



A New Penetration Test Method: Protection Efficiency of Glove and Clothing Materials Against Diphenylmethane Diisocyanate (MDI)

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ABSTRACT

Reported cases of allergic contact dermatitis caused by methylenediphenyl diisocyanate (MDI) have increased and thereby increased the need for adequate skin protection. Current standardized permeation and penetration test methods give information about efficacy of protective materials against individual components of the polyurethane systems. They do not give information of what kind of clothing materials workers should wear against splashes when handling mixed MDI-polyurethane formulations, which contain MDI, its oligomers, and polyols. The aim of this study was to develop and validate a sensitive penetration test method that can be used to select clothing that is protective enough against uncured splashes of MDI-polyurethane, still easy to use, and also, to find affordable glove materials that provide adequate protection during a short contact. The penetration of MDI through eight representative glove or clothing materials was studied with the developed test procedure. One MDI hardener and two polymeric MDI (PMDI)-polyol formulations representing different curing times were used as test substances. The materials tested included work clothing (woven) fabric, arm shields (nonwoven fabric), old T-shirt, winter gloves, and gloves of nitrile rubber, leather, vinyl (PVC), and natural rubber. A drop (50 µl) of test substance was added to the outer surface of the glove/clothing material, which had Tape Fixomull attached to the inner surface as a collection medium. After penetration times of 5 or 20 min, the collecting material was removed and immediately immersed into acetonitrile containing 1-(2-methoxyphenyl)-piperazine for derivatization. The formed urea derivatives of 2,4'-MDI and 4,4'-MDI were analysed using liquid chromatography with mass spectrometric and UV detection. The precision of the test method was good for the material with high penetration (work clothing fabric) of MDI, as the relative standard deviation (RSD) was 14 and 20%. For the arm shield with a low penetration (the nonwoven fabric), the precision was lower with RSDs of 35 and 50%. For two clothing materials, the penetration was high (134–577 µg cm⁻²). Low penetration (<0.5 µg cm⁻²) was shown by the arm shield and the natural rubber glove. Three glove materials showed no detectable MDI penetration (<0.002 µg cm⁻²). Two affordable glove materials (natural rubber and nitrile rubber) and one clothing material (dust proof arm shield) that can provide adequate protection during short contact with solvent free PMDI formulations were found. The new test procedure should be standardized in order to get a new international penetration standard.

KEYWORDS: clothing; gloves; isocyanates; MDI; penetration; protective materials; sensitizer; testing

INTRODUCTION

Isocyanates are respiratory and skin sensitizers and a well-known cause of occupational asthma. The awareness of health risks caused by inhalation exposure has resulted in more efficient protection against airborne isocyanates and thereby decreasing exposure to these harmful substances. Meanwhile, reported cases of allergic contact dermatitis have increased and especially for methylenediphenyl diisocyanate (MDI) after commercial MDI (polymeric MDI [PMDI]) and methylenedianiline (MDA) were included into the patch test battery (Goossens *et al.*, 2002; Aalto-Korte *et al.*, 2012; Engfeldt *et al.*, 2012). Nowadays, according to the Finnish Register of Occupational Diseases (2008–2011), the annual mean number of diagnosed allergic contact dermatitis caused by MDI has reached the same level as for the reported asthma cases (3).

Due to its low volatility, PMDI has become the dominant isocyanate produced and technically used world-wide. The skin of workers handling PMDI in gluing and foaming is often exposed to small splashes of formulations containing both MDI and polyols, without solvent dilution. Skin exposure caused by MDI penetration through gloves and clothing is also possible, but these hazards are not always recognized at workplaces. Permeation and penetration test methods do not give information of what kind of clothing the workers should wear against splashes of the glue and foam at work. The right type of glove for direct contact with PMDI and for washing the work equipment with solvents can be chosen based on work of the International Isocyanate Institute in 1993 and 1996 (American Chemistry Council, 2013). However, for most of the working time, starting with the mixing process, workers are mainly in contact with the mixture of PMDI and polyol, not with the MDI hardener as such. This contact time is for practical reasons very short, 10–20 min, due to the ongoing hardening process.

