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TNO report

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The release of MDI during the filling of cable joints with a two compound polyurethane resin.

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Summary

Lovink Enertech is a company which develops and manufactures cable joints for medium and low voltage purposes. The insulation used for the cable joints consists of an electrical insulation based on a silicone compound and a mechanical insulation based on a two part polyurethane resin.

One part of the polyurethane resin consist of methylenediphenyl diisocyanate (MDI) and is considered as harmful. The applied MDI is a mixture of 2,2 and 2,4 and 4,4, MDI. During the process of pouring the resin into the cable joint, it might be possible that MDI vapours/aerosols are released into the air and are potentially inhaled by the operators.

Therefore Lovink Enertech has asked TNO Department of Applied Environmental Chemistry to perform measurements for MDI in order to investigate the possible emissions of MDI during the mixing and filling operation of cable joints.

The findings of the investigation are as follows:

- Compared to daily practice where cable joints are filled in the ambient air, personal air sampling experiments during filling of cable joints were carried out in a so called worst-case scenario in two separate inside rooms without ventilation.
- The measured concentration of 4,4,MDI in the breathing zone of technician 1, who carried out the filling of the cable joints with polyurethane (for experiment 1 and 2), are equal or less than 0,1 % of the levels used for occupational exposure of MDI (NIOSH, OSHA, ACGIH).
- For both experiments 1 and 2, no concentrations of 4,4 MDI were measured in the breathing zone of technician 2.
- For both technicians, no concentration levels of 2,2 MDI and 2,4 MDI were measured in the breathing zone.

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1 Introduction and study objective

Lovink Enertech is a company which develops and manufactures cable joints for medium voltage purposes. The insulation used for the cable joints consists of an electrical insulation based on a silicone compound and a mechanical insulation based on a two part polyurethane resin.

Both parts of the polyurethane resin are packed separated from each other in a twin compartment foil pouch.
For use in the field the sealed frontier between both parts are opened for mixing. After mixing both parts, the liquid mixture of polyurethane resin is ready to pour into the cable joint.

One part of the polyurethane resin consist of methylenediphenyl diisocyanate (MDI) and is considered as harmful. During the process of pouring the resin into the cable joint, it might be possible that MDI vapours/aerosols are released into the air and are potentially inhaled by the operators.

Therefore Lovink Enertech has asked TNO Department of Applied Environmental Chemistry to perform measurements for MDI in order to investigate the possible emissions of MDI during the mixing and filling operation of cable joints.

The main study objective is:

1. Determination of MDI vapour and aerosol concentration in the breathing zone of workers during the processing of mixing and filling cable joints with the polyurethane resin.
2. Evaluation of the measured MDI concentrations by comparison to the TLV's (threshold limit values) for occupational exposure.

2 Exposure limits and normative references

For this study the following International regulatory and advisory concentration limits for occupational exposure to MDI are used:

- The NIOSH (National Institute for Occupational Safety and Health) ceiling value, expressed as a 10 minutes average: 200 µg/m^3
- The NIOSH REL (recommended exposure limit), expressed as a 8 hour time-weighted average: 50 µg/m^3
- The UK HSE STEL (short term exposure limit), expressed as a 15 minutes average: 70 µg/m^3
- The UK HSE (Health and Safety Executive) TWA (time weighted average), expressed as a 8 hour time-weighted average: 20 µg/m^3
- The OSHA (Occupational Safety and Health Administration) PEL (permissible exposure limit) ceiling value, expressed as a 15 minutes average: 200 µg/m^3
- The ACGIH (American Conference of Governmental Industrial Hygienists) TLV (threshold limit value), expressed as a 8 hour time-weighted average: 51 µg/m^3

The following International Standards are (partly) used for the determination of MDI in air.

