Danish Ministry of the Environment
Environmental Protection Agency

Survey of certain isocyanates (MDI and TDI)

Part of the LOUS-review

Version of Public Hearing

October 2013

Title:
Survey of certain isocyanates (MDI and TDI), part of the LOUS-review

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Published by:

The Danish Environmental Protection Agency
Strandgade 29
1401 Copenhagen K
Denmark
www.mst.dk/english

Year:

2013

ISBN no.

[xxxxxx]

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Preface

Background and objectives
The Danish Environmental Protection Agency's List of Undesirable Substances (LOUS) is intended as a guide for enterprises. It indicates substances of concern whose use should be reduced or eliminated completely. The first list was published in 1998 and updated versions have been published in 2000, 2004 and 2009. The latest version, LOUS 2009 (Danish EPA, 2011), includes 40 chemical substances and groups of substances which have been documented as dangerous or which have been identified as problematic using computer models. For inclusion in the list, substances must fulfil several specific criteria. Aside from the risk of leading to serious and long-term adverse effects on health or the environment, only substances which are used in an industrial context in large quantities in Denmark, i.e. over 100 tonnes/year, are included in the list.

Over the period 2012-2015, all 40 substances and substance groups on LOUS have been or will be surveyed. The surveys include collection of available information on: the use and occurrence of the substances, internationally and in Denmark; environmental and health effects; alternatives to the substances; existing regulations; monitoring and exposure, and regarding ongoing activities under REACH, among others.

On the basis of the surveys, the Danish EPA will assess the need for any further information, regulation, substitution/phase out, classification and labelling, improved waste management or increased dissemination of information.

This survey concerns certain isocyanates (MDI and TDI). The entry in LOUS 2009 for these substances is "Certain Isocyanates - MDI and TDI". The reason for the inclusion in LOUS was that MDI and TDI are classified as suspected carcinogens and that, in addition, MDI is classified with R48 (Danger of serious damage to health by prolonged exposure) according to the Dangerous Substances Directive (67/548/EEC).

The main objective of this study is, as mentioned, to provide background for the Danish EPA's consideration regarding the need for further risk management measures.

The process
The survey has been undertaken by COWI A/S (Denmark) in cooperation with the Technological Institute (Denmark) from March to October 2013. The work has been followed by an advisory group consisting of:

- Louise Grave-Larsen, Lone Schou and Kathrine Smidt, Danish EPA
- Thomas Brønnum, The Danish Plastics Federation – PUR Section
- Bente Fabech and Charlotte Legind, Danish Veterinary and Food Administration
- Susanne Høyer, Danish Working Environment Authority
- Nils H. Nilsson, Danish Technological Institute
- Frans Møller Christensen, COWI

Data collection
The survey is based on the available literature on the substances, information from databases and direct inquiries to trade organisations and key market actors. The data search included (but was not limited to) the following:

- Legislation in force from Retsinformation (Danish legal information database) and EUR-Lex (EU legislation database);
- Ongoing regulatory activities under REACH and intentions listed on ECHA's website (incl. Registry of Intentions and Community Rolling Action Plan);

- Relevant documents regarding International agreements from HELCOM, OSPAR, the Stockholm Convention, the PIC Convention, and the Basel Convention.
- Data on harmonised classification (CLP) and self-classification from the C&L inventory database on ECHAs website;
- Data on ecolabels from the Danish ecolabel secretariat (Nordic Swan and EU Flower);
- Pre-registered and registered substances from ECHA's website;
- Production and external trade statistics from Eurostat's databases (Prodcom and Comext);
- Export of dangerous substances from the Edexim database;
- Data on production, import and export of substances in mixtures from the Danish Product Registry (confidential data, not searched via the Internet);
- Date on production, import and export of substances from the Nordic Product Registries as registered in the SPIN database;
- Information from Circa on risk management options (confidential, for internal use only, not searched via the Internet)
- Monitoring data from the National Centre for Environment and Energy (DCE), the Geological Survey for Denmark and Greenland (GEUS), the Danish Veterinary and Food Administration, the European Food Safety Authority (EFSA) and the INIRIS database.
- Waste statistics from the Danish EPA;
- Chemical information from the ICIS database;
- Reports, memorandums, etc. from the Danish EPA and other authorities in Denmark;
- Reports published at the websites of:
  - The Nordic Council of Ministers, ECHA, the EU Commission, OECD, IARC, IPCS, WHO, OSPAR, HELCOM, and the Basel Convention;
  - Environmental authorities in Norway (Klif), Sweden (KemI and Naturvårsverket), Germany (UBA), UK (DEFRA and Environment Agency), the Netherlands (VROM, RIVM), Austria (UBA). Information from other EU Member States was retrieved if quoted in identified literature;
  - US EPA, Agency for Toxic Substances and Disease Registry (USA) and Environment Canada; and
- PubMed and Toxnet databases for identification of relevant scientific literature.

As well, direct enquiries were sent to Danish and European trade organisations and a few key market actors in Denmark.

Summary and conclusions

Substance group and terminology
This report addresses two groups of diisocyanates:
- Methylene diphenyl diisocyanate (MDI)
- Toluene diisocyanate (TDI)

Methylene diphenyl diisocyanate (MDI) is an aromatic diisocyanate with the chemical formula $C_{15}H_{10}N_2O_2$ where the two aromatic rings are connected by a methylene group. Three isomers - 2,2'-MDI, 2,4'-MDI, and 4,4'-MDI - exist. Toluene diisocyanate (TDI) is an aromatic diisocyanate with the formula $CH_3C_6H_3(NCO)_2$. Six isomers are possible, of which 2,4-TDI and 2,6-TDI are commercially the most important.

Seven (mixes of) MDI/TDI monomers are within the key scope of this project:
- **2,2'-MDI** (Diphenylmethan-2,2'-diisocyanate); CAS-number: 2536-05-2; EC-number: 219-799-4
- **2,4'-MDI** (Diphenylmethan-2,4'-diisocyanate); CAS-number: 5873-54-1; EC-number: 227-534-9
- **4,4'-MDI** (Diphenylmethan-4,4'-diisocyanate); CAS-number: 101-68-8; EC-number: 202-966-0
- **MDI - unspecified mix of isomers**: CAS-number: 26447-40-5; EC-number: 247-714-0
- **2,4-TDI** (2,4-toluene diisocyanate):CAS-number: 584-84-9; EC-number: 204-825-9
- **2,6-TDI** (2,6-toluene diisocyanate): CAS-number: 91-08-7; EC-number: 202-039-0
- **TDI-mixed** (2,4-TDI:2.6-TDI often indicated as 80:20 and 65:35 mixes): CAS-number: 26471-62-5; EC-number 247-714-0.

The three “pure” MDI isomers have been registered under REACH, whereas the CAS-number for a mix of isomers (CAS-number: 26447-40-5) has not been registered as such. However, dialogue with industry has revealed that registration has actually taken place under other CAS/EC-numbers because of REACH technicalities. The EU 2005 risk assessment of MDI generally referred to CAS-number 26447-40-5 with the understanding that this CAS-number would cover all (combinations of) isomers. However, some confusion has been created because CAS-number 26447-40-5 is not REACH registered as such.

2,4-TDI and TDI-mixed have been registered, whereas the technically difficult-to-isolate 2,6-TDI has not.

TDIs are generally marketed in their monomeric form, whereas MDIs are marketed in various other forms as well:
- *Polymeric MDI* is (refined) reaction products from the MDI manufacturing process consisting of approx. 40-50% 4,4’- MDI, 2.5-4.0% 2,4’-MDI, 0.1-0.2% 2,2’-MDI and 50-60% Homologues;
- *Oligomeric MDI* is the crude reaction product of the above process, containing a mix of monomeric and polymeric MDI, but with a homologue/polymer content below 50%, and
- *Modified/prepolymer MDI*s are prepared from monomeric or polymeric MDIs via a potentially catalyzed partial reaction with themselves or with hydroxyl- or amino-compounds resulting in molecules terminated with isocyanate groups. This group includes MDI homopolymers, which consists of MDIs that have been reacted with themselves.

Polymeric MDI has not been registered under REACH as industry considers it a polymer according to the OECD polymer definition (>50% polymer content), whereas oligomeric MDI and a range of modified MDIs have been registered.

Terminology around the various forms in which MDI is marketed is not straightforward, and it has been the experience of the authors that ambiguities and different understandings and uses of the terms exist. Further complicating the issue is that generic terms such as "polyisocyanates" and "co-polymers" are sometimes used without defining these terms with any precision. However, ISOPA[1] member companies stress that all forms of MDI, including polymeric MDI and modified/prepolymer MDI are classified and labelled in line with monomeric MDI and exposures/risks should be controlled similarly. The project, however, has identified that some modified/prepolymer MDIs are marketed as being less toxic than monomeric MDIs.

Regulation
The seven (mixes of) TDI and MDI within the scope of this project are subject to harmonised classification under the CLP regulation. They are all classified as suspected of causing cancer, as dermal and respiratory sensitisers, for acute toxicity following inhalation, as well as eye, skin and respiratory irritants. Furthermore, MDI is classified for potential to cause damage to liver and kidney following repeated exposure, whereas TDI is classified for environmental effects (harmful to aquatic life with long lasting effects).

MDI is subject to an EU restriction on the use of MDI-containing consumer products and a Commission recommendation related to MDIs used professionally. 2,4-TDI, 2,6-TDI, 2,4'-MDI and 4,4'-MDI are on the positive list of the plastic food contact material regulation with certain restrictions and TDIs are prohibited in cosmetics. "Isocyanates" (including MDI and TDI) are specifically indicated to be within the scope of the IPPC (Integrated Pollution Prevention and Control) and PRTR (Pollutant Release and Transfer Register) directives. TDI is specifically mentioned in Annex 1, Part 2 of the Seveso Directive. Isocyanate waste (nomenclature: "08 05 01 waste isocyanates") is regulated as hazardous waste. Finally, a Commission recommendation states that Member States should address occupational diseases caused by isocyanates.

For the Danish situation, an array of national legislation is in place in relation to occupational handling of isocyanates, including the need for training, labelling, handling, security measures, limitations of spray applications and the establishment of Danish Occupational Exposure Limits. Most of these requirements are also applicable off-shore and on ships.

MDI and TDI are generally not addressed in international agreements, except that TDI is specifically addressed by the UNECE Convention on the Transboundary Effects of Industrial Accidents (in parallel with being specifically addressed by the Seveso directive) and isocyanates waste, classified as hazardous waste, falls under the provisions of the Basel Convention.

Isocyanates are addressed by a few EU and Nordic eco-labelling criteria, in particular in relation to TDI in adhesives, furniture and textiles.

In general there is some ambiguity as to whether some or all TDI and MDI isomers are addressed by a given requirement and whether other forms, such as prepolymer and polymeric isocyanates, have been considered in relation to drafting the requirements. It should be noted that most of the specific Danish requirements are also applicable to prepolymers.

TDI and MDI are currently undergoing REACH substance evaluation and further risk management considerations in the EU, which might lead to further action at EU level. These activities are thus far subject to confidentiality, but the Danish EPA has direct access to the activities and the related documents.