PMDI-polyol formulations cannot be used as test chemicals using the existing permeation test or penetration methods since these components would react forming solid polyurethane which would destroy the testing equipment (EN ISO 6529, 2001; EN 374-3, 2003; EN ISO 6530, 2005; ASTM F 739, 2012). Due to lack of suitable test methods, there is no information available on what type of clothing or gloves the worker should wear against splashes of the glue or foam. The

test results of MDI permeation bring about the need for leak-tight chemical protective suits (Forsberg and Mansdorf, 2007), which are burdensome and create physical stress. In addition, a new penetration method is needed since the existing penetration methods in use are based on weighing of the penetrated chemicals (EN ISO 6530, 2005). Weighing is not a selective method for the MDI component and is not sensitive enough for a chemical that is able to sensitize at low concentrations.

Penetration is described as a movement of a chemical through porous materials, seams, pinholes, or other imperfections in a material. Permeation is a diffusion process in which the chemical first has to absorb into the intact material and also desorb out of the material (EN 374-1). Neither penetration nor permeation test methods can differentiate which process causes the movement of chemical through the material. The developed method was called a penetration method, because of the ability to test penetration through porous materials.

The aim of this study was to develop and validate a penetration method that can be used to select clothing that is protective enough against splashes, still easy to use, and also, to find affordable glove materials that provide adequate protection during the short (5–20 min) contact with formulations of PMDI and polyol. The developed technique utilizing disposable equipment was used to measure the penetration of MDI from PMDI formulations of different curing times through eight representative glove or clothing materials. The test results are compared to results from permeation testing and to suggested safety limits for protective materials.

MATERIALS AND METHODS

Study design

After choice of collection medium, the tape collection was validated and then the developed method was used to test the penetration of MDI through eight different materials. Test conditions during the different phases of development of the penetration test and during the testing are summarized in Table 1.

Test formulations

MDI hardeners (PMDI) are chemically a mixture of monomeric and oligomeric MDI. MDI or pure

Table 1. Study design of test conditions during method development and testing of MDI penetration

Test	Test time (min)	Material	MDI formulation
Evaluation of two collection media	5 and 20	Woven fabric	Medium-curing B1
	5 and 20	Arm shield	Medium-curing B1
Validation of tape collection	20	Woven fabric	Slow-curing A and medium-curing B1
	20	Arm shield	Slow-curing A and medium-curing B1
Penetration testing using tape collection	5 and 20	All eight test materials	A, B1, and B2

MDI is a mixture of primarily 4,4'-MDI with small amounts of 2,4 and 2,2' isomers. PMDI typically contains 25–65% MDI monomers with the balance consisting of oligomeric polyisocyanate homologues of MDI.

The following test formulations that can be used for both glues and foams were used:

A: Slow-curing PMDI (MDI hardener A, 100%); full cure will take >24 h.

B1: Medium-curing formulation of PMDI (MDI hardener B) and castor oil derivative (Albodur 901); full cure in 2 h. The portion of PMDI was 31% (w/w).

B2: Fast-curing formulation of PMDI (MDI hardener B) and castor oil derivative; full cure in 15 min. The fast curing was achieved by addition of 250 ppm of dibutyl tin dilaurate (Aldrich, St Louis, MO, USA).

Huntsman (Everberg, Belgium) delivered the test chemicals, the mixing ratios for the formulations and approximated times for full cure. Albodur 901 is bio-based polyol made from castor oil. According to analysis results, MDI hardener A contained 3.7% 2,4'-MDI and 23% 4,4'-MDI. The PMDI (hardener B) used for medium and fast-curing formulations contained 9.4% 2,4'-MDI and 64% 4,4'-MDI.

Glove and clothing test samples

The tested materials represented widely different types of materials worn in Finnish working places while handling PMDI formulations.

1. Work clothing fabric, 'woven fabric', twill, 65% polyester, 35% cotton, 300 g m⁻² (as reported by the manufacturer), domestic washing five times in accordance with the EN ISO 6330 before the tests (EN ISO 6330, 2000), average thickness 0.49 mm
2. Old 'T-shirt', knitted fabric, 100% cotton, average thickness 0.50 mm
3. 'Arm shield', nonwoven polypropylene fabric with a microporous polyethylene film, protection against dust, powders and limited protective performance against liquid chemicals, L. Brador DC 20, average thickness 0.22 mm
4. 'Leather gloves', thickness 1.0 mm
5. 'PVC gloves' (vinyl gloves), examination gloves for healthcare, thickness 0.07 mm
6. 'Natural rubber gloves', thickness 0.53 mm, classification: EN 374-1 Chemical protective gloves
7. Single-use 'nitrile rubber gloves', Worksafe Nimex Premium, average thickness 0.10 mm, classification: EN 374-1 Chemical protective gloves
8. 'Winter gloves', Guide 49W, leather gloves with thermoplastic polyurethane insulation and double fleece lining, average thickness 1.9 mm, Classification EN 388, gloves against mechanical hazards

Test samples were punched from the fabrics and the palms of the glove. The round material samples had a diameter of 8 cm. The material thicknesses were

measured in accordance with the ISO 4648 standard (ISO 4648, 1991). Hereafter, the materials will be identified according to the designations in quotes above. Nevertheless, the results cannot be generalized for all the materials with the same designation.

