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Cases of worker exposure to PUR thermal degradation products based on literature screening

A lous follow-up project

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Cases of worker exposure to PUR thermal degradation products based on literature screening

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1. Introduction

1.1 Background

The LOUS Survey of certain isocyanates (MDI and TDI) (Danish EPA Environmental project no. 1537, Christensen et al., 2014) – from now on the 'LOUS survey' – found that thermal degradation of polyurethane (PUR) products might lead to generation of carbon monoxide, oxides of nitrogen, traces of hydrogen cyanide, free isocyante monomers, amines and other toxic degradation products. The thermal degradation (oxidation and pyrolysis) takes place between 200 °C and about 600 °C – the exact temperatures depending on the type of PUR.

A Danish report from 2001 identified a range of industries (car workshops, work with district heating pipes, textile manufacturing, wood industry, manufacturing of building materials) in which products/coated PUR product might be heated due to cutting, boring/drilling, grinding, soldering, welding, casting, etc. (Pratt and Engelund, 2001).

Within the scope of the LOUS survey, no information sources addressing actual exposure estimations/measurements associated with thermal degradation of PUR-products were identified. Neither any human case reports were identified.

1.2 Overall objective

This project is aiming at identifying further information regarding occurrence and possible impacts associated with thermal degradation of PUR products as an input to ongoing considerations regarding the LOUS strategy follow-up on MDI and TDI.

1.3 Scope

1.3.1 Foreseen activities

The current project shall initially:

- Examine MDI and TDI REACH registration dossiers to reveal whether thermal degradation of PUR products has been addressed in the relevant exposure scenarios of the Chemical Safety Reports (CSRs). *NB! This activity has been reported in a separate confidential report and will thus not be addressed further in this memo.*
- Contact the following stakeholders regarding possible information about human cases involving thermal degradation of PUR products
  - The poison information center at Bispebjerg hospital
  - The Danish Register of Occupational Diseases
  - The PUR section of the Danish Plastics Federation
  - Selected polyurethane experts
- Screen literature for description of cases causing worker exposure and impacts as a result of exposure to PUR thermal degradation products.

2. Methodology/approach

2.1 Public registers

The poison information center at Bispebjerg hospital and the Danish Working Environment Authority (hosting the Danish Register of Occupational diseases) have been approached with an explanation about the background for the project (in line with Section 1.1) and asked to conduct specific searches for possible human cases involving thermal degradation of PUR products.

2.2 Stakeholders

Contact was taken with Thomas Brønnum from the PUR section of the Danish Plastics Federation and with a number of plastics/polyurethane experts from the Danish Technological Institute to learn about their view/experiences with thermal degradation of PUR products.

2.3 Literature search and review

A literature search was conducted in order to identify scientific articles and otherwise published literature covering thermal degradation of PUR products, especially in relation to generation of thermal degradation products during working operations and related exposure and effects in humans/workers. A range of key words were used as search terms, either alone or together in different combinations. "PUR", "PUR products" or "polyurethane" were combined with the following search word: "thermal degradation", "human", "worker exposure", "heating", "monomers", "metal work*", "insulation material". The words "isocyanates" and "aminoisocyanates" were also combined with "thermal degradation". The searches were primarily conducted in December 2014 in PubMed, and supplemented with searches in Web of Science, DTU FindIt and Google.

Based on the titles of the search outcome, 20 potentially relevant scientific articles were identified. Within the scope of this project, these articles have been further screened and where relevant summarised, largely based on the abstracts.

3. Findings

3.1 Poison center

The poison information center at Bispebjerg hospital has not responded to the enquiry within the time frame of the project.

3.2 Register of Occupational diseases

Extracts from the Danish Register of Occupational diseases for the period 2004 to 2013 were provided by the Danish Working Environment Authority.

Extracts from this register proved challenging for the following reasons:

- Entries involving chemicals are generally associated with handling of the chemicals as such, e.g. from products containing isocyanate monomers rather than polymers made from the monomers. Thus possible cases associated with thermal degradation might be difficult to locate via searches in the register as they might have been filed differently.

- Associated with the above, the description of the cases/entries (made by the medical doctor registering the case) are very different in style and content and does often not provide enough information to decide whether a given entry/case is associated with handling products with free isocyanates or products from which the isocyanates are released due to thermal degradation.

- The register often lists several possible chemicals associated with a given case/entry, e.g. brominated flame retardants as well as isocyanates in relation to polymers.

Thus, there could be more entries not identified due to difficulties associated with the search strategy and some cases thought to be associated with thermal degradation might be due to exposure to products with free isocyanates or to other chemicals.

In light of these uncertainties, the following discussion of entries possibly associated with thermal degradation of PUR products should not be over-interpreted.