Manufacture, use and applications
Manufacture
MDI and TDI are manufactured on a large scale in a few EU facilities not located in Denmark.

[1] The European Diisocyanate and Polyol producers Association

Overall volumes and trends
Volume-wise, MDI and TDI account for about 95% of the use of isocyanates with an estimated:

- EU consumption of about 1.5 million tonnes/year;
- Nordic market consumption of about 67,000 tonnes/year, and
- Danish consumption of about 9,000 – 14,000 tonnes/year.

The global, EU and Nordic consumption is steadily increasing. A similar trend is expected for Denmark.

Applications and split between MDIs and TDIs
Main applications of TDIs and MDIs are:

- Flexible PUR (e.g. for furniture upholstery and mattresses) (largely TDI-based, but about 10% MDI), and
- Rigid PUR (e.g. for insulation, district heating tubes, refrigeration, construction) (purely polymeric MDI-based).

"C.A.S.E.":

- **C**oatings (surface treatment such as paints and lacquers) (Nordic data indicate that about 70% of these are MDI-based, the rest TDI-based);
- **A**dhesives (Nordic data indicate that about 80% of these are MDI-based, the rest TDI-based);
- **S**ealants (e.g. fillers/joint fillers/foam sealants) (largely MDI-based) , and
- **E**lastomers (e.g. rubber and thermoplastic elastomers) (almost purely MDI-based).

In addition:

- Binders (used for binding particles together mainly for chipboards) (purely MDI based).

Flexible and rigid PUR, as well as elastomers (E) are typically supplied as already cured products, whereas for coatings (C), adhesives (A), sealants (S) and binders, the curing itself forms part of the functionality of the products during/after use.

In the EU and Nordic market, 80% and 83%, respectively, of TDI and MDI consumption for production are applied for PUR production (rigid, flexible and elastomer). Binders for the production of chipboards account for 10% of the EU market and 11% of the Nordic market. This leaves about 10% (EU) and 6% (Nordic) for production of coatings, adhesives and sealants.

Please note that these figures represent the MDI and TDI 'consumption for production' and not the consumption of PUR products or consumption of products containing MDI/TDI (such as coatings, adhesives and sealants), as the latter are affected by import/export.

For the Danish market, it has not been possible to obtain precise data on the distribution of the MDI/TDI volumes among the main application groups. However, it is assumed that the majority of MDI and TDI are used for PUR production; the Danish Plastics Federation estimates that about 6,000 tonnes TDI/year and 6,000 tonnes MDI/year are used for production of flexible, rigid and elastomeric products. The Danish Plastics Federation notes that Danish production of rigid PUR has decreased in recent years, leaving a relatively high production of flexible PUR, which is largely TDI-based.

To our knowledge, no board production using MDI binders is taken place in Denmark.

Although no exact data have been found, but considering data collected for EU and the Nordic market, it is estimated that about 10% overall of the Danish MDI and TDI volume is accounted for in coatings, adhesives and sealants, corresponding to approx. 1000 tonnes/year. However, it should be stressed that this is an estimate made with a high level of uncertainty.

Adhesives and sealants are supplied to consumers, including MDI in aerosol cans and products containing TDI (e.g. joint sealants and yacht wood sealers). It should be noted that no EU consumer restriction is in place for

TDI-based products similar to the one applicable for MDI-based products. Finally, it is also speculated whether it is possible for consumers to get access to more professional grades of products, such as e.g. coatings and paints.

A significant range of PUR-based consumer products is available on the Danish market, including e.g. foam in automotive seats, mattresses and furniture, as well as PUR in shoes, textiles (fibres or as coating), hoses, foamed facecloths, food contact materials and briefcases. As will be discussed in the section addressing human health effects, there is some ambiguity as to the content of residual monomers and amine degradation products in these PUR products.

Production in Denmark
Dialogue with Danish trade organisations has provided the following figures for Danish productions facilities using MDI and TDI:

- Rigid PUR production: 9 companies;
- Flexible PUR production: 2 companies;
- PUR elastomer production: 3 companies;
- Coatings/paints: A few companies;
- Adhesives/Sealants: None, and
- Chipboards using MDI based binders: None (assumed).

Waste Management
Waste from manufacture of MDI and TDI
There is no manufacturing in Denmark of MDI and TDI and, therefore, no production waste.

Waste fraction containing free MDI and TDI monomers
According to interviews with a number of producers, there is no MDI and TDI waste from the production of rigid and flexible PUR. From trials in research and development, small amounts of MDI/TDI might end up as waste. This is send to Nord (former Kommunekemi).

From production and professional use of coatings, adhesives and sealants, interviews with coating/paint companies indicate that the waste is disposed of as hazardous waste "Isocyanate", waste code: 08 05 01. From the Danish EPA waste statistics, data regarding waste code 08 05 01 has been extracted for 2012. According to this extract, 244 tonnes (99%) are incinerated and less than 1 % recycled. Isocyanates will degrade completely during combustion.

Waste from use of coatings, adhesives and sealants by consumers should ideally be collected as hazardous waste, but may end up in household waste or in various fractions at the recycling stations. It is assumed that it is minor items and that they will go to incineration, where the isocyantes will be degraded.

PUR production waste amounts and treatments
Recycling of production waste from the production of district heating insulated pipes (rigid PUR) is done by glycolysis (100 % recovery as new regenerated polyol for production). The Danish producer of such pipes in Denmark confirms that the amount of PMDI used for production is unchanged (2012) from the amount in Danish EPA (2005a): 6,500 tonnes, but the amount of internal waste has decreased to 3%, which is recycled in the above mentioned glycolysis process.

Production waste of flexible PUR products is used for new applications after milling (carpet backing), according to information provided by producers. This is an important recycling process for flexible PUR as there is a high amount of production waste (23 %) in the cutting process.

Recycling possibilities for flexible PUR are continuously improved, requiring higher demands regarding the purity of the raw materials. The amount of production of flexible foam products in Denmark is judged to be unchanged from the amount in Danish EPA (2005a): 22,200 tonnes.

Product waste amounts and treatments

Waste treatment is strictly regulated by Danish law as well as at the European level with regard to PUR WEEE[2] waste. The PUR waste from end-of-life cooling furniture is not recycled, but rather incinerated with energy recovery, thereby also removing previous (CFCs, HCFCs) and current (cyclo-pentane) blowing agents. End-of-life PUR products from other sources (cars, furniture, building insulating foams, etc.) is, to our knowledge, incinerated with energy recovery or deposited to landfill; it is not recycled. One issue with PUR which makes recycling difficult is that PUR is often laminated to other materials (e.g. in sandwich panels), thus complicating separation. The amount of PUR products which ends up in the waste stream is unknown, except for cooling furniture (one company treats about 18,000 tonnes of PUR from this source annually).

Incineration

Isocyanates and polyurethanes will degrade completely during incineration at municipality waste incineration plants.

Environmental effects and exposure

Based on existing risk assessments from authoritative bodies, MDI and TDI do not seem to constitute any risk to the environment, although TDI is classified as harmful for the environment.

Ongoing REACH substance evaluations re-examine this issue, including possible PBT properties of MDI and TDI hydrolysis products (amines).

The Danish EPA has access to the confidential substance evaluations and can use the outcomes to evaluate whether further action in relation to MDI/TDI and the environment is appropriate.

Human health effects and exposure

MDI and TDI are classified as suspected of causing cancer, as dermal and respiratory sensitisers, as toxic following inhalation and as eye, skin and respiratory irritants. In particular, their ability to cause respiratory sensitisation is of concern. Inherently, TDI, having a vapour pressure about three orders of magnitude above that of MDI, is more likely to cause inhalation exposure and TDI exerts higher inhalation toxicity. However, MDI applications using aerosols and spraying also take place. Possible toxicity to fertility has been highlighted as an issue, e.g. in the 2005 MDI risk assessment (EU, 2005) and CMR properties of MDI/TDI and their degradation products (primary aromatic amines) is one of the reasons why both substances are subject to REACH substance evaluations. In parallel, a number of investigations regarding possible implementation of further risk management are ongoing at EU level. These activities are in the process of summarising hazards and the situation regarding exposure at the EU level. These activities are ongoing and/or confidential and can therefore not be summarised here. However, the Danish EPA has full access to all activities and documentation and can use that material as background for possible further action on these substances. Therefore, the main focus in this project is on the Danish situation, as a supplement to the EU activities.

Occupational exposure limits for MDI and TDI are in place in an array of EU and non-EU countries and the Danish values are similar to those in most other countries. In terms of exposure measurement and control, biomonitoring methods exist to measure the corresponding primary aromatic amines (MDA for MDI and TDA for TDI) following hydrolysis of isocyanate-protein adducts in urine and blood. A good correlation is found between inhalation exposure and this type of biomonitoring. Germany and the UK have established biological monitoring guidance values to assist in control of occupational exposure.

In terms of exposure, and thereby risk, most attention should probably be paid to professional and consumer use of coatings, adhesives and sealants.

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[2] Waste Electrical and Electronic Equipment

Extracts from Danish statistics over occupational diseases show a constant level of 10-15 registrations per year related to isocyanate exposure. Most of these are related to use of coatings, adhesives and sealants; the majority are related to airway diseases and a lower number to skin disorders.

This survey has shown that MDI- and TDI-containing adhesives and sealants are marketed for Danish consumers, with some MDI products marketed as aerosols. Furthermore, as e.g. also speculated by recent US EPA action plans on MDI and TDI, it cannot be excluded that consumers can get access to products intended for the professional market, e.g. via the Internet.

Consumer use of TDI-based products seems to be a cause for concern, as TDI is not subject to an EU restriction (as is MDI) requiring that products are provided with gloves and extended safety information. This is triggered by the fact that TDI is both more volatile than MDI and exerts higher inhalation toxicity.

MDI-containing products in aerosol cans might also be a cause for concern, as consumers would likely not use such products with appropriate ventilation and risk management controls.

Altogether, there seems to be a knowledge gap in relation to coatings, adhesives and sealants marketed and/or accessible to Danish consumers, including TDI-based products and MDI-based products involving spraying/aerosol generation.

MDI and TDI monomers (as residual monomers and/or degradation products) have been detected in a number of PUR consumer products, including e.g. baby mattresses. Their presence seems to conflict with chemical and thermodynamic arguments, which, according to the understanding of European isocyanate and PUR products trade organisations, show that analytically determined MDI and TDI in such products must be artefacts related to the analytical techniques.

It is generally acknowledged that liberation of MDI, TDI, amines and other degradation products might appear as a result of thermal degradation. Such degradation might take place e.g. during ironing and during a range of heat generating processes such as grinding and welding in a range of branches. No overview has been identified quantifying such emissions and related risk management measures put in place to reduce exposure.