Chemical analysis

2,4'-MDI and 4,4'-MDI were measured by first reacting them with 1-(2-methoxyphenyl)piperazine (2MP) to form stable urea derivatives (ISO 16702, 2007). The formed urea derivatives were analysed using a liquid chromatograph (LC; Thermo Accela) coupled with a triple quadrupole mass spectrometer (MS/MS; Thermo TSQ Quantum Access). The spray voltage was 5000 V and the capillary temperature was 250°C. Separation took place on a Symmetry C18 column (150 × 2.1 mm; Waters Corp.) using a gradient mobile phase of acetonitrile–water with 0.1% formic acid giving retention times of 12–14 min. The flow rate was 0.2 ml min⁻¹. Positive ions were monitored in the electrospray mode. The parent ion was the doubly charged molecular ion (M+2H)²⁺. The daughter ion monitored was the 2MP fragment at *m/z* = 193. The derivatives were also monitored with a photodiode array detector (Thermo Accela). Concentrations >5 µg per sample were calculated from the UV signal at 254 nm. The external standard method was used. The sum of the two MDI-isomers is reported and expressed as MDI. To find out if the recovery of MDI monomers from the tape was acceptable, the tape was spiked directly with known amounts (MDI levels of 0.1 and 0.5 µg, in triplicate) of PMDI (B). The recovery from the glass fibre was not determined for this task as it was used in only one test and was already known to have good recoveries for isocyanates when 2MP in acetonitrile is used as a desorption solvent. As the recovery of MDI from the tapes was >95%, results were not corrected for recovery. The limit of detection (LOD) of the method is ~5 ng per sample.

Validation of the penetration test method

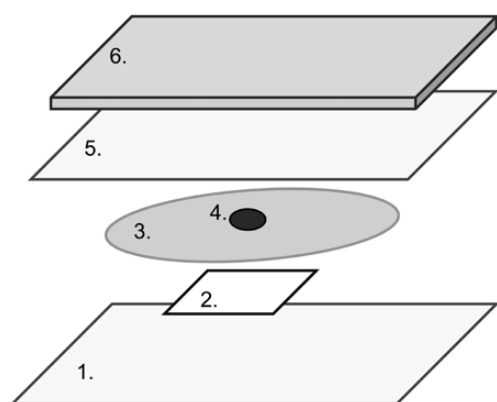
Validation of the penetration test covered the determination of the repeatability including all steps in the procedure. It also covered the choice of collecting medium. Two collection media were evaluated for the test. They were an adhesive tape (3.3 × 4 cm, Fixomull®; BSNmedical, Hamburg, Germany) and a glass fibre filter (diameter 25 mm) free of organic

binders (Whatman GF/B). Commercial PERMEA TEC™ pads (CLI Laboratories, Inc.) were also used in the validation tests to visually detect penetrated MDI. According to the supplier, their pads are sensitive to 3–5 µg of isocyanate.

The precision of the developed penetration test method was determined as relative standard deviation (RSD). The precision was determined separately for the application step by weighing of the 50 µl dosage, and for the whole method (application + penetration + extraction + analysis) by analysis of the 2MP derivatives extracted from the tape after 20 min of penetration. The determinations were designed to generate two different levels of penetration (low and high). The test samples used to achieve these different levels were the 'arm shield' and the 'woven fabric'. The test chemicals were the slow-curing PMDI A and the medium-curing formulation B1. Six replicates of each combination were used to determine the standard deviation.

