



# Exposure to MDI During the Process of Insulating Buildings with Sprayed Polyurethane Foam

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Buildings are often insulated with sprayed-in-place polyurethane foam in spite of the fact that few studies have been carried out on exposure levels to isocyanates during the spraying process. This paper is meant to provide new data on personal exposure to methylene-bis (4-phenylisocyanate) (MDI) while dwellings and office buildings are being insulated with polyurethane foam. An impinger using a 1-(2-methoxyphenyl)piperazine toluene solution as absorbent was used to take personal samples for the sprayer and helper during indoor and outdoor applications. The analytical results show that the levels of exposure were significant, especially for the sprayer, with values of up to  $0.077 \text{ mg m}^{-3}$  and  $0.400 \text{ mg m}^{-3}$  during outdoor and indoor applications, respectively. The helper's exposure was always lower. © 1999 British Occupational Hygiene Society. Published by Elsevier Science Ltd. All rights reserved.

*Keywords:* MDI; isocyanates; insulation; polyurethane foam; spray foam

## INTRODUCTION

The reaction of di- or polyisocyanate with a polyhydroxylated organic compound in the presence of a foaming agent produces the popular polyurethane foams. These foams, which can be either flexible or rigid, are obtained principally from diisocyanates. Sprayed-in-place polyurethane foams have been widely used in insulation in recent years.

Studies by Peterson *et al.* (1962) (during indoor spraying of polyurethane foam) and by Hosein and Farkas (1981) (during outdoor spraying) dealt with concentrations of toluene diisocyanate (TDI), the isocyanate component most often used to produce flexible foams. However, now there is a tendency to use rigid foams based on methylene-bis (4-phenylisocyanate) (MDI) to insulate buildings.

Although polyurethane is considered safe for humans, isocyanates are notoriously toxic. Isocyanates are very reactive substances and, as Woolrich (1982) explained, are irritant to the mucous membranes of the eyes and respiratory tract at airborne concentrations of between 0.1 and 1 ppm. At concentrations greater than 1 ppm, there is danger of an acute toxic effect. Continuous inhalation of its vapours or mists can produce nausea, headaches, cough, nose and throat irritation, and

respiratory problems; massive exposure can cause severe fits of coughing and bronchitis, and some individuals can become sensitized and later suffer asthma attacks when they are exposed to small concentrations. Contact with liquid isocyanates can produce reddening of the skin, irritation, dermatitis and, in some individuals, sensitization.

As shown by Dharmarajan (1979), MDI is usually aerosolized in spraying operations at ambient temperature or is easily condensed to form aerosols because of its low vapour pressure ( $5 \times 10^{-6}$  mmHg at  $25^\circ\text{C}$ ).

The basic components of rigid insulating foams are MDI and an organic polyol (main components at a proportion of approximately 1:1) with a fluorocarbonated derivative as a foaming agent and small amounts of a catalyst, usually a tertiary amine. Other fireproofing agents or surfactants may also be present.

During the application, the MDI and the polyol, which contain the necessary additives, are pumped from separate containers through a proportioning and heating unit to a spray-gun, where they are mixed. Electrically-heated, insulated hoses help control the temperature and viscosity of the products on the way to the spray-gun. The sprayed mixture polymerizes exothermally at ambient temperature, and the reaction is completed in a few minutes.

Environmental conditions greatly affect the foaming process, so spraying is not advisable at ambient temperatures below  $10^\circ\text{C}$  or when relative humidity

Received 15 July 1998 in final form 25 February 1999  
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is above 80%. To optimize the yield of the foaming process, the catalyst-foaming agent mixture is adjusted in each season of the year according to these variables.

There are few previous studies on MDI concentrations at the workplace during these spraying operations. Fitzpatrick *et al.* (1964) and Nemery and Lenaerts (1993) referred to a specific application in underground mines. Concerning applications in construction, Bilan *et al.* (1989) studied the MDI exposure levels of the workers involved in this activity (sprayer and helper). The sampling was carried out exclusively during the spraying operation itself, using the modified Marcali colorimetric method. Of the eight applications considered, five were carried out indoors, and three outdoors (roofs). However, none of the indoor applications were for dwellings or offices, and none of the outdoor applications were for façades. The greatest concentrations of MDI observed around the sprayer were 0.129 ppm (indoors, mill barn) and 0.05 ppm (roof), while the concentrations around the helper were 0.018 ppm (inside the barn) and 0.021 ppm (roof). In outdoor applications, MDI concentrations for a “windscreen holder” reached 0.038 ppm. [The MDI time-weighted average exposure limit for an 8-h workday (TWA value) according to the ACGIH (1998) is 0.005 ppm].