Isocyanate-containing laminates/adhesives are used in plastic food contact materials. The risk for formation of primary aromatic amines from uncured isocyanate monomers, which could migrate to the food, is a subject of attention and an EU migration level has been established. A control campaign conducted by the Danish Food Directorate in 2001/2002, however, showed that even for laminates taken directly from the stores (with a higher expected content of uncured isocyanates), only two samples out of 33 showed primary aromatic amines above the detection level, but still considerably below the EU migration level at that time, as well as that in place today.

MDA (the primary aromatic amine generated from MDI hydrolysis) has been found at high levels in plastic kitchen utensils imported from China and Hong Kong. These levels could stem from degradation of MDI in the products. Regulation has been put in place to monitor and control the level of primary aromatic amines in such products.

Alternatives

Substitution of the volatile TDI with less volatile MDI, including modified/prepolymer MDI, has been undertaken and continues to take place, but may have reached a limit for technical reasons.

Blocking and encapsulation technologies “masking” the isocyanate groups to avoid/reduce exposure are being developed. To restore reactivity, this masking/blocking will disappear when the products are heated during processing.

Some alternative isocyanates substances like naphtalen-1,5-diisocyanate (NDI), Hexamethylene diisocyanate (HDI) and 1-(isocyanatomethyl)-3,5,5-trimethyl-cyclohexan (IPDI) are available for some applications. They possess some of the same hazardous properties as MDI and TDI, not the least of which is respiratory sensitising properties.

For the larger application areas of MDI and TDI for PUR products (flexible foam for furniture, rigid foam for district heating pipes, board stock, sprayed foam, one-component foam, etc.), given the need for high reactivity, it is foreseen that the products will largely continue to be based on the free isocyanates MDI/PMDI and TDI. When possible, they may be supplemented with modified/prepolymeric MDI according to best available technology (BAT) processes with focus on protection of the workers against exposure to the free isocyanates.

From the identified literature, it is foreseen that non isocyanate-based polyurethane (NIPU) will primarily find a market in the coating/paint, adhesive and sealant segments in the short term, the segment to which consumers also have access to products with monomeric MDI/TDI. Promising NIPUs are based on the reaction between polycyclic carbonate oligomers and aliphatic or cycloaliphatic polyamines with primary amino groups. Innovation in relation to using NIPU is ongoing, as supported by several identified patent applications.

The availability of alternatives for coatings, adhesives and sealants has partially been confirmed by contact with a number of Danish importers/producers of coatings, adhesives and sealants, although quality, price and tradition might limit the use of alternatives. For example, it has been stated that isocyanate free foam on a silane/STP (Silane Terminated Polymer) basis is about 8-9 times more expensive than the PUR based foam.

Toxicity of alternatives is rather complex to judge as generally "systems" ("silan-based" or "polycyclic carbonate-based") are described as isocyanate free products, but without information on the toxic evaluation of the alternatives. Assessments comparing health and safety aspects of alternatives with those based on isocyanate chemistry in a systematic way have not been identified, but e.g. US EPA in their recent MDI and TDI action plans note that environmentally friendly substitution seems difficult.

Overall, to reduce exposure and risk, it seems advisable to:

- continue the search for substituting TDI with the three orders of magnitude less volatile MDI, including modified/prepolymer MDIs. The potential for further substitution in this vein is, however, uncertain;
- further exploit the use of blocked and encapsulated MDIs/TDIs, as well as NIPU technology, and
- focus on process substitution/optimisation (and education) with the aim of minimising consumer and worker exposure. This focus would apply to MDI/TDI as well as any substitute chemistry, which is generally based on highly reactive and therefore potentially toxic chemistry in order to fulfil the required technical function.

Gaps

Based on the documentation reviewed and generated in this project, the main information gaps and gaps in relation to consensus/common understanding among stakeholders are assessed to be:

- *Use of CAS-numbers and terminology*. In documents reviewed for this project, there appears to be different practices in relation to use of CAS-numbers and terminology. This in particular relates to MDI, which can be supplied in various forms, including monomeric, modified, prepolymer, polymeric and oligomeric. Key issues in relation to this issue are:
  - Industry generally states that all MDI forms are considered equal from a hazard point of view and therefore handling, exposure control and other risk management should be equal for the different forms. To this end it should be noted that some modified MDIs appear to be marketed as less toxic than monomeric MDI.
  - Care should be taken when interpreting statistics, reviewing literature etc. as terms are used differently and sometimes interchangeably by some authors.
  - In relation to scope of legislation, some ambiguity exists as to whether all monomeric forms are addressed (not all relevant monomeric MDI/TDI CAS-numbers are always listed) and non-monomeric MDI forms (polymeric, modified etc.) are not (consistently) addressed, although as noted above, these should generally be considered equally hazardous.

- *Presence of monomeric MDI/TDI as residual monomer and primary aromatic amines in PUR products*. Analytical evidence appears to conflict with theory (thermodynamic/chemical considerations). Consequently, possible consumer and occupational exposure to MDI/TDI and primary aromatic amines during handling of these products is uncertain. The on-going REACH substance evaluations might address this issue.
- *MDI and TDI in consumer products*. No Danish statistics/overview exist as to the presence of MDI- and TDI-containing consumer products on the market or professional grade products that consumers can get access to (e.g. via the Internet). From an exposure/risk perspective, the project has identified that consumers have access to aerosols containing MDI (high likelihood of inhalation exposure) and some sealants/sealers containing TDI. TDI may be of specific concern given its three orders of magnitude higher vapour pressure and higher inhalation toxicity compared with MDI, as well as the fact that TDI is not covered by a similar EU consumer restriction as MDI (including requiring that gloves are provided with the product and that specific use instruction are communicated).
- *Thermal degradation*. No recent review has been identified regarding MDI, TDI, amines and other degradation products liberated during heating of PUR products and PUR coated products/materials. This gap includes the extent to which such processes are used in occupational and consumer settings, as well as possible risk management measures in place during such processing, which would reduce the resulting exposure levels.
- *Alternatives assessment*. Compared to other projects/analysis, which generally conclude that no (limited) alternatives are available, this project has identified a range of emerging alternative substances and technologies (in particular for specific applications, including consumer applications). However, no systematic assessment of the alternatives' health and environmental performances are identified. This gap might be associated with the fact that these alternatives are based on different chemical "systems", e.g. "silan-based".

Sammenfatning og konklusion

Stofgruppe og terminologi
Denne rapport omhandler to grupper af diisocyanater:

- Metylen-bisfenyl-isocyanat / diphenylmethan-diisocyanat (forkortet MDI efter det engelske "Methylene diphenyl diisocyanate")
- Toluen-diisocyanat (TDI)

Metylen-bisfenyl-isocyanat (MDI) er en aromatisk diisocyanat med den kemiske formel C15H10N2O2, hvor de to aromatiske ringe er forbundet med en metylengruppe. Der eksisterer tre isomere: 2,2'-MDI, 2,4'-MDI og 4,4'-MDI. Toluen-diisocyanat (TDI) er en aromatisk diisocyanat med formlen $CH_3C_6H_3(NCO)_2$. Der findes seks mulige isomere, hvoraf 2,4-TDI og 2,6-TDI er de kommercielt vigtigste.

Syv (blandinger af) MDI/TDI monomerer er indenfor rammen af dette projekt:

- **2,2'-MDI** (Diphenylmethan-2,2'-diisocyanat); CAS-nummer: 2536-05-2; EC-nummer: 219-799-4
- **2,4'-MDI** (Diphenylmethan-2,4'-diisocyanat); CAS-nummer: 5873-54-1; EC-nummer: 227-534-9
- **4,4'-MDI** (Diphenylmethan-4,4'-diisocyanat); CAS-nummer: 101-68-8; EC-nummer: 202-966-0
- **MDI** – uspecificeret **blanding af isomerer**: CAS-nummer: 26447-40-5; EC-nummer: 247-714-0
- **2,4-TDI** (2,4-toluen-diisocyanat): CAS-nummer: 584-84-9; EC-number: 204-825-9
- **2,6-TDI** (2,6-toluen-diisocyanat): CAS-nummer: 91-08-7; EC-nummer: 202-039-0
- **TDI – blandet** (2,4-TDI:2.6-TDI er ofte angivet som 80:20 og 65:35 blandinger): CAS-nummer: 26471-62-5; EC-nummer 247-714-0.

De tre "rene" MDI isomere er registreret under REACH, mens CAS-nummeret for blandingen af isomere ikke er blevet registreret som sådan. Dialog med industrien har imidlertid vist, at registreringen har fundet sted under andre CAS/EC-numre på grund af REACH teknikaliteter. EU 2005 risikovurderingen af MDI refererede generelt til CAS-nummeret 26447-40-5 med den forståelse, at dette CAS-nummer dækkede alle (kombinationer af) isomere. Dog har dette skabt en vis forvirring, i og med at CAS-nummeret 26447-40-5 ikke er REACH registreret som sådan.

2,4-TDI og TDI-blandinger er blevet registreret, hvorimod 2,6-TDI, som er vanskeligt at isolere teknisk, ikke er registreret.

TDI bliver generelt markedsført som monomer, mens MDI også markedsføres i flere andre former:

- *Polymert MDI* består af (raffinerede) reaktionsprodukter fra fremstillingsprocessen af MDI, bestående af omkring 40-50% 4,4'- MDI; 2,5-4,0% 2,4'-MDI; 0,1-0,2% 2,2'-MDI og 50-60% Homologer;
- *Oligomert MDI* er det rå reaktionsprodukt fra ovennævnte proces, bestående af en blanding af monomert og polymert MDI, men med et homolog/polymer-indhold under 50%, og
- *Modificeret/præpolymert MDI* er fremstillet fra monomert eller polymert MDI, gennem en potentielt katalyseret partiel reaktion mellem MDI monomererne eller mellem MDI og hydroxyl- eller aminoforbindelser, hvilket resulterer i molekyler med isocyanatgrupper i enderne. Denne gruppe inkluderer MDI homopolymere, som består af MDI'er, som har reageret med sig selv.

Polymert MDI er ikke blevet registeret under REACH, da industrien betragter det som en polymer ud fra OECDs definition af polymerer (>50% polymer-indhold), hvorimod oligomert MDI og en række modificerede MDI'er er blevet registret.

Terminologien omkring de forskellige former, hvorpå MDI er markedsført er ikke ligetil, og det er forfatternes opfattelse, at der eksisterer uklarheder og forskellige forståelser og brug af disse termer. Dette forhold kompliceres yderligere af, at generiske termer såsom "poly-isocyanater" og "co-polymere" sommetider anvendes uden en klar definition. ISOPAs[3] medlemsfirmaer understreger dog, at alle former for MDI, herunder polymert og modificeret/præpolymert MDI er klassificeret og mærket på linje med monomert MDI og at eksponering/risiko skal kontrolleres som sådan. Dette projekt har imidlertid identificeret, at nogle modificerede/præpolymere MDI' er markedsføres som værende mindre giftige end monomert MDI.