Penetration testing with the developed test method

Using a 1 ml syringe (BD Plastipak), one drop (50 µl) of test formulation was added to the outer surface of the glove/clothing material, which had the collection medium in close contact with the inner surface. An adhesive tape (3.3 × 4 cm, Fixomull®; BSNmedical) was used as the choice for the collecting medium. A light weight (a board, 25 × 29 cm, 11 kg m⁻²) was applied on top of the samples to ensure contact of the test chemical with the material. Between the weight and the test chemical, a plastic film (size A4 from plastic document pockets) was used to rule out contamination of the weight. In Fig. 1 is a sketch of the test system. With this system, one to six pieces of material samples could be tested at the same time. The test times were 5 and 20 min. The tests were run in triplicate. The Fixomull tape was used for all test samples except for the 'PVC gloves', for which a glass fibre filter was used (Whatman GF/B). Both collection media were evaluated for purity by LC-MS/MS. No MDI was detected. After penetration times of 5 or 20 min, the collecting medium was removed and immediately immersed into the analysis solution for derivatization with 3 mg ml⁻¹ of 2MP in acetonitrile (5 ml). The amount of 2MP derivatization reagent was optimized for the MDI amount in the test formulations. At least one day was allowed for derivatization. The spreading



1 Sketch of the test system. 1. plastic film, size A4, 2. collection medium, 3.3 × 4.0 cm, 3. round glove or clothing sample specimen (diameter 8 cm), 4. test chemical, 50 µl, 5. plastic film, and 6. weight (board, 11 kg m⁻²).

area of the applied drop on the test material was measured with a ruler after the penetration test was finished and the mean diameter of two diagonal measurements was used to calculate the penetrated MDI amount as µg cm⁻². Blank tests without addition of test formulations were done regularly to check for interfering impurities on the collection medium.

RESULTS

Validation of the penetration test method

Two different collection media were evaluated for the test. The penetration results are presented in Table 2. Materials generating two different penetration levels (low and high) were used. At the high penetration level, the glass fibre filter collected about five times more than the tape during the same time. At the low penetration level, MDI were detected only on the tape and after a test time of 20 min. MDI penetration was measurable on the filter only when a heavy weight was applied to the arm shield to ensure close contact to the filter.

The precision of the application (50 µl drop) expressed as RSD was 16% ($n = 10$) for slow-curing PMDI (A) and 9% for the medium-curing formulation B1 ($n = 8$). The precision results for the whole method are presented in Table 3.

Penetration testing with the developed test method

No detectable penetration (MDI < 0.002 µg cm⁻²) was noticed for three of the five tested glove materials ('nitrile rubber gloves', 'winter gloves', and 'PVC

Table 2. MDI penetration test results using two different collection media and the medium-curing test formulation B1

Test material	Test time (min)	MDI penetration ^a	
		µg/tape	µg/filter
Woven fabric	5	578	2566
	20	401	2527
Arm shield	5	<0.005	<0.005
	20	0.07	<0.005

^aMean concentration for determinations in triplicate.

gloves'). For the 'arm shield' (nonwoven fabric), penetration was measurable only when the test time was 20 min. Even then the penetration was very low, at most 0.014 µg cm⁻² for the medium-curing formulation B1 (Table 4). This penetration could not be seen as a colour reaction on Permea-Tec pads. The woven fabric and T-shirt demonstrated the highest penetration with mean concentrations of MDI in the range 134–577 µg cm⁻². The penetration was at the same level for both test times. The penetration was also seen on Permea-Tec pads as a colour reaction. Penetration of MDI from the slow-curing A resulted in tape concentrations that were two to four times higher than for penetration of MDI from medium-curing B1 and fast-curing B2 formulations of PMDI and polyol, although the 50 µl drops contained about the same amounts of MDI monomers (13.8 and 12.2 mg, respectively). The penetrated MDI amount was 2–5% of the applied dose for the medium-curing B1 and fast-curing B2 formulations. For the slow-curing A formulation, the penetrated MDI amount was 6–8% of the applied dose.

DISCUSSION

Evaluation of collection media

Permeation test methods and traditional penetration test methods do not give information on what kind of clothing the workers should wear against unreacted MDI in splashes of glue and foam during work. Therefore, a penetration method that can be used to detect small amounts of MDI from PMDI-polyol formulations was developed and validated. Two collection media candidates were evaluated for the penetration study: Fixomull tape and glass fibre filters

Table 3. Precision of the developed penetration test method with an applied dose of 50 µl determined as RSD of penetrated MDI during 20 min

Test material	Test formulation	MDI penetration ^a		
		% ^b	µg/tape	RSD (%)
Woven fabric	Slow-curing A	7.7	1073	14
	Medium-curing B1	3.2	393	20
Arm shield	Slow-curing A	0.00046	0.064	50
	Medium-curing B1	0.00050	0.061	35

^aMean values of six replicates.