In recent years, high performance liquid chromatography (HPLC), which Rosenberg and Pfäffli (1982) proved to be a more precise and sensitive analytical technique, has been used instead of the colorimetric method to measure airborne organic isocyanates. The reagent most commonly used now as impinger absorbent is 1-(2-methoxyphenyl)piperazine, rather than the nitro-reagent (*N*-4-nitrobenzyl-*N*-*n*-propylamine) used by these authors.

The evaluation of workplace exposure to airborne organic isocyanates can be approached in two ways: determination of concentrations ( $\text{mg m}^{-3}$ ) of specific monomeric isocyanates [as described in Method 5521, 4th ed., of the United States National Institute for Occupational Safety and Health (NIOSH-USA, 1994)] or determination of concentrations of isocyanates (including monomers and oligomers), shown as a function of the free isocyanate groups present ( $\mu\text{g NCO m}^{-3}$ ) [as in Method MDHS 25/2 of the United Kingdom Health and Safety Executive (HSE, 1994)]. The applicable reference values should of course agree with the criterion adopted. Therefore, the ACGIH threshold limit values are consistent with the NIOSH-USA method. To date, there is no international agreement on which criterion is the most suitable.

The purpose of this study was to ascertain the spray-gun operator and helper’s personal exposure to MDI while spraying polyurethane foam insulation on blocks of flats, terrace houses, and office buildings. The applications studied were carried out

indoors and outdoors (roofs and façades). The HPLC analytical method was used for samples taken with an impinger.

## METHOD

Personal samples of airborne MDI were taken at 17 construction sites run by different companies. These included a large office building, two groups of terrace houses, and 14 blocks of flats. Thirteen of the applications sampled were indoors (sprayed on the inside of the exterior wall) and five were outdoors (two facades and three roofs). One block of flats received both an indoor and a roof application. More indoor applications were studied because they were more frequent than outdoor applications. The foam applications were carried out by several specialized companies. The doors and windows had not yet been installed in the flats, so the work areas could be considered semi-open. In some cases, natural ventilation was impeded by provisional screens installed in the window voids to keep the foam from being sprayed outside and causing damage.

Depending on the type of application, the common thicknesses and densities of the foam were within the ranges shown in Table 1.

MDI exposure levels for the sprayer and helper were determined with Method MTA/MA-034/95, established in Spain by the National Institute for Occupational Safety and Health (NIOSH-Spain, 1995) for determining the airborne concentrations of certain monomeric diisocyanates. Although this method’s sampling procedure and analytical technique are similar to those of Method 5521 and Method MDHS 25/2 mentioned above, the results foreseen follow the criterion of the former and are expressed in  $\text{mg m}^{-3}$  of monomeric isocyanate.

The samples were taken with an impinger, using a  $2 \times 10^{-4}$  M solution of 1-(2-methoxyphenyl)piperazine in toluene as the absorbent, with 20–75 min per sample and a flow rate of  $1 \text{ l. min}^{-1}$ . After acetylation with acetic anhydride, the absorbent solution evaporated to dryness, and the residue was dissolved in 1 ml of the chromatographic eluent mixture [60% (v/v) acetonitrile/40% sodium acetate buffer, pH 6.0]. It was later analysed by HPLC, using a dual ultraviolet (242 nm, photodiode array, PDA) and electrochemical (+0.8 V, Ag/AgCl) detection system.

The pauses for changing the equipment to another room or floor or to clean the spray-gun were included in the sampling to obtain representative results of the most common work conditions during the entire spraying operation. These pauses are usually short (only a few minutes), and the sampling unit was left on.