- NEN-ISO 16702, Workplace air quality - Determination of total organic isocyanate groups in air using 1-(2-methoxyphenyl)piperazine and liquid chromatography, 2007
- ISO 17736, Workplace air quality - Determination of isocyanate in air using a double-filter sampling device and analysis by high pressure liquid chromatography, 2010

3 Experimental design

In order to investigate the emissions during the whole process of mixing and filling cable joints, two experiments were carried out in two different rooms inside the facility of Lovink Enertech. In both rooms the ventilation was switched off in order to create a minimum of ventilation. Compared to real situations where mixing and filling takes place in the ambient air, the chosen experimental design is more or less worst-case.

The following experiments were carried out:

Experiment 1

Filling and mixing took place in the LSR room of the facility. Before the start of the experiment a background concentration level of MDI was determined from the indoor air of the room. The mixing and filling experiment was carried out by two technicians, both shaking the bags (type peelable seal, figure 1), one technician was involved in pouring the resin into the joint (figure 2). The other technician stood nearby and performed assistant tasks which consists of mixing the bags. Both technicians were equipped with personal air samples near by the breathing zone. Three bags of resins were used to fill the joint in a time period of approximately 8-10 minutes.

Figure 1. Bag with the separated two compound polyurethane resin (peelable seal)

Figure 2. Filling of the cable joint (exp 1)

Experiment 2

Filling and mixing took place in the E room of the facility
Experiment 2 was carried out in the same way as for experiment 1, with the exception of the type of bag, which was of the type Pouch Clip.
Figure 3 shows a Pouch Clip bag with the two compound polyurethane resin. Figure 4 shows the filling of the cable joint for experiment 2.

Figure 3. Bag with the separated two compound polyurethane resin (Pouch Clip)

Figure 4. Filling of the cable joint (experiment 2)

4 Methods and materials

4.1 Sampling equipment

Sampling is performed in accordance with NEN-ISO 16702:2007 (Workplace air quality – Determination of total isocyanate groups in air using 1-(2-methoxyphenyl)piperazine and liquid chromatography).
A measured volume of air at a rate of approximately 1.5 L/min is drawn through a filter 37mm sampling cassette in which a glass fiber (GF) filter impregnated with 1-(2-methoxyphenyl)piperazine (1-2MP). The personal air sampling pump is a Gilian pump Model HFS-513A.

4.2 Analytical procedure

Analysis is performed in accordance with NEN-ISO 16702:2007 (Workplace air quality – Determination of total isocyanate groups in air using 1-(2-methoxyphenyl)piperazine and liquid chromatography). Instead of the 'classical' EC/UV detection, mass spectrometry (MS) detection is used because it's more sensitive, provides improved identification and is easier to use.

Samples are analyzed using reversed phase high pressure liquid chromatography and electro spray MS detection (RP-LC-MS), monitoring positive ions.
Quantification is made by using an external standard and monitoring selected ions m/z = 635 and m/z = 193 (SIM mode). The LC-MS system consist of a Agilent 1100 LC with a Agilent 6140 Single Quad Mass Spectrometer. The LC-column is Phenomenex Luna PFP2 (150 x 3 mm, 3µm) column. The mobile phase is a gradient with ammonium formate (5mM) and acetonitrile.

5 Results

5.1 MDI concentrations

The experiments were carried out on Tuesday 23th, April 2013 at the facility of Lovink Enertech in Terborg, The Netherlands. In Table 1 the MDI analysis results are shown of experiment 1 and 2. The concentrations are given in µg/m^3 MDI for the three different isomers of MDI and in isocyanate equivalents (table 2). The concentrations of 2,4 and 2,2 MDI are semi –quantitative, calculated based on the response of 4,4, MDI.