^bPercentage penetration of the applied dose.

free of organic binders representing widely different adsorption properties. Fixomull tape has also been successfully used to collect MDI from the skin in a skin exposure study (Liljelind *et al.*, 2010).

The thick and porous glass fibre filter adsorbed about five times more MDI than the tape when a 'woven fabric' representing high penetration was the test material (Table 2). For the 'arm shield' representing a material with low MDI penetration, MDI was detected on the tape only after the longer (20 min) test time (Table 2). A heavy weight was needed to press MDI into contact with the filter to get measurable amounts. Evidently, the close contact provided by the thin adhesive layer on the tape to the test material seems to promote the penetration of MDI through materials with low penetration compared to the MDI collection by the glass fibre filter. For those materials through which the penetration was high, the thick and porous glass filter had capacity to adsorb MDI more efficiently than the tape. The tape was chosen as collection medium for further studies in order to make it possible to detect low penetration levels, since the general interest is to find efficient protective materials with the method. The maximum absorbed amount on the tape was still suitable for analysis as 2MP derivatives. If the material to be tested for some reason sticks too efficiently to the tape and the tape cannot be released for analysis, then glass fibre filters free of organic binders is proposed to be used. For this reason, PVC gloves were tested using glass fibre filters as collection medium. However, to get comparable test results with different collection media, the influence of pressure on penetration need to be studied in more detail.

Commercial Permea-Tec pads showed colour reactions only in contact with the 'woven fabric' and not when they were in contact with the 'arm shield'. According to the supplier, their pads are sensitive to 3–5 µg of isocyanate corresponding to ~2 µg cm⁻². Thus, these pads can be used to screen for materials with high penetration of MDI. For materials with low penetration (<3–5 µg), reliable test results can only be achieved by using the developed test method.

Precision and applicability of the developed test method

According to validation results, the precision of the test method was good for the material with high penetration ('woven fabric'), as the RSD was 14 and 20% (Table 3). For the material with low penetration (the 'arm shield'), the precision was lower with RSDs of 35 and 50%. The low precision may be due to a nonuniform quality of the material, as well as to low analytical precision at this concentration level. The RSD of the extraction and analysis step at this MDI level was 22%. In practice, the precision of the developed method should be acceptable for routine testing.

Eight different materials representing both gloves and clothing commonly used when handling PMDI formulations in the work place were chosen to test the developed penetration method. The MDI penetration results spanned several orders of magnitude (Table 4). The 'woven fabric' and 'T-shirt' demonstrated the highest penetration, with the penetrated amount representing 2–8% of the applied dose. For the 'arm shield' material, the penetration was much lower (~0.0005% [5 ppm] of the applied dose) and for three glove

Table 4. MDI penetration through three clothing materials and two glove materials with test formulations of different curing rate and at two different test times. Penetration was not detected for the gloves made from PVC and nitrile rubber, and winter gloves

Test material	Test formulation	MDI penetration ($\mu\text{g cm}^{-2}$)			
		5 min		20 min	
		Mean	Actual	Mean	Actual
Woven fabric	Slow-curing A	577	395, 545, 791	512	367, 470, 699
	Medium-curing B1	241	159, 279, 284	167	124, 178, 200
	Fast-curing B2	286	245, 269, 343	185	168, 192, 196
T-shirt	Slow-curing A	471	379, 432, 601	476	399, 487, 543
	Medium-curing B1	140	82, 104, 234	144	122, 132, 178
	Fast-curing B2	175	162, 177, 187	134	108, 125, 169
Arm shield	Slow-curing A	<0.001	all < 0.001	0.006	0.004, 0.006, 0.010
	Medium-curing B1	<0.001	all < 0.001	0.010	0.005, 0.011, 0.014
	Fast-curing B2	<0.001	all < 0.001	0.0029	0.002, 0.003, 0.004
Leather gloves	Slow-curing A	0.004	0.002, 0.002, 0.008	0.011	0.008, 0.011, 0.012
	Medium-curing B1	0.19	0.016, 0.21, 0.36	2.02	0.010, 1.84, 4.21
	Fast-curing B2	<0.002	all < 0.002	<0.002	all < 0.002
Natural rubber gloves	Slow-curing A	<0.002	all < 0.002	0.044	0.004, 0.022, 0.11
	Medium-curing B1	<0.002	all < 0.002	<0.002	all < 0.002
	Fast-curing B2	0.008	<0.002, <0.002, 0.021	0.12	0.005, 0.010, 0.34

materials, the penetration was not detectable (MDI LOD = 5 ng, representing ~0.00004% [0.4 ppm] of the applied dose). The two glove materials ('leather' and 'natural rubber') with measurable penetration of MDI showed great variations between actual results (Table 4). This may be explained by a nonuniform material. In such cases, the test should be repeated by doing at least six replicates to get reliable results and reporting the highest.