Regulering

De syv (blandinger af) TDI og MDI, som er inden for rammerne af dette projekt, er underlagt harmoniseret EU klassificering under CLP-forordningen. De er alle klassificerede som mistænkt for at fremkalde kræft, som sensibiliserende ved hudkontakt og inhalation, for akut toksicitet ved indånding, samt som irriterende ved kontakt med hud, øjne og ved inhalation. Ydermere er MDI klassificeret for potentielt at forårsage skade på lever og nyre som følge af gentagen eksponering, hvorimod TDI er klassificeret for miljømæssige effekter (skadelig for vandlevende organismer, med langvarige virkninger).

MDI er omfattet af en EU-anvendelsesbegrænsning for MDI-holdige forbrugerprodukter, samt en henstilling fra Kommissionen angående professionel brug af MDI. 2,4-TDI, 2,6-TDI, 2,4'-MDI og 4,4'-MDI er på positivlisten i forordningen for fødevarekontakt-materialer af plastic med visse restriktioner og TDI er forbudt i kosmetik. "Isocyanter" (herunder MDI og TDI) er specifikt angivet som værende inden for rammerne af IPPC (Integrated Pollution Prevention and Control) og PRTR (Pollutant Release and Transfer Register) direktiverne. TDI er eksplicit nævnt i Seveso-direktivets Annex 1, Part 2. Isocyanat-affald (nomenklatur: 08 05 01 Isocyanataffald) er reguleret som farligt affald. Derudover angives det i en henstilling fra Kommissionen, at medlemslandene bør adressere erhvervsmæssige sygedomme forårsaget af isocyanter.

I Danmark eksisterer en række nationale lovgivninger i relation til erhvervsmæssig håndtering af isocyanater, herunder krav om uddannelse, mærkning, håndtering, sikkerhedsforanstaltninger, begrænsning af spraysanvendelser og etablering af danske grænseværdier. De fleste af disse krav er også gældende off-shore og om bord på skibe.

MDI og TDI er generelt ikke behandlet i internationale aftaler/konventioner, med undtagelse af at TDI er eksplicit nævnt i UNECE-konventionen om "The Transboundary Effects of Industrial Accidents" (parallelt med at være eksplicit nævnt i Seveso-direktivet) og at isocyanat-affald, klassificeret som farligt affald, falder under bestemmelserne i Basel Konventionen.

Isocyanater adresseres specifikt i enkelte EU og nordiske miljømærkekriterier, særligt i forbindelse med TDI i lime, møbler og tekstiler.

Generelt er der en vis usikkerhed om, hvorvidt kun nogle eller alle TDI- og MDI-isomere er omfattet af en given lovgivning/bestemmelse og om hvorvidt andre former, så som præpolymere og polymere isocyanater, er taget i betragtning i forbindelse med udarbejdelsen af den pågældende lovgivning/bestemmelse. Det skal bemærkes at hovedparten af de specifikke danske krav også gælder specifikt for præpolymere.

TDI og MDI undergår i øjeblikket stof-evalueringer under REACH, samt overvejelser angående yderligere EU risikoreduktionsforanstaltninger, hvilket på et senere tidspunkt kan føre til yderligere EU-regler. Disse aktiviteter er indtil videre omfattet af fortrolighed, men den danske Miljøstyrelse har direkte adgang til disse aktiviteter og relaterede dokumenter.

Fremstilling, brug og anvendelser

Fremstilling

MDI og TDI fremstilles i stor skala i nogle få EU-virksomheder, hvoraf ingen er placeret i Danmark.

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[3] The European Diisocyanate and Polyol producers Association

Samlet volumen og tendenser
Mængdemæssigt tegner MDI og TDI sig for omkring 95% af brugen af isocyanater med et anslået:

- EU-forbrug på omkring 1,5 millioner ton/år;
- Nordisk forbrug på omkring 67.000 ton/år, pg
- Dansk forbrug på mellem 9.000 og 14.000 ton/år.

Det globale, EU og nordiske forbrug er støt stigende. En lignende tendens forventes for Danmark.

Anvendelser og opdeling mellem MDI'er og TDI'er
De vigtigste anvendelser af TDI og MDI er:

- Fleksibelt PUR (f.eks. til møbelpolstring og madrasser) (hovedsageligt TDI-baseret, men omkring 10% MDI), og
- Stift PUR (f.eks. til isolering, fjernvarmerør, køleanlæg, byggeri) (udelukkende baseret på polymert MDI).

"C.A.S.E.":

- **C**oatings (Overfaldebehandlingsmidler, såsom maling og lak) (Nordiske data viser, at omkring 70% af disse er MDI-baseret, resten er TDI-baseret);
- **A**dhesives (Klæbemidler/klæbere, såsom lime og laminater) (Nordiske data viser, at omkring 80% af disse er MDI-baseret, resten er TDI-baseret);
- **S**ealants (Fugemasser/tætningsmidler/skum fugemasse) (hovedsageligt MDI-baseret), og
- **E**lastomerer (f.eks. gummi og termoplastiske elastomere) (næsten udelukkende MDI-baseret).

Derudover:

- Binders (Bindemidler - anvendes til at binde partikler sammen, hovedsageligt til spånplader)

Fleksibelt og stift PUR, samt elastomere (E) bliver typisk leveret som allerede udhærdede produkter, hvorimod selve hærdningen for overfladebehandlingsmidler (C) , klæbemidler (A), fugemasser (S) og bindemidler er en del af funktionaliteten af produktet under/efter brug.

I EU og på det nordiske marked anvendes henholdsvis 80% og 83% af den forbrugte mængde TDI og MDI i PUR produktionen (stift, fleksibelt og elastomere). Bindemidler til produktionen af spånplader udgør 10% af det europæiske og 11% af det nordiske marked. Det efterlader omkring 10% (EU) og 6% (Norden) til produktionen af overfladebehandlingsmidler, klæbemidler og fugemasser.

Bemærk at disse tal repræsenterer MDI og TDI 'forbrugt til produktion' og ikke forbruget af PUR produkter eller forbruget af produkter der indeholder MDI/TDI (såsom overfladebehandlingsmidler, klæbemidler og fugemasser), da selve forbruget er påvirket af import/eksport.

For det danske marked har det ikke været muligt at indhente nøjagtige oplysninger om fordelingen af MDI/TDI mængder for de forskellige typer af anvendelser. Imidlertid antages det, at størstedelen af MDI og TDI anvendes til PUR produktion; Brancheforeningen, Plastindustrien, estimerer at omkring 6.000 ton TDI/år og 6.000 ton MDI/år bruges til produktionen af fleksible, stive og elastomere produkter. Plastindustrien gør opmærksom på, at produktionen af stift PUR er faldet i de seneste år, hvilket efterlader en relativ stor produktion af fleksibelt PUR, som hovedsageligt er TDI-baseret.

Så vidt vides, er der ingen spånpladeproduktion baseret på MDI-bindemidler i Danmark.

Til trods for at der ikke er nogen nøjagtig information, men ud fra oplysninger for EU og det nordiske marked, estimeres det, at omkring 10% af den samlede danske mængde af MDI og TDI forefindes i overfladebehandlingsmidler, klæbemidler og fugemasser, hvilket svarer til omkring 1.000 ton/år. Det skal understreges, at dette estimat er behæftet med en høj usikkerhed.

Klæbemidler og fugemasser markedsføres til forbrugere, inklusiv MDI i aerosolbeholdere og produkter indeholdende TDI (f.eks. i fugemasser og i tætningsmidler til træskibe). Det skal bemærkes, at der ikke er nogen EU anvendelsesbegrænsning for TDI-baserede produkter svarende til den, der findes for MDI-baserede forbrugerprodukter. Derudover er der overvejelser omkring, hvorvidt det er muligt for forbrugerne at få adgang til mere professionelle produkter, så som overfladebehandlingsmidler og maling.

En bred vifte af PUR-baserede forbrugerprodukter er tilgængelige på det danske marked, herunder bl.a. skum i bilsæder, madrasser og møbler, såvel som PUR i sko, tekstiler (fibre eller coatings), slanger, skumgummivaskeklude, fødevare-kontaktmaterialer og dokumentmapper. Som det også vil blive diskuteret i afsnittet om sundhedsskadelige virkninger, er der en vis uklarhed omkring muligt indhold af rest-monomere og aminer som nedbrydningsprodukter i disse PUR-produkter.

Produktion i Danmark
Dialog med de danske brancheorganisationer har givet følgende tal for danske produktionsvirksomheder, som anvender MDI og TDI:

- Produktion af stift PUR: 9 virksomheder;
- Produktion af fleksibelt PUR: 2 virksomheder;
- Produktion af PUR elastomere: 3 virksomheder;
- Overfladebehandlingsprodukter/maling : nogle få virksomheder ;
- Klæbemidler og fugemasser: ingen, og
- Spånplader, der bruger MDI-baseret bindemidler: ingen(antaget).

Affaldshåndtering
Affald fra fremstilling af MDI og TDI
Der er ingen fremstilling af MDI og TDI i Danmark, og derfor intet affald fra fremstilling.

Affaldsfraktioner indeholdende frie MDI og TDI monomerer
Baseret på interviews med en række producenter er der intet MDI og TDI affald fra produktionen af stift og fleksibelt PUR. Forsknings- og udviklings-forsøg kan dog genere små mængder MDI/TDI affald. Dette affald sendes til Nord (tidligere Kommunekemi).

Interviews med virksomheder der producerer overfladebehandlingsprodukter indikerer, at affald fra produktionen og professionel anvendelse af overfladebehandlingsmidler, klæbemidler og fugemasser bortskaffes som farligt affald under affaldskoden 08 05 01 Isocyanataffald. Information om affald med koden 08 05 01 er blevet ekstraheret fra Miljøstyrelsens affaldsstatistik for 2012. Ifølge disse oplysninger blev 244 ton (99%) afbrændt og mindre end 1% blev genanvendt. Isocyanater bliver fuldstændigt nedbrudt ved forbrænding.

Affald fra forbruger-anvendelser af overfladebehandlingsmidler, klæbemidler og fugemasser bør ideelt indsamles som farligt affald, men kan ende i husholdningsaffaldet eller i forskellige fraktioner på genbrugsstationer. Det antages, at dette vil være mindre emner og at disse ender i forbrændingen, hvor isocyanaterne vil blive nedbrudt.

Mængder og behandling af affald fra PUR produktion
Genanvendelse af affald fra produktionen af isolerede fjernvarmerør (stift PUR) sker ved glykolyse (100% genindvinding som ny-genereret polyol til produktionen). Den danske producent af disse rør bekræfter, at den samme mængde PMDI anvendt til produktion er uændret (2012), sammenlignet med mængden i 2005 (estimeret i Danish EPA (2005a)): 6.500 ton/år, men at mængden af det interne affald er faldet til 3%, som altså genanvendes i den ovennævnte glykolyse-proces.

Ifølge producenterne bliver affald fra produktionen af fleksible PUR-produkter brugt til nye anvendelser efter formaling (tæppe-bagsider). Dette er en vigtig genvindingsproces af fleksibelt PUR, eftersom der er store mængder produktionsaffald (23%) efter udskæringsprocessen.