Overall, however, for the 10-year period (2004-2013), it is assessed that the following entries might be associated with exposure to degradation products generated by thermal degradation of PUR products:

- Welding: 2 entries

- Machining (sawing, grinding, ….): 2 entries

- Thermal degradation of insulation materials: 1-2 entries

- Thermal degradation associated with manufacturing: 1 entry

3.3 PUR section of the Danish Plastics Federation

Thomas Brønnum from the PUR section of the Danish Plastics Federation refers to the following:

- The report "Littorin et al. 2003. Isocyanater – Medicinske risker, biologiske mekanismer samt medicinsk och social prognos (AFA/AMF/AGSs projekt 474). Slutrapport 2003-03-05. Yrkes- och miljömedicin, Universitetssjukhuset, 221 85 Lund."

- A Swedish case: www.arbetsmiljoforskning.se/isocyanater/slipskiva-sadede-r%C3%B6rl%C3%A4ggarens-lungor-f%C3%B6r-livet

Littorin et al. (2003), among others, address measurements from two facilities handling "filters with FINNMOP". It is not entirely clear what FINNMOP refers to, but measurements show high levels of amines (ICA) resulting from thermal degradation of PUR. It is concluded that such releases from MDI-PUR might cause chronic inflammation in the mucous membranes of the nose. It is also noted that further information on the health effects of thermal degradation from PUR products is needed.

The case study describes a case from 2012, where a pipe fitter using a sanding disc containing PUR has had his lungs permanently damaged by released isocyanates. As a consequence, the sanding disc manufacturer (3M) has stopped the manufacture of this type of disc.

3.4 Plastics experts

A number of plastics experts at the Danish Technological Institute have been interviewed.

To their memory, they have not observed any "cases" involving exposure to thermal degradation products from PUR products.

They commonly doubt that e.g. machining of pure PUR products will generate enough heat to cause thermal degradation.

Thus, they would assume that thermal degradation of PUR products would be associated with e.g. heating/hotwiring of electrical installations involving PUR insulation materials and/or where e.g. metal parts coated with PUR are machined.

3.5 Literature review

The initially identified 20 scientific articles were further screened for relevance within the scope of this project.

This resulted in deselection of 11 of these papers, including papers addressing measurements of PUR thermal degradation in the laboratory (e.g. Melin et al., 2001 and Zitting et al., 1980) and papers addressing exposure during application of products with free isocyanates, including gluing operations with or without heating (e.g. Littorin et al. 2000, 2002; Dalene, 1997).

The remaining 9 articles all relate to observations involving thermal degradation or PUR products in the workplace. The review of these have been divided into studies: i) solely addressing exposure in the workplace, ii) studies addressing measurements of biomarkers in workers, and iii) studies addressing observations of health effects in exposed workers.

TABLE 1: SUMMARY OF IDENTIFIED SCIENTIFIC ARTICLES ADRESSING EXPSOURE TO PUR THERMAL DEGRADATION RPODUCTS

Working process	Exposure characteristics	Symptoms observed	Reference	Other comments
Exposure studies				
Welding in car body repair shops	MDI	Not studied	Pronk et al. (2006)	-
Cutting, grinding and orbital sanding operations in a car paint body repair shop	Most abundant isocyanates: MDI, TDI, HDI, IPDI and methyl isocyanate	Not studied	Boutin et al. (2006)	"... a rapid decrease of the isocyanate concentration was observed while moving away from the emission source."
- Welding of district heating pipes - Welding of PUR-coated metal sheets	Eleven isocyanates, three amines and five aminoisocyanates	Not studied	Karlsson et al. (2002)	- "The compounds were present in both the gas and particles phases"
Cutting and welding operations in a car repair shop	MDI, TDI and other ioscyanates	Not studied	Karlsson et al. (2000)	- "Isocyanates with low volatility were mainly found in the particle phase, but isocyanates with a relatively high volatility such as TDI, were found in both the particle and the gas phase"
- Car repair workshop: i) grinding and ii) welding operations - Welding of district heating pipes - Turning of a PUR-coated metal cylinder	Elevated levels of MDI and other isocyanates measured during work processes	Not studied	Henriks-Eckerman et al. (2002)	- It is noted that "The diisocyanate concentrations were in general higher near the emission source than in the workers' breathing zone."
Biomarker studies				
Pipe layers welding PUR insulated pipes	Thermal degradation products including MDI	Increased isocyanate-derived amine (TDA) in acid-hydrolysed urine and in plasma	Dalene et al. (1996)	- In urine samples, MDA seems to be present only for a short period after exposure, whereas MDA in plasma seems to "give a rather good estimate of exposure to MDI during the preceding months."