Table 1. Common thicknesses and densities for sprayed-in-place polyurethane foam

	Roof	Façade	Indoors
Thickness (cm)	2–6	4–5	2–3
Density (kg m <sup>-3</sup> )	35–45	30–35	30–50

## RESULTS AND DISCUSSION

When applying polyurethane foam, workers spend from 2 to 5 days at each construction site, and work conditions vary greatly. The working day may be longer or shorter depending on productivity or on the development of the particular construction project, transportation to and from the construction site and installation and transfer of the unit within the building. Natural ventilation and ambient pollution at the workplace are widely influenced by the structural characteristics of the building and atmospheric conditions. The spraying operations studied were carried out by seven firms, which may have used different procedures, equipment, or raw materials. These circumstances contributed to the great differences observed in the analytical results of the samples taken during different spraying operations (Table 2).

The levels of personal exposure to MDI (mean weighted concentrations with respect to the sampling time in each spraying operation) deduced from the analytical results are shown in Table 2 and are linked to the ambient conditions during the spraying period on each working day. The values recorded show that the most unfavourable conditions occur indoors, as could be expected, because these partially closed spaces favour the accumulation of contaminants. During open-air spraying (roofs and façades), natural dilution by wind obviously reduces the presence of contaminants in the work area.

The helper always receives less exposure than the sprayer because he is not always in the area where the work is going on, and he stands further away from the spray-gun.

The workday for this activity usually includes variable periods during which no spraying is performed (trips between the spraying company's headquarters and the construction site, assembly and disassembly of the spraying unit, or breakdowns), and for which MDI exposure would probably be zero. Therefore, the exposure level for an 8-h workday (8 h TWA values) including these periods when no spraying is carried out would obviously be lower than the calculated levels shown in Table 2.

The length of the different spraying periods sampled has been estimated at 3–7 h/day, although the periods would commonly be situated between 4 and 5.5 h/day (2–4 h a day was estimated for the periods with no spraying). Consequently, in most cases the applicable 8 h TWA values would

approach 50–70% of the exposure levels calculated, at times reaching 40–90%.

No limiting value has yet been established in Spain for evaluating airborne MDI exposure in the workplace, although the ACGIH criteria are provisionally being used. In the interior applications studied, the foreseeable 8 h-TWA MDI levels for the sprayer usually exceeded the current ACGIH (1998) limit for MDI (0.051 mg m<sup>-3</sup>, 8 h-TWA value); this level was occasionally exceeded in the helper's position. In exterior applications, the reference limit was surpassed in exceptional cases in the sprayer's position.

The ACGIH has no reference value for the short exposures to high concentrations (during indoor applications, up to 0.570 mg m<sup>-3</sup> for the sprayer and 0.408 mg m<sup>-3</sup> for the helper) that were observed.

## CONCLUSIONS

Personal MDI sampling carried out by absorption in a 1-(2-methoxyphenyl)piperazine solution while rigid polyurethane foam is being sprayed on buildings shows that exposure levels to this contaminant may reach significant levels, especially for indoor applications, where they may greatly exceed the ACGIH TWA reference value. Levels are usually acceptable in outdoor applications.

The high MDI levels that may occur during this activity require careful use of personal protection equipment, above all for the sprayer while he is working indoors.

In the applications studied, the usual protective measures against contact with the aerosol particles included closed work clothes, a head covering, gloves, and anti-stick face lotion. For breathing protection, disposable half masks or particle filters (obviously inadequate for MDI vapours) and/or filters for organic vapours (effective against MDI, but with the limitations observed below) were used. The visor of the eye protection equipment was covered with a film of disposable transparent material (cellophane or plastic) to avoid the loss of visibility from adhesion of aerosol particles. Occasional symptoms described by the workers were skin irritation, reddening or watering of the eyes, and difficulty in breathing.

Controlling ambient pollution with a forced draught is impracticable because application time is fast and the workers are constantly moving from one part of the building to the other.

Table 2. Personal exposure to MDI in the insulation of building with sprayed-in-place polyurethane foam\*

Type of application/No. of applications	Job	No. of samples/No. of applications	Individual samples (min-max)†	Exposure level (min-max)‡
Roofs (3)	Sprayer	5/3	0.010–0.100	0.020–0.077
	Helper	4/3	0.001–0.055	0.004–0.045
Façades (2)	Sprayer	5/2	0.017–0.060	0.018–0.057
	Helper	2/1	0.029–0.038	0.034§
Indoors (13)	Sprayer	29/13	0.012–0.570	0.017–0.400¶
	Helper	16/9	0.006–0.408	0.025–0.308

\* Concentrations in  $\text{mg m}^{-3}$ .