Table 1 Results of the measurements, expressed in µg/m^3 MDI

Code TNO	Description of samples	4,4'-MDI µg/m^3	2,2'-MDI µg/m^3	2,4'-MDI µg/m^3
52013092-005	Blank measurement of the workplace air in LSR room (exp 1)	< 0,001	< 0,001	< 0,001
52013092-006	PAS measurement technician 1 during mixing/filling of the cable joint (exp 1)	0,009	< 0,008	< 0,008
52013092-007	PAS measurement technician 2 around filling of the cable joint (exp 1)	< 0,008	< 0,008	< 0,008
52013092-008	Blank measurement of the workplace air in E-room (exp 2)	< 0,0003	< 0,0003	< 0,0003
52013092-009	PAS measurement technician 1 during mixing/filling of the cable joint (exp 2)	0,027	< 0,008	< 0,008
52013092-010	PAS measurement technician 2 around filling of the cable joint (exp 2)	< 0,008	< 0,008	< 0,008

< = LOQ (limit of quantification)

PAS =personal air sampling in breathing zone

Table 2 Results of the measurements, expressed in µg/m^3 Isocyanate (NCO)

Code TNO	Description of samples	4,4'-MDI µg nco/m3	2,2'-MDI µg nco/m3	2,4'-MDI µg nco/m3
52013092-005	Blank measurement of the workplace air in LSR room (exp 1)	< 0,0002	< 0,0002	< 0,0002
52013092-006	PAS measurement technician 1 during mixing/filling of the cable joint (exp 1)	0,003	< 0,003	< 0,003
52013092-007	PAS measurement technician 2 around filling of the cable joint (exp 1)	< 0,003	< 0,003	< 0,003
52013092-008	Blank measurement of the workplace air in E-room (exp 2)	< 0,0001	< 0,0001	< 0,0001
52013092-009	PAS measurement technician 1 during mixing/filling of the cable joint (exp 2)	0,009	< 0,003	< 0,003
52013092-010	PAS measurement technician 2 around filling of the cable joint (exp 2)	< 0,003	< 0,003	< 0,003

< = LOQ (limit of quantification)

PAS =personal air sampling in breathing zone

5.2 Occupational exposure risks

There are several regulatory and/or advisory concentration limits used for occupational (NIOSH, OSHA, ACGIH) exposure to MDI:

1. The NIOSH ceiling and OSHA PEL (permissible exposure limit) ceiling value for MDI is 200 µg/m^3; this concentration should not be exceeded at any time. This value is expressed as a 10 or 15 minutes average.
2. The NIOSH REL (recommended exposure limit) and ACGIH TLV (threshold limit value) for MDI is respectively 50 µg/m^3 and 51 µg/m^3, this is the concentration of MDI to which most workers can be exposed without adverse effects and is expressed as an 8 hour time-weighted average.

3. UK HSE occupational exposure limits: STEL (short term exposure limit): 70 µg/m³ expressed as a 15 minutes ceiling value and TWA (time weighted average): 20 µg/m³, expressed as an 8 hour time-weighted average.

The measured concentration of 4,4,MDI in the breathing zone of technician 1, who carried out the filling for experiment 1 and 2, are equal or less than 0,1 % of the levels used for occupational exposure of MDI (NIOSH, OSHA, ACGIH). No concentrations of 4,4 MDI were measured in the breathing zone of technician 2. For both technicians, no concentration levels of 2,2 MDI and 2,4 MDI were measured in the breathing zone.

6 Conclusions

Within the context of research towards possible exposure to MDI around mixing and filling cable joints with polyurethane resin, an investigation was conducted with the purpose of gaining more insight into the following questions:

- Determination of MDI (vapor and aerosol) concentration in the breathing zone of workers during the processing of mixing and filling cable joints with the polyurethane resin.
- Evaluation of the measured MDI concentrations by comparison to the TLV's (threshold limit values) for occupational exposure.

The findings of the investigation are as follows:

- Compared to daily practice where cable joints are filled in the ambient air, personal air sampling experiments during filling of cable joints were carried out in a so called worst-case scenario in two separate inside rooms without ventilation.
- The measured concentration of 4,4,MDI in the breathing zone of technician 1, who carried out the filling of the cable joints with polyurethane (for experiment 1 and 2), are equal or less than 0,1 % of the levels used for occupational exposure of MDI (NIOSH, OSHA, ACGIH).
- For both experiments 1 and 2, no concentrations of 4,4 MDI were measured in the breathing zone of technician 2.
- For both technicians, no concentration levels of 2,2 MDI and 2,4 MDI were measured in the breathing zone.

7 Autentication

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