Mulighederne for genvinding af fleksibelt PUR forbedres løbende og skrappere krav til renligheden af råmaterialerne påkræves. Mængden af produktionen af fleksibelt skum i Danmark skønnes at være uændret fra mængden i 2005 (Danish EPA (2005a): 22.200 ton.

Mængder og behandling af affald fra produkter

Med hensyn til PUR WEEE[4] affald er affaldsbehandlingen strengt reguleret af dansk lovgivning, såvel som på europæisk plan. PUR-affaldet fra udtjente kølemøbler bliver ikke genanvendt, men brændt med energigenvinding. Derved nedbrydes tidligere (CFC'er, HCFC'er) og nuværende (cyklo-pentan) opskumningsmdiler. Udtjente PUR produkter fra andre kilder (biler, møbler, isoleringsskum fra bygninger, etc.) bliver, så vidt vides, forbrændt med energigenvinding eller deponeret på lossepladser; det bliver ikke genanvendt. Et problem med PUR-produkter, der vanskeliggør genanvendelse er, at PUR ofte er lamineret til andre materialer (f.eks. i sandwich paneler), hvilket komplicerer adskillelse. Mængden af PUR-produkter, der ender op i affaldsstrømmen kendes ikke, bortset fra kølemøbler (et firma behandler årligt omkring 18.000 ton PUR fra denne kilde).

Forbrænding

Isocyanater og polyurethaner vil nedbrydes fuldstændigt under forbrænding i kommunernes forbrændingsanlæg.

Miljømæssige effekter og eksponering

Baseret på eksisterende risikovurderinger fra autoritative instanser, lader det ikke til, at MDI og TDI udgør nogen risiko for miljøet, selvom TDI er klassificeret som skadelig for miljøet. De igangværende stofevalueringer under REACH revurderer mulige miljøeffekter, herunder mulige PBT-egenskaber for MDI og TDI hydrolyseprodukter (aminer).

Den danske Miljøstyrelse har adgang til de fortrolige stofvurderinger og kan bruge resultaterne til at vurdere, om yderligere tiltag i relation til MDI/TDI og miljøet er nødvendige.

Sundhedsmæssige effekter og eksponering

MDI og TDI er klassificerede som mistænkt for at fremkalde kræft, som sensibiliserende ved hudkontakt og inhalation, som giftige efter inhalation og som irriterende ved kontakt med hud, øjne og ved inhalation. Særligt er deres evne til at forårsage respiratorisk sensibilisering bekymrende. TDI, som har et damptryk omkring tre størrelsesordner større end MDI, har en større sandsynlighed for at forårsage inhalationseksponering og TDI udviser større toksicitet ved indånding. Dog kan anvendelser med MDI som aerosoler og i spray-applikationer også finde sted. Mulig fertilitetstoksicitet er også fremhævet som et problem, f.eks. i risikovurderingen af MDI fra 2005 (EU, 2005), og CMR-egenskaberne for TDI og MDI og deres nedbrydningsprodukter (primære aromatiske aminer) er en af grundene til, at begge stofferne er underlagt stofevalueringer under REACH. Sideløbende hermed er en række aktiviteter vedrørende eventuel iværksættelse af yderligere risikostyring i gang på EU-plan. Disse aktiviteter er i færd med at opsummere farerne og situationen med hensyn til eksponering på EU-plan. Da de er igangværende og/eller fortrolige kan de ikke opsummeres her. Den danske Miljøstyrelse har dog fuld adgang til alle aktiviteter og dokumentation og kan bruge dette materiale som baggrund for mulige yderligere tiltag for disse stoffer. Hovedfokus i dette projekt er derfor på den danske situation, som et supplement til EU-aktiviteterne.

Grænseværdier for arbejdsmiljøet for MDI og TDI er fastsat i en række europæiske og ikke-europæiske lande, og de danske værdier er på samme niveau som i de fleste andre lande. I forbindelse med måling og kontrol af eksponering, findes der metoder til biomonitering, som kan måle de tilsvarende primære aromatiske aminer (MDA for MDI og TDA til TDI) efter hydrolyse af isocyanat-protein addukter i urin og blod. Der en fundet en god sammenhæng mellem inhalationseksponering og denne type af biomonitering. Tyskland og Storbritannien har etableret vejledende biologiske grænseværdier til at hjælpe med at kontrollere den erhvervsmæssige eksponering.

Med hensyn til eksponering og den medfølgende risiko, skal opmærksomheden hovedsageligt vendes mod professionelle og forbrugermæssige anvendelser af overfladebehandlingsmidler, klæbemidler og fugemasser.

[4] Waste Electrical and Electronic Equipment

Uddrag fra dansk statistik over erhvervsbetingede lidelser viser et konstant niveau på 10-15 årlige registreringer relateret til eksponering for isocyanater. De fleste af disse er relateret til brug af overfladebehandlingsmidler, klæbemidler og fugemasser; hovedparten er relateret til luftvejssygdomme, mens en mindre del relaterer sig til hudlidelser.

Denne kortlægning har vist at MDI- og TDI-holdige klæbemidler og fugemasser markedsføres til danske forbrugere, hvoraf nogle MDI-produkter markedsføres som aerosoler. Derudover, som også påpeget i nylige US EPA Action Plans for MDI og TDI, kan det ikke afvises at forbrugere, f.eks. via Internettet, kan få adgang til produkter som er beregnet til det professionelle marked.

Forbrugeres anvendelse af TDI-baserede produkter kunne skabe anledning til bekymring, da TDI ikke på samme vis som MDI er reguleret via en EU anvendelses-begrænsning, som kræver at produkter markedsøres sammen med handsker og udvidet information om sikker anvendelse. Dette underbygges af den kendsgerning at TDI er mere flygtigt end MDI og udviser større toksicitet ved indånding.

MDI-holdige produkter i aerosoldåser kan også være en årsag til bekymring, da forbrugere sandsynligvis kan anvende sådanne produkter uden tilstrækkelig ventilation og risikobegrænsende foranstaltninger.

Alt i alt ser der ud til at være datamangel vedr. overfladebehandlingsmidler, klæbemidler og fugemasser, som markedsføres og/eller er tilgængelige for danske forbrugere, herunder TDI-baserede produkter og MDI-baserede produkter, hvis anvendelse involverer dannelsen af aerosoler.

MDI og TDI monomere (som restmonomere og/eller nedbrydningsprodukter) er blevet påvist i en række PUR forbrugerprodukter, herunder f.eks. babymadrasser. Et sådan indhold ser ud til at være i modstrid med kemiske og termodynamiske argumenter, som, ifølge de europæiske brancheforeninger for isocyanater og PUR produkter, viser at analytisk bestemt indhold af MDI og TDI i sådanne produkter må være fejl/artefakter relateret til de anvendte analytiske teknikker.

Det er generelt accepteret at frigivelse af MDI, TDI, aminer og andre nedbrydningsprodukter kan forekomme som følge af termisk nedbrydning. En sådan nedbrydning kan forekomme, f.eks. ved strygning og i forbindelse med en lang række varme-genererende processer såsom slibning og svejsning i en lang række brancher. Der er ikke identificeret nogen kortlægning af sådanne emissioner og relaterede risikohåndteringsforanstaltninger for at reducere eksponeringen.

Isocyanat-holdige laminater/klæbemidler anvendes i fødevarekontaktmaterialer. Risikoen for dannelse af primære aromatiske aminer fra uhærdede isocyanat-monomere, som ville kunne migrere til fødevarer, er genstand for opmærksomhed og EU har fastsat en migrationsgrænse. I 2001/2002 gennemførte Fødevaredirektoratet en kontrolkampagne, som viste, at selv for laminater, som tages direkte fra lager (med højere forventet indhold af uhærdet isocyanat), var der kun to af 33 prøver som viste indhold af primære aromatiske aminer over detektionsgrænsen, men stadig anseeligt under EU migrationsgrænserne, der var gældende på den tid, såvel som de i dag gældende.

MDA (den primære aromatiske amin som dannes ved hydrolyse af MDI) er fundet i høje koncentrationer i køkkenredskaber af plast importeret fra Kina og Hong Kong. Dette indhold kunne stamme fra nedbrydning af MDI i disse produkter. Der er indført lovgivning for at monitorere og kontrollere koncentrationer af primære aromatiske aminer i sådanne produkter.

Alternativer
Substitution af flygtigt TDI med det mindre flygtige MDI, herunder modificeret/præpolymert MDI, har fundet sted og fortsætter med at finde sted, men er af tekniske årsager muligvis ved at nå grænsen hvad der er muligt.

Teknologier til blokering og indkapsling, som "maskerer" isocyanat-grupperne for at undgå/reducere eksponeringen, er under udvikling. For at genskabe reaktiviteten, opvarmes produkterne under anvendelse, hvorved maskeringen/blokeringen forsvinder.

Nogle alternative isocyanater, såsom naftalen-1,5-diisocyanat (NDI), hexamethylen diisocyanate (HDI) og 1-(isocyanatomethyl)-3,5,5-trimethyl-cyklohexan (IPDI) er tilgængelige for nogle anvendelser. Disse stoffer besidder nogle af de samme farlige egenskaber som MDI og TDI, ikke mindst evnen til at forårsage sensibilisering ved inhalation.

For de større anvendelsesområder af MDI og TDI til PUR produkter (fleksibelt skum til møbler, stift skum til fjernvarmerør, spånpladematериale, skum spray, en-komponent skum, osv.), forudses det, at produkterne i stor udstrækning vil fortsætte med at være baseret på de frie isocyanater MDI/PMDI og TDI, da disse anvendelser kræver høj reaktivitet. Hvor muligt, vil disse suppleres af modificeret/præpolymert MDI under anvendelse af processer baseret på bedst tilgængelige teknologi (BAT) med fokus på beskyttelse af arbejderne mod eksponering for frie isocyanater.

Baseret på den identificerede litteratur, forudses det, at "ikke isocyanat-baseret polyurethan" (NIPU- Non isocyanate-based polyurethane) på kort sigt hovedsageligt vil finde anvendelse i markedet for overfladebehandlingsmidler, klæbemidler og fugemasser; MDI/TDI produkter som også forbrugerne har adgang til. Lovende NIPU-teknologier er baseret på reaktionen mellem polycykliske karbonat oligomere og alifatiske eller cykloalifatiske polyamider med primære amino-grupper. Innovation i relation til anvendelse af NIPU pågår, hvilket ses af flere identificerede patentansøgninger på området.

Tilgængeligheden af alternativer til overfladebehandlingsmidler, klæbemidler og fugemasser er delvist blevet eftervist gennem kontakt til en række danske importører og producenter af overfladebehandlingsmidler, klæbemidler og fugemasser, dog kan kvalitet, pris og tradition begrænse anvendelsen af disse alternativer. F.eks. er det blevet fremført at isocyanatfrit skum på basis af silan/STP (Silane Terminated Polymer) er ca. 8-9 gange dyrere en PUR baseret skum.

Toksiciteten af alternativer er kompleks at vurdere, da der generelt er tale om alternative "systemer" ("silan-baseret" eller "polycyklisk karbonat-baseret") beskrevet som "frie for isocyanater", men uden information om toksiciteten. Der er ikke identificeret systematiske sammenlignende vurderinger af isocyanat-holdige produkter mod alternativer, men US EPA anfører i deres Action plans for MDI og TDI, at miljøvenlig substitution må anses for at være svært.