† Minimum and maximum values observed throughout the individual samples.

‡ Minimum and maximum values of the mean weighted concentrations with respect to the sampling time in each spraying operation.

§ Associated with 0.057 (sprayer).

¶ Nine of the thirteen values were between 0.1 and  $0.3 \text{ mg m}^{-3}$ .

|| Seven of the nine values were less than  $0.1 \text{ mg m}^{-3}$ .

The use of air tanks is not advisable because it would limit the worker's movement and add to the weight and discomfort associated with this type of job.

The best type of personal protection would be a positive air pressure mask or hood with a visor cover made of some disposable transparent material to protect against aerosol particles. A provisional alternative would be the use of a mask with a mixed A2-P3SL filter (against organic vapours and solid or liquid particles), but this would have certain drawbacks. The passage of air would be reduced by the deposition of aerosol particles on the filter, and it would be difficult to avoid excessive exposure because of filter saturation, as the smell threshold of MDI vapour (0.4 ppm) is much greater than the limit value of exposition (0.005 ppm, ACGIH 8 h-TWA value).

*Acknowledgements*—The authors would like to thank the construction companies and insulation companies that have made this study possible. We would also like to thank Dr E. Toledano from the National Centre for Protective Equipment (NIOSH-Spain) in Seville for preparing the samples, and Licentiate F. Pollo from the National Centre for New Technologies in Madrid (NIOSH-Spain) for the HPLC analyses.

## REFERENCES

- ACGIH (1998) *Threshold Limit Values for Chemical Substances and Physical Agents. Biological Exposure Indices*. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, U.S.A.
- Bilan, R. A., Hafidson, W. O. and McVittie, D. J. (1989) Assessment of isocyanate exposure during the spray application of polyurethane foam. *Am. Ind. Hyg. Assoc. J* **6**, 303–306.
- Dharmarajan, V. (1979) Occupational exposures to methylene bisphenylisocyanate (MDI): gaseous or aerosol? *J. Environ. Path. Toxicol* **2**, 1–8.
- Fitzpatrick, M., Craft, R., Warren, J. W., Laird, F. H., Watson, H. A., Harris, E. J., Beatty, R. L. and Schell, L. D. (1964) An industrial hygiene survey of polyurethane foam application in an underground mine. *Am. Ind. Hyg. Assoc. J* **25**, 569–577.
- Hosein, H. R. and Farkas, S. (1981) Risk associated with the spray application of polyurethane foam. *Am. Ind. Hyg. Assoc. J* **42**, 663–665.
- HSE (1994) Laboratory Method using 1-(2-Methoxyphenyl)piperazine Solution and High Performance Liquid Chromatography. In *MDHS 25/2 Methods for the Determination of Hazardous Substances, Organic Isocyanates in Air*. Occupational Medicine and Hygiene Laboratory, Health and Safety Executive, London, U.K.
- Nemery, B. and Lenaerts, L. (1993) Exposure to methylene diphenyl diisocyanate in coal mines. *Lancet* **341**, 318.
- NIOSH-Spain (1995) MTA/MA-034/A95—Methods for sampling and analysis. In *Determination of airborne organic isocyanates (2,6- and 2,4-toluene-diisocyanate, hexamethylenediisocyanate, 4,4'-diphenylmethane-diisocyanate)*, derivation and ultraviolet and electrochemical double detection method/High Performance Liquid Chromatography. National Institute for Occupational Safety and Health, Madrid, Spain.

- NIOSH-USA (1994) *Method 5521—Isocyanates, monomeric. Manual of Analytical Methods*, 4th ed. National Institute for Occupational Safety and Health, Department of Health and Human Services, Cincinnati, Ohio, U.S.A.
- Peterson, J. E., Copeland, R. A. and Hoyle, H. R. (1962) The hazards of spraying polyurethane foam out-of-doors. *Am. Ind. Hyg. Assoc. J* **23**, 345–352.
- Rosenberg, C. and Pfäffli, P. (1982) A comparison of methods for the determination of diphenylmethane diisocyanate (MDI) in air samples. *Am. Ind. Hyg. Assoc. J* **43**, 160–163.
- Woolrich, P. F. (1982) Toxicology, industrial hygiene and medical control of TDI, MDI and PMPPi. *Am. Ind. Hyg. Assoc. J* **43**, 89–97.