Factors affecting penetration of MDI through different clothing and glove material

Generally splashes of PMDI are expected to contain more MDI available for penetration than splashes from formulations of similar PMDI mixed with polyol. When high penetration was recorded, as for 'woven fabric' and 'T-shirt', then according to the results in Table 4, the penetration of MDI from the slow-curing

one component PMDI was at least two times higher compared to MDI penetrating from the medium and fast-curing formulations, although the applied dose contained about the same amount of MDI when the test started. In these cases, it seems that the presence of polyol in some way affected the penetration process by lowering the unreacted amount of MDI available for penetration even for a short curing/penetration time of 5 min.

As the precision of the determinations is low for materials showing low penetration (Table 2), no conclusion can be drawn about the influence of curing rate on MDI penetration through such materials as arm shields, leather gloves, and natural rubber gloves (Table 4). Although the test formulations represented widely different times to reach full cure, the penetration levels were still on the same magnitude for the same material. Therefore, the penetration test can be

performed with one or, at most, two test formulations and still give useful results. The first choice as test chemical could be the MDI hardener in use without addition of polyol just to make the test procedure simpler. The formulation used in the work place is recommended as the other choice.

The effect of test time (5 or 20 min) on MDI penetration of the same material was marginal for high penetration except for the fast-curing test formulation B2 (Table 4). One explanation may be that the maximum absorption capacity of the tape was reached, at least for the slow-curing PMDI (A). For the fast-curing PMDI (B2), the penetration was ~30% less after 20 min of testing compared to the 5 min testing for both the 'woven fabric' and the 'T-shirt', which can be explained by polymerization. For materials with low penetration of MDI, the test time may be critical, as penetration may not be detectable if the test time is too short. A test time of 20 min will cover most working situations and these test results can be applied to choose proper skin protection and to make decisions about safe periods of use for the chosen material.

No detectable penetration was noticed for nitrile rubber gloves, winter gloves, and PVC gloves. The main reason for it is watertight glove materials (nitrile rubber and PVC) and for the winter gloves also the thickness together with the polyurethane film.

A light weight (11 kg m⁻²) was used to simulate the pressure of e.g. the fold of the clothing to the skin. Sleeves and midriff of the clothing are seldom under extra pressure. Gloves, on the other hand, may be used under extra pressure, since hands and fingers are used for carrying and using tools at work. Therefore, the use of a heavier weight when penetration testing glove materials may give some extra information for safe use.

Assessment of penetration test results

A comparison to test results obtained for the same tested materials by a permeation test method in another study is presented in Table 5 (Mäkelä *et al.*, 2014). The test chemical in the permeation testing was the PMDI containing 64% 4,4'-MDI, which was used in the medium-curing B1 and fast-curing B2 formulations in this study. Permeation was measured as 4,4'-MDA in acid water (Mäkelä *et al.*, 2014). If the

material cannot be tested against permeation, then penetration can at least be determined by tape collection and LC-MS/UV-analysis. For screening purposes, Permea-Tec pads can be used. Penetration results for protective gloves can also be assessed by comparing to the suggested safety limit, 1 µg cm⁻², corresponding to an acceptable level of cumulative permeation (Mäkelä *et al.*, 2014). For clothing, a higher safety limit (10 µg cm⁻²) is recommended, as clothing materials are not in such close contact with the skin as the gloves are (Mäkelä *et al.*, 2014).

The test results for the arm shield showed levels below the suggested safety limit of 10 µg cm⁻², but the 'woven material' and the 'T-shirt' did not (Table 4). Splashes and other direct contact of PMDI formulations on the clothing may result in penetration of amounts that are able to sensitize the skin. During a dermal uptake study, an applied MDI dose of 800 µg cm⁻² sensitized two volunteers (Hamada *et al.*, 2012). In our test, the applied dose was one drop (=50 µl) and 2–8 % of MDI in that amount penetrated the test materials resulting in MDI amounts of 134–577 µg cm⁻² on the collection tape (Table 4). If there is a moderate to high risk of PMDI contamination of the work clothing, then at least aprons and arm shields should be used to improve protection. Protective overalls made of material with similar penetration properties as the tested 'arm shield' could be the choice for protection during work involving spraying of MDI foams onto surfaces, but testing with a higher material variety is needed than was possible within this study.