Working process	Exposure characteristics	Symptoms observed	Reference	Other comments
Flame lamination factory applying a thin layer of TDI-based flexible PUR foam onto textile fabric, involving partly melting of the PUR foam by an open flame	TDI	Increased isocyanate-derived amine (TDA) in acid-hydrolysed urine Increased TDA in plasma and erythrocytes	Lind et al. (1997)	- "..history of exposure can be determined by biomarkers in plasma an erythrocytes. Recent exposure does not greatly affect the P-TDA and E-TDA levels."
- Car repair workshops - Milling and turning of PUR coated cylinders - Welding of district heating pipes	MDI and TDI as PUR thermal degradation products	Increased isocyanate-derived amines (MDA and/or TDA) in acid-hydrolysed urine	Rosenberg et al. (2002)	- Levels not as high as in workers handling monomeric isocyanates - Increased levels not found in relation to: i) injection moulding of thermoplastic PUR, ii) joint welding of PUR floor covering
Effect studies				
Pipe layers, in particular PUR welding tasks (n = 163)	"Thermal degradation products", not further specified	Adverse effects on mucous membranes, including: - Reduced FEV1 - Irritative eye symptoms - congestion of the nose - dryness of the throat	Jakobsson et al. (1997)	- No confounding effect of other welding

Within the scope of this project, the following can be concluded based on the literature review performed:

- Thermal degradation products, including MDI and TDI monomers can be released when PUR products are heated, e.g. directly via an open flame or welding, and via machining operations (cutting, grinding, milling, turning) of metal products coated with PUR.
- Biomarkers of isocyanate exposure resulting from thermal degradation products can be measured in urine (relatively short time after exposure) and in plasma and erythrocytes (good indicators for exposure during preceding months).
- Adverse health effects on mucous membranes have been reported in one of the peer-reviewed articles.
- References are relatively old – the most recent are from 2006. Whether this is a result of lack of interest among scientist or an indication that exposure management has increased over the past years is not known.

- Concentrations of diisocyanates seem to drop rapidly with distance from the emission source. Thus as a first measure, worker exposure can be significantly reduced if distance between the source and the breathing zone can be established.
- Looking further into the authors and affiliations of the articles reviewed reveal that quite some of the evidence in the scientific literature originates from a research group at Lund University in Sweden in the late 1990's/early 2000's. These authors also published the report summarised in Section 3.3.

4. Conclusion

Based on information received from: i) a number of experts, ii) from the Danish Register of Occupational diseases, and iii) from a screening literature review, it appears that thermal degradation products, including MDI and TDI from PUR products can be released from the following operations:

- Heating of PUR products, including heating PUR films and heating of insulation materials in electrical installations
- Welding of PUR coated products, including district heating pipes
- High energy impact on PUR coated metal products; including machining such as cutting, grinding, milling, turning, drilling/boring, sawing
- High energy operations involving tools containing PUR (e.g. sanding discs)

It has been reported that diisocyanate biomarkers can be measured in urine, plasma and erythrocytes in workers exposed to PUR thermal degradation products and a few studies have reported effects on mucous membranes, including chronic inflammation.

Most of the evidence identified is more than 10 years old and to a large extent associated with activities around Lund University.

It is unclear whether this is a result of better exposure management today or lack of scientific interest.

In any case, concentrations of diisocyanates seem to drop rapidly with distance from the emission source. Thus as a first measure workers exposure can be significantly reduced if distance between the source and the berating zone can be established.

Overall, the information identified clearly shows that thermal degradation of PUR products might occur in the working environment and lead to exposure/effects in exposed workers. It is not possible to assess the real magnitude/frequency/severity of cases associated with exposure to thermal degradation products from PUR products based on evidence identified in this study.

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Appendix 1: Abbreviations

E-TDA	Erythrocytes- Thiodianiline
ICA	Isocyanic acid
IPDI	1-(isocyanatomethyl)-3,5,5-trimethyl-cyklohexan
HDI	Hexamethylene diisocyanate
MDA	Methylenedianiline
MDI	Methylene diphenyl diisocyanate
TDA	Thiodianiline
TDI	Toluene diisocyanate
P-TDA	Plasma- Thiodianiline
PUR	Polyurethane

Cases of worker exposure to PUR thermal degradation products based on literature screening

This is a literature screening identifying information regarding occurrence of MDI and TDI as well as possible impacts associated with thermal degradation of PUR products as an input to ongoing considerations regarding the LOUS strategy on MDI and TDI. It is a follow-up of the Danish EPA's List of Undesired Substances (LOUS) review 2012-2015.

Dette er en litteraturscreening, der identificerer viden om forekomst af MDI og TDI samt mulige konsekvenser forbundet med termisk nedbrydning af PUR-produkter som et input til igangværende overvejelser om den danske strategi for MDI og TDI. Det er et opfølgningsprojekt i forbindelse med Miljøstyrelsens arbejde med Listen over uønskede stoffer (LOUS) 2012-2015.

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