For at reducere eksponering og risiko må det alt i alt vurderes tilrådeligt at:
- fortsætte med at afsøge mulighederne for at substituere det tre størrelsesordener mere flygtige TDI med det mindre flygtige MDI, herunder modificeret/præpolymert MDI. Potentialet for yderligere substitution på dette område er dog uvis;
- fortsætte udforskningen af anvendelsen af blokerede og indkapslede MDI'er/TDI'er, såvel som NIPU teknologier, og
- fokusere på substituering/optimering af processer (og på uddannelse) med det mål at reducere eksponeringen af forbrugere og arbejdere. Dette fokus skal rette mod MDI/TDI såvel som alternative kemiske løsninger, som generelt også er meget reaktive for at opfylde de tekniske krav, og derfor har potentiale for at forårsage toksiske effekter.

Mangler
Baseret på den dokumentation som er gennemgået og fremskaffet i dette projekt er de væsentligste informationsmangler og mangler på konsensus blandt interessenter vurderet at være:
- *Anvendelse af CAS-numre og terminologi.* I de dokumenter der er gennemgået i denne rapport, forekommer der at være forskellig praksis for brug af CAS-numre og terminologi. Ikke mindst for MDI, som markedsføres i forskellige former, herunder som monomert, modificeret, præpolymert, polymert og oligomert MDI. Væsentlige områder i relation til dette emne er:
  – Industrien anfører generelt, at alle former af MDI anses for at have samme farlige egenskaber og derfor at håndtering, eksponeringskontrol og andre risikohåndteringsforanstaltninger skal være ens for alle former. Til dette skal det noteres, at nogle modificerede MDI'er tilsyneladende bliver markedsført som mindre toksiske en MDI monomere.

  - Man skal udvise forsigtighed i forhold til fortolkning af statistikker, gennemgang af litteratur mv. da termer anvendes forskelligt og nogle gange i flæng af forskellige forfattere.
  - I relation til anvendelsesområde af forskellige lovgivninger eksisterer der nogen usikkerhed i relation til om alle monomere er adresseret (ikke alle relevante CAS-numre for MDI/TDI monomere er altid angivet) og ikke monomere MDI former (polymert, modificeret, osv.) er ikke (konsekvent) adresseret, også selvom disser former, som angivet ovenfor, bør anses som ligeså toksiske som monomere.
- *Forekomst af monomert MDI/TDI som restmonomere og primære aromatisk aminer i PUR produkter.* Analytiske målinger ser ud til at være i modstrid med teorien (termodynamiske/kemiske overvejelser). Mulig eksponering for MDI/TDI og primære aromatiske aminer af forbrugere og arbejdere ved håndtering af PUR produkter er derfor usikker. De igangværende stofevalueringer under REACH adresserer muligvis dette emne.
- *MDI og TDI i forbrugerprodukter.* Der forefindes ingen dansk kortlægning eller statistik til belysning af forekomsten af MDI- og TDI-baserede forbrugerprodukter eller professionelle produkter, som forbrugere kan få adgang til (f.eks. via Internettet). Ud fra et eksponerings/risiko perspektiv har projektet identificeret at forbrugere har adgang til aerosolprodukter som indeholder MDI (med høj risiko for inhalationseksponering) og en række fugemasser indeholdende TDI. TDI kan udgøre en specifik bekymring, da TDI er tre størrelsesordener mere flygtigt og mere inhalationstoksisk end MDI og tillige ikke er omfattet af samme anvendelsesbegrænsning som MDI (herunder krav om at handsker skal vedlægges produktet og særlige risikohåndteringsforanstaltninger kommunikeres sammen med produktet).
- *Termisk nedbrydning.* Der er ikke identificeret nogen nylig kortlægning over frigivelsen af MDI, TDI, aminer og andre nedbrydningsprodukter i forbindelse med opvarmning af PUR-produkter eller produkter overfadebehandlet med PUR. Denne datamangel inkluderer omfanget af anvendelsen af sådanne processer i forbruger- og arbejdsmæssige-sammenhænge, såvel som anvendelse af mulige risikoreduktionsforanstaltninger for at reducere eksponeringsniveauet.
- *Vurdering af alternativer.* Sammenlignet med en række andre projekter/analyser, som på et generelt grundlag konkluderer at ingen/få alternativer eksisterer, har dette projekt identificeret en række alternative stoffer og teknologier, som er ved at vinde indpas/blive udviklet, særligt for specifikke applikationer, herunder forbrugerprodukter. Der er ikke identificeret en systematisk vurdering af miljø- og sundhedseffekterne af alternativer. Denne mangel kan hænge samen med det faktum at alternativerne er baseret på alternative kemiske "systemer", f.eks. "silan-baseret".

1. Introduction to the substance group

1.1 Definition of the substance group and substances within the scope of this report

Organic compounds that contain an isocyanate group are referred to as isocyanates. "Isocyanate" is the functional group with the formula –N=C=O (Figure 1).

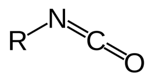

FIGURE 1
ISOCYANATE CONSTITUING AN ISOCYANATE GROUP (-N=C=O) ATTACHED TO AN ALIPHATIC OR AROMATIC GROUP ("R")

An isocyanate with two isocyanate groups is known as a diisocyanate. This report addresses two groups of diisocyanates:

- Methylene diphenyl diisocyanate (MDI)
- Toluene diisocyanate (TDI).

1.1.1 Methylene diphenyl diisocyanate (MDI)

Methylene diphenyl diisocyanate (MDI) is an aromatic diisocyanate with the chemical formula $C_{15}H_{10}N_2O_2$ where the two aromatic rings are connected by a methylene group. Three isomers - 2,2'-MDI, 2,4'-MDI, and 4,4'-MDI - exist. These are indicated as "pure MDIs" in Figure 2.

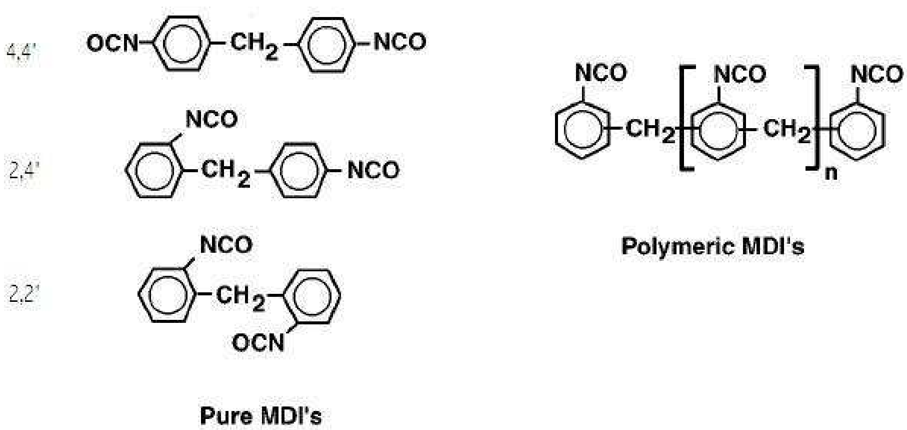

FIGURE 2
MDI ISOMERS

The "pure MDI's" and mixes of these are within the scope of this report (some synonyms appear in brackets):

- **2,2'-MDI** (Diphenylmethan-2,2'-diisocyanate/2,2'-Diphenylmethan-diisocyanat); CAS-number: 2536-05-2; EC-number: 219-799-4
- **2,4'-MDI** (Diphenylmethan-2,4'-diisocyanate/2,4'-Diphenylmethan-diisocyanat/2,4'-diisocyanatodiphenylmethan); CAS-number: 5873-54-1; EC-number: 227-534-9
- **4,4'-MDI** (Diphenylmethan-4,4'-diisocyanate/4,4'-Diphenylmethan-diisocyanat/p,p'-Diphenylmethan-diisocyanat); CAS-number: 101-68-8; EC-number: 202-966-0
- **MDI - unspecified mix/mixture[5] of isomers**: CAS-number: 26447-40-5; EC-number: 247-714-0.

As will be further elaborated upon in Chapter 3, the three pure isomers have been registered, whereas the CAS-number for a mix of isomers (CAS-number: 26447-40-5) has not been registered as such. Following correspondence with industry, there are several explanations for this issue[6]:

- For mixes where one isomer constitutes more than 80% (the main constituent), the mix can be named after the main constituent. This would normally be the 4,4'-MDI isomer, being the most prevalent isomer coming out of MDI manufacturing. Thus in this case mixes will be registered under the 4,4'-MDI CAS-number 101-68-8 and considered a substance under REACH;
- Sometimes the pure MDI isomers are combined to create this product. In this case, the product would be considered a mixture consisting of different substances (the pure isomers) and the pure isomers would have to be registered;
- Finally, the product can also be produced directly from purification of the crude MDI coming out of the MDI manufacturing process. For some technical reasons, this is not registered under CAS-number 26447-40-5 (EC-number: 247-714-0), but under other substance identities. One example of such a registration is EC-number 905-806-4 (no CAS-number available).

The MDI production process and registered substances will be further elaborated upon in Chapter 3.

The EU risk assessment of MDI (EU, 2005) generally referred to CAS-number 26447-40-5 with the understanding that this CAS-number would cover all (combinations of) isomers. However, it has created some confusion that CAS-number 26447-40-5 is not registered as such.

Further complexity exists as MDI is not only supplied as (mixes of) pure monomers.

Polymeric MDI

MDI can also be supplied as polymeric MDI (PMDI, see Figure 2), which according to the EU risk assessment of MDI (EU, 2005) has the following composition:

- 40-50% 4,4'- MDI
- 2.5-4.0% 2,4'-MDI
- 0.1-0.2% 2,2'-MDI
- 50-60% Homologues[7].

Dialogue with ISOPA (the European Diisocyanate and Polyol Producers Association) member companies reveals that industry generally supports this understanding of PMDI, although it is stressed that the content of homologues is about 55-60%. Based on the homologue content of >50%, ISOPA companies consider PMDI as a polymer according to the OECD polymer definition[8]. To complicate matters further, REACH requires that the monomeric units of polymers are registered. However, these would not be the monomeric MDI isomers, but aniline and formaldehyde.

[5] A mix, understood as "what comes out of the reaction vessel", is a substance under REACH. A mixture (in Danish "Blanding") on the other hand consists of several substances (formerly known as a "preparation"). CAS-number 26447-40-5 may be a mix as well as a mixture.
[6] Interviewed industry persons prefer to remain anonymous.
[7] Homologues consist of at least 3 aromatic rings.
[8] http://www.oecd.org/env/ehs/oecddefinitionofpolymer.htm

Although not registered, ISOPA companies stress that PMDI is considered as having the same hazard as monomeric MDI and is thus assigned the same classification; consequently, exposures/risks are managed in the same ways as for monomeric MDI.

