be appropriate.
5. Air samples obtained for mutagenicity testing indicate that frame-shift mutagens were present in the particulates within each of the surveyed facilities. The source and identity of the active compound(s) are not known. Furthermore, it is not known if the results predict an increased risk from cancer or reproductive disorders. Since many of the workers in this industry are young females, the possible reproductive effects are especially of concern. Epidemiological studies are needed to determine risk, and detailed studies are needed to identify the active compound(s) so that material substitution or better controls may be effectively implemented.

Acknowledgments

The success of this study was due to the many field survey participants and the chemists who analyzed the samples. Special thanks to James Arnold, Organic Method Development Section, NIOSH, for the analysis of toluenediamine, and to G. David Foley and Dr. Gangadhar Choudhary, Measurement Research Support Branch, NIOSH, for the analysis of aliphatic amines, nitrosamines, and flame retardants. Airborne mutagen samples were collected and analyzed by John Stewart from the Microbiology Section, DRDS, NIOSH, in Morgantown, West Virginia. Additional analyses were performed under contract to UBTL, Inc., Salt Lake City, Utah. The managements of each facility surveyed are also thanked for their cooperation during the surveys and for sharing information that may help provide for a safer industry.

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Received 11/10/88; review decision 8/17/89; revision 11/21/90; accepted 12/13/90