The penetration test results for glove materials revealed that 'leather gloves' did not pass the safety limit 1 µg cm⁻², as some actual results exceeded 1 µg cm⁻² (Table 4). 'PVC gloves' could not be tested using tape as collection medium, as the tape could not be released for analysis after testing. This may explain the test results below detection limit for those gloves. Thin 'PVC gloves' are fragile and therefore not suitable for urethane work despite the promising permeation test results reported by Mäkelä *et al.* (2014, Table 5). The 'natural rubber glove' passed the safety limit with good margin in the penetration testing. The 'nitrile rubber glove' for single use was the only glove with no measurable penetration or permeation (Table 5). Thus, the

Table 5. Comparison of MDI penetration results to permeation results of MDI through the tested materials. The penetration test time was 20 min. The cumulative permeation at the test time of 20 min was calculated from permeation test data reported by Mäkelä *et al.* (2014)

Test material	Thickness (mm)	Test formulation	Penetration	Permeation
			($\mu\text{g MDI cm}^{-2}$)	($\mu\text{g MDI cm}^{-2}$)
Woven fabric	0.49	Slow-curing A	512	
		Medium-curing B1	167	
		MDI hardener B		— ^a
T-shirt	0.50	Slow-curing A	476	
		Medium-curing B1	144	
		MDI hardener B		— ^a
Arm shield	0.22	Slow-curing A	0.0064	
		Medium-curing B1	0.010	
		MDI hardener B		0.7
Leather glove	1.0	Slow-curing A	0.011	
		Medium-curing B1	2.02	
		MDI hardener B		— ^a
PVC glove	0.07	Slow-curing A	<0.002	
		Medium-curing B1	<0.002	
		MDI hardener B		0.7
Natural rubber glove	0.53	Slow-curing A	0.044	
		Medium-curing B1	<0.002	
		MDI hardener B		ND ^b
Nitrile rubber glove	0.10	Slow-curing A	<0.002	
		Medium-curing B1	<0.002	
		MDI hardener B		ND ^b
Winter glove	1.9	Slow-curing A	<0.002	
		Medium-curing B1	<0.002	
		MDI hardener B		0.1

^aTechnically not possible to do the permeation test.

^bPermeation not detected (=ND).

small test set in this penetration study did come up with two affordable glove materials that can provide adequate protection during short contact with MDI hardeners both before and after addition of polyol. According to the manufacturer, the tested ‘winter gloves’ had a polyurethane film in their structure.

The film together with the thickness are the probable reason for the winter gloves to pass the safety limit (Table 5). The structure of the ‘winter gloves’ does not allow their classification as chemical protective gloves in accordance with their requirements in the European Union.

CONCLUSIONS AND RECOMMENDATIONS

A simple and sensitive method to test MDI penetration through different protective materials was developed. The method allows mixed MDI hardener and polyol components of polyurethane to be used as test chemical using test equipment that is inexpensive enough for one-time use. The precision of the penetration test method was good for materials with high MDI penetration and acceptable for materials with very low MDI penetration. The sensitivity of the test method was high due to the use of LC-MS/MS for analysis; 5 ng from a dosage of 50 µl could be detected, which correspond to a penetration of only 0.00005% or 0.001–0.002 µg cm⁻². It was also demonstrated that widely different protective materials, both gloves and clothing, representing low and high penetration of MDI from both PMDI and PMDI formulations could be tested using the tape as collection medium. Affordable glove and clothing materials that can provide adequate protection during short contact with MDI were found, e.g. dustproof arm shields, natural rubber gloves, nitrile rubber gloves for single use. Ordinary woven working clothes or T-shirts do not protect efficiently enough from PMDI formulations.

The test procedure should be standardized in order to get an international standard (EN ISO) for testing MDI penetration through widely different protective materials. The formulation and test time should be chosen according to the demands of the work task and be the same for all material candidates to be evaluated for a certain work task. A test time <15 min is not recommended.

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DISCLAIMER

The findings and conclusions in this paper are those of the authors and do not necessarily represent the views

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