It appears from the review done in this project that the terminology regarding PMDI is not always clear and that different authors may have different understandings. The generic CAS-number 9016-87-9 is often assigned to PMDI. This CAS-number has not been registered under REACH.

Oligomeric MDI
Oligomeric MDI is the crude reaction product containing a mix of monomeric and polymeric MDI, but with a polymer content below 50%. Thus, oligomeric MDIs are registered under REACH (CAS-number 32055-14-4).

Modified/prepolymer MDIs
Modified MDIs are prepared from MDIs via a potentially catalyzed partial reaction with themselves or with hydroxyl- or amino-compounds, resulting in molecules terminated with isocyanate groups.

Prepolymers are modified MDIs reacted with hydroxyl or amino compounds.

MDI Homopolymer is a modified MDI created by the reaction between MDI monomers with themselves. MDI Homopolymer is the terminology often assigned with the CAS-number 25686-28-6.

Modified MDIs can substitute monomeric MDIs in the production of polyurethanes by further reaction with polyols in some processes. The terms "modified MDIs" and "prepolymer MDIs" are often used interchangeably. REACH registrations of modified/prepolymer MDIs are addressed in Chapter 3.

Finally, MDI can also be reacted with hydroxyl compound polymers, e.g. CAS-number 9048-57-1 and 59650-39-4, where MDI is reacted with Poly Propylene Glycol (PPG). These are considered polymers and therefore not registered under REACH.

Terminology around the various forms in which MDI is marketed is not straightforward, and it has been the experience of the authors that ambiguities and different understandings and uses of the terms exist. Further complicating the issue is that generic terms such as "polyisocyanates" and "co-polymers" are used without defining these terms with any precision. However, ISOPA member companies stress that all forms of MDI, including polymeric MDI and modified/prepolymer MDI are classified and labelled in line with monomeric MDI and exposures/risks should be controlled similarly[9].

Non-monomeric and modified/prepolymer MDIs are not within the key scope of this report, but will be discussed as appropriate when data on these are identified, in particular in the chapter on manufacture and use (Chapter 3) and alternatives (Chapter 7), as the generally lower volatility of prepolymers reduces the risk of inhalation exposure. As noted above, all forms of MDI are considered as hazardous as monomeric MDI; therefore, Chapters 5 and 6 on Environmental and Human Health would generally apply to non-monomeric MDIs as well.

1.1.2 Toluene diisocyanate (TDI)

Toluene diisocyanate (TDI) is an aromatic diisocyanate with the formula $CH_3C_6H_3(NCO)_2$. Six isomers are possible, of which 2,4-TDI and 2,6-TDI are commercially the most important. 2,4-TDI is shown in Figure 3.

[9] However, as is seen in chapter 7, there may not be 100% agreement as some modified MDIs are considered less toxic than monomeric MDI.

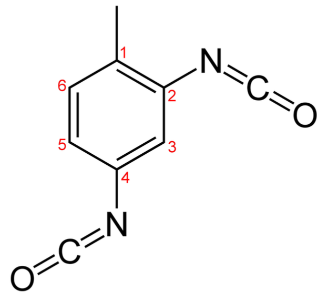

FIGURE 3
2,4-TDI.

2,4-TDI and 2,6-TDI and mixes of these are within the scope of this report (some synonyms appear in brackets):

- **2,4-TDI** (2,4-toluene diisocyanate; 2,4-Diisocyanato-1-methylbenzene; Isocyanic acid, 4-methyl-meta-phenylene ester; 2,4-Diisocyanatotoluene): CAS-number: 584-84-9; EC-number: 204-825-9
- **2,6-TDI** (2,6-toluene diisocyanate; 1,3-Diisocyanato-2-methylbenzene; Isocyanic acid, 2-methyl-meta-phenylene ester; 2,6-Diisocyanatotoluene): CAS-number: 91-08-7; EC-number: 202-039-0
- **TDI-mixed** (2,4-TDI:2.6-TDI often indicated as 80:20 and 65:35 mixes) (toluene diisocyanate; 1,3-Diisocyanatomethylbenzene; Isocyanic acid, methyl-meta-phenylene ester; Diisocyanatotoluene): CAS-number: 26471-62-5; EC-number 247-714-0.

As is further detailed in Chapter 3, mixes of TDIs (CAS-number: 26471-62-5) and 2,4-TDI have been registered under REACH and 2,6-TDI has not been registered.

Terminology confusion is less problematic for TDIs, which are in generally marketed in monomeric form.

1.2 Function, main applications and reactivity of diisocyanates

Isocyanate groups react with hydroxy/alcohol groups to form urethanes. Typically MDI and TDI are reacted with polyols in the production of polyurethane (PUR), which accounts for the main application of these substances.

The main groups of PUR plastic products are:

- Flexible PUR (Traditionally TDI-based, but with increasing content of MDI);
- Rigid PUR (blown) (MDI-based)/Solid (non-blown) PUR (MDI-based), and
- Elastomeric polyurethanes used both as rubber and as thermoplastic elastomers (mainly MDI based).

For these types of PUR, one distinguishes between polyester and polyether types having different resistance towards weathering (See Section 1.4).

Other well-known areas of use are PUR based coatings/paints/lacquers, adhesives and sealants, in which MDI as well as TDI is used and the reactive monomers form part of the curing/bonding functionality of the products.

Various ways of grouping MDI and TDI applications have been encountered in various references reviewed as the background for Chapter 3. The most frequently applied and the one we strive to use in this report are:

- Flexible PUR
- Rigid PUR

“C.A.S.E.”:

- Coatings;
- Adhesives;
- Sealants, and
- Elastomers.

“Binders” (largely used for chipboard production) are also often included in statistics.

When data allow, application areas are further detailed within these main groups.

In both MDI and TDI, the isocyanate groups in the fourth position are the most reactive. In 2,4'-MDI, the reactivity of the group in the 4-position is about four times as great as the group in the 2-position (Randall and Lee, 2003). Therefore, overall, the order of reactivity of MDIs is:

4,4'-MDI > 2,4'-MDI > 2,2'-MDI

For sterical hindering reasons, this appears logical in comparison with Figure 2. As will be shown in the remaining parts of the report, the 4,4'-MDI isomer is the most widely used, being the main component of many MDI mixes.

Similar to MDI, the 4-positions in TDI is also about four times as reactive as the 2- and 6-positions. The 2- and 6-positions are symmetrical and thus have similar reactivity. Thus 2,4-TDI is more reactive than 2,6-TDI (Randall and Lee, 2003).

Finally, it should be noted that for MDI as well as TDI, the reactivity of one group is affected if the other group reacts.

1.3 Specificity

It appears that the addressed diisocyanates are largely referred to as "MDI" and "TDI" in legislation, when discussing with trade associations, as well as in the literature, including health and safety assessments. As an example, in the EU risk assessment of MDI (generally addressing the mix/mixture MDI CAS-number 26447-40-5), it is stated: "*Data gained on any mixture of MDI isomers, regardless of relative isomer proportions, as well as on any individual isomer, are considered representative for the purpose of hazard evaluation and risk assessment*." (EU, 2005). For TDI, for example, the Environmental Health Criteria from IPCS (WHO, 1987) address TDI isomers and mixtures as one group. LOUS 2009 (Danish EPA, 2011) has also included MDI and TDI as generic groups. The current report will, therefore, generally not distinguish between the isomers within the groups of MDI and TDI.

Although the reactivity of the isomers is different, the literature reviewed in this project does not indicate any differences in e.g. toxicity between isomers. In regulative contexts, including REACH registrations, it will be specified when CAS-numbers, and thereby isomer form(s), are indicated.

Therefore, in line with what appears to be the consensus and for reasons of readability, this report will generally use the simple abbreviations "MDI" and "TDI”[10] (when relevant, including an indication of the locations of the isocyanate groups).

[10] As also noted in the list of abbreviations, TDI can be confused with “Tolerable Daily Intake”. However, we would not find it justified to deviate from the generally agreed upon abbreviation for toluen diisocyanate in this report.

1.4 Residual monomers and degradation products

Introduction

Of specific attention in this report will be the presence of residual/unreacted MDI and TDI monomers in polyurethane and polyurethane-containing products or other products where MDI and TDI are used as reactive monomers/cross-linkers.

Similarly to residual monomers, the possibility of formation of toxic degradation products is important.

Given the expected importance of this subject in several chapters in this document, this section addresses these issues in some detail upfront to form the needed background.

Degradation mechanisms and products

Polyurethanes may degrade by various mechanisms.

Gajewski (1990) gives an overview of degradation mechanisms. Degradation creates isocyanates and aromatic amines. The most common degradation mechanism for PUR is hydrolysis of the urethane bond. Polyether-based PUR is more resistant to hydrolysis than polyester-based PUR, the latter indicated to degrade two to four times faster (Gajewski, 1990). By hydrolysis, the urethane chemical bond is cleaved by water whereby carbon dioxide will be liberated and the isocyanate group will be converted to an amine group. The amines formed will be aromatic and can be a threat to health, especially for the primary aromatic amines formed from MDI and TDI monomers directly.

Higher temperatures significantly promote degradation. Degradation depends on the exact chemistry of the system, but for illustration, Gajewski (1990) showed in a TDI-based system at 50◦C that the polyester and polyether systems had half-lives of 4-5 months and almost two years, respectively. At 70◦C the half-lives were reduced to about two and five weeks. At 100◦C half-lives were reduced to days. According to Gajewski (1990), this may involve a partly reversible dissociation of the urethane to the isocyanates and polyols from which it was formed. The isocyanate might in turn hydrolyse to create aromatic diamines by liberating CO_2 in an irreversible reaction.

Degradation of PUR (especially polyester PUR) can take place at room temperature, but as shown above, an elevated temperature accelerates the degradation. The rule of thumb is that the reaction rate doubles for every 10 °C increase in temperature (Brown, 2001). The principle behind this rule of thumb is designated "the Arrhenius relationship".

According to Dolezel (1978), degradation by weathering depends on the formulary and the raw materials used (linear or cross-linked). Many PUR foamed products degrade rapidly when exposed to light even when protected by window glass. However, PUR-based elastic fabrics are more stable to weathering than nylon (polyamides) and as stable as polychloroprene or polysulphide rubber (Dolezel, 1978).

Typically, weathering makes the polyurethanes yellow. Photochemical degradation is exemplified with a model compound and it is concluded that it is light with wavelengths between 334 nm and 411 nm that is responsible for the degradation. It is the carbonyl group which dissociates and the CN bond is cleaved with the creation of several different species: e.g. by reaction with water, amines are created. By using UV absorbers and other additives the yellowing effect can be reduced. Polyester urethanes are more resistant to light than polyether urethanes, which on the other hand are less resistant to hydrolysis as the ester bond is much more easily cleaved by water (Dolezel, 1978).

Substantiating that hydrolysis and not oxidation is the main degradation mechanisms was the subject of Lowett and Eastop (2003) in accelerated tests carried out at 70° C in an oven at varying humidity, and in experiments with oxygen and non-oxygen contents in dry conditions. It was shown through a study of tensile strength that degradation was fast at high humidity. At 100% humidity after 4 weeks, the tensile strength (breaking load) was zero newtons. In the oxygen experiments, the tensile strength increased at high oxygen concentrations, probably due to further cross-linking. The study was carried out because of the observation that PUR foam-laminated dresses (from 1960) were degraded and dusty. It was observed that acidic volatile molecules were liberated during the degradation of the PUR foam. Both authors developed sore eyes and allergic rhinitis while examining the dresses.

It must be stressed that by breaking the ester bond, the PUR polymer chain gets shorter without the formation of the primary aromatic diamines (methylenedianiline (MDA) and toluenedianiline (TDA)). Only if the urethane bond is hydrolysed on both sides of the MDI or TDI monomer in PUR, can MDA and TDA be formed.

According to Swift and Glass (1990), step-grown polymers (such as PUR) are biodegradable to a greater or lesser extent, depending on:

- Chemical functional groups: esters> ethers>amides>urethanes (esters degrade fastest, urethane slowest);
- Molecular weight: Lower is faster;
- Morphology: Amorphous degrades faster than crystalline;
- Hardness: Softer degrades faster, and
- Hydrophilicity: More hydrophilic degrades faster.

As the biodegradation of the polyurethanes is due to hydrolysis/cleavage of chemical bonds by enzymes in wet conditions, it can be concluded that the most difficult bond to cleave is the urethane bond. This finding questions the conclusions of Gajewski (1990), proposing hydrolysis of the urethane bond as the most likely degradation mechanism.

Polyester PUR is degraded by microorganisms due to the hydrolysis of the ester bond by esterases. The solid-polyester-degrading enzyme (PUR esterase) derived from *Comamonas acidovorans* TB-35 can degrade polyester PUR particularly effectively. The enzyme has a hydrophobic PUR-surface-binding domain and a catalytic domain and both in combination are essential for degradation (Nakajima-Kambe et al., 1999).

The degradation products from PUR can be used as nutrition for microorganisms and, for this reason, biocides as well as stabilisers to prevent degradation might be added to the PUR formularies. These include steric hindered phenols used as antioxidants, benzoxazoles used as light protection agents and polycarbodiimid, used for protection against hydrolysis (Uhlig, 1998).

Residual monomers and degradation products during production and in finished products

The only way MDI and TDI can remain as residual monomers in polyurethane products or other products where MDI and TDI are used as reactive chemicals (e.g. cross-linkers) is by slowing the reaction at the end of the polymerisation process, e.g. cross-linking processes where the reactants are more distant from each other than at the beginning of the polymerisation. If present, residual monomers are judged to be in low concentrations due to their high intrinsic reactivity with amines, alcohols and water.

Another possibility is that MDI and TDI are formed by depolymerisation (e.g. by heat) in the finished PUR products. According to PPG Industries (2003), PUR, when heated to high temperatures e.g. in a fire, will degrade in a complex manner due to pyrolysis and oxidation. According to Danish EPA (2005b), a thermoset PUR will not melt when heated but rather degrade/pyrolyse in the temperature range 200°C to 600°C. At temperatures higher than 600°C nitriles, aliphatic and aromatic hydrocarbons will be formed.

Fumes, gases and vapours formed by these processes may include, but are not limited to, carbon monoxide, oxides of nitrogen, traces of hydrogen cyanide, and free isocyanate (PPG Industries, 2003). A review study by Pratt and Engelund (2001) found that MDI, TDI, amines and other degradation products might be generated when heating PUR to 200-300 ◦C. According to information from industry (data source not disclosed), free isocyanates (TDI) might be formed at lower temperatures, e.g. by ironing of PUR containing washing clothes.

The review performed by Pratt and Engelund (2001) identified a range of industries (car workshops, work with district heating pipes, textile manufacture, wood industry, manufacturing of building materials) in which PUR products/coated PUR products might be heated due to cutting, boring, grinding, soldering, welding, casting, etc. The review, however, concludes that worker exposure depends on the risk management in place. No review has been identified analysing actual exposure to MDI/TDI.

On request, ISOPA (the European Diisocyanate and Polyol Producers Association) has stated that no monomeric TDIs are left in finished polyurethane products due to their high reactivity based on the following arguments for TDI (ISOPA, 2013):

- Reaction between TDI and water is rapid, with a half-life of approx. 1 min., and
- TDI in air degrades due to reaction with OH radicals, with a half-life of approx. 1 day.

ISOPA has furthermore advised that if the corresponding aromatic diamines are liberated from degradation of TDI by hydrolysis in the process, they will immediately react with another TDI molecule with the formation of polyureas. The half-life for theoretical back cleavage of TDA from polyurea is in the order of millennia (18,000-300,000 years). Although not specifically mentioned by ISOPA (2013), it is judged that the same will be the case for MDI due to the high reactivity of the isocyanate groups with nucleophiles, like aromatic diamines.

Substantiating the above, ISOPA (2013) makes reference to a document “Response to Polish Authority” (BASF, 2013) sent to the Polish competent authority conducting the TDI substance evaluation under REACH (see Chapter 2), as well as a brief summary of some additional key literature on TDI.

Regarding lack of residual TDI monomers in polyurethane flexible foam products, ISOPA (2013) also refers to BASF (2013). It is stated that there are no free diamines as residues in finished products resulting from hydrolysis, as they are converted to polyureas by reaction with another diisocyanate with a much faster rate than the reaction with water.

However, MDI and TDI monomers have been identified in a number of Danish EPA projects. In the project addressing chemical exposure to 2-year-old children (Danish EPA, 2009), by means of GC/MS screening analysis, MDI was found on the outer fabric of jackets (5 items/pieces) in amounts of up to 410 mg/kg and, in a zipper strap, 1,600 mg/kg was found. For mittens/gloves (5 items), TDI was found in the Velcro closure in amounts up to 250 mg/kg and in the outer fabric TDI was found in amounts of up to 870 mg/kg. Other isocyanates (aliphatics) were also identified. Migration experiments by exposure to artificial saliva and analysis for TDI and MDI after derivation with (2-pyridyl)-piperazin and HPLC analysis carried out in the above project showed that only a minor part of the two diisocyanates migrated.

In another consumer protection project concerning exposure of babies to chemical substances (Danish EPA, 2008), MDI was detected by GC/MS screening in foamed facecloths (amount not quantified) and in baby mattresses in an amount of 22 mg /kg. The project report concluded that the positive identification of MDI in the clothes might be due to a depolymerization in the GC/MS inlet, but a recent discussion with the laboratory technician who carried out the analysis cast doubt on that conclusion.

For a customer (identity cannot be disclosed), the laboratory at Technological Institute recently confidentially validated a similar GC/MS analysis for TDI with success, so the conclusion regarding the formation of a false positive detection of free isocyanates by depolymerization may in fact be incorrect.

In bilateral correspondence, ISOPA and EuroPUR (European Association of Flexible Polyurethane Foam Blocks Manufacturers) stress that any findings of MDI/TDI in PUR products have been shown to be created by the analytical method and, therefore, constitute artefacts rather than actual presence of MDI/TDI in such products.

Nevertheless, the above cited data indicate that residual TDI and MDI monomers might be left in products where these diisocyanates have been used, but the data are too scarce for making general conclusions regarding presence of residual TDI and MDI (or MDI and TDI as a result of degradation) in products where MDI/TDI has been used during manufacturing. Further, some ambiguity related to the analytical methods exists.

In a study of "Primary aromatic amines (PAAs) in black nylon and other food contact materials, 2004-2009 (Trier et al., 2010), 4,4´- methylenedianiline (MDA) was found in a large number of products, especially black kitchen utensils imported to Denmark from China. The samples were analysed by HPLC-MS_MS by an accredited test method for contact with aquatic food simulants and the risk assessment and estimates were concluded to be of major concern. It was stated that sources for the MDA could be aromatic isocyanates (MDI) or azo-colours. It is known that MDI is used as cross-linker in nylons; therefore, MDI might be the source of the formation of the dianiline, but that has not been concluded in the study.

From this limited study it cannot be concluded that diamines corresponding to TDI and MDI (TDA and MDA) will be present in MDI- and TDI-based finished products. To verify or exclude this possibility, further studies are required.

In general, it seems advisable to further investigate the presence of residual monomers and degradation products, based on theoretical (chemical and thermodynamic considerations) as well as practical experience, incl. strengths and weaknesses of various analytical methods.

However, as the formularies (recipes) for PUR products are base-catalyzed by the presence of amines (e.g. tertiary aliphatic organic amines) reacting with the diisocyanates, it seems logical that the diisocyanates will not survive as isocyanates, but the possibility exists that the corresponding diamines (TDA and MDA) are formed in small concentrations due to hydrolysis.

Other substances of concern related to PUR products

For a long period, PUR products were blown with freons (CFCs) and later, HCFCs, which are now banned. For this reason, foamed PUR with these gasses will still end up in the PUR waste stream and care must be taken that during waste handling these gasses will not be liberated to the environment. This issue will be further addressed in Chapter 4.

Summary

Hydrolysis of PUR is one of the major routes to degradation of polyester-based polyurethanes. Through hydrolysis of polyester-based PUR, the degradation products are shorter PUR polymer chains where the ester bond is broken. Only if the urethane bond on both sides of the diisocyanate monomer used in the polymerisation is broken, might the primary aromatic diamines (TDA and MDA) be formed.

For polyether-based PUR, the resistance to hydrolysis is high, but the polyether-based PUR is less resistant to photo-oxidation than the polyester-based PUR. However, the photodegradation of polyester-based PUR is accelerated in the presence of water.

For the above-mentioned degradation mechanisms, the addition of stabilizers to the formularies of PUR may be needed to prevent oxidation or hydrolysis or microbial degradation.

Chemicals of concern that are or could be formed or left in MDI- and TDI-based products during handling, production and end-of-life are judged to be:

- Residual monomers of MDI and TDI;
- Depolymerisation of PUR at elevated temperatures resulting in liberation of isocyanate monomers (e.g. TDI and MDI), and
- Aromatic diamines derived from MDI and TDI by degradation either by photo-oxidation or hydrolysis of the urethane bond.

MDI and TDI and other diisocyanates or the corresponding diamines are found in PUR products in some studies. This finding conflicts with the information from ISOPA/EuroPUR that no monomer MDI or TDI or primary aromatic diamines (MDA and TDA) remain. One open question is whether the analysis for free diisocyanates sometimes generates false positives (e.g. depolymerisation in GC/MS inlet) and sometimes might be actual positives (e.g. identification by HPLC and derivatisation).

The primary aromatic amine MDA, possibly from degradation of MDI, has been found in some food contact materials, especially black kitchen utensils.

1.5 Physicochemical properties

The physicochemical properties of MDI and TDI (isomers indicated when specified) are shown in Table 1 and Table 2. A main concern for MDI and TDI is the possibility to cause health effects following inhalation; it is therefore of importance that TDI has a considerably higher vapour pressure than MDI (also at higher temperatures).

The table also shows that due to their rapid reactivity with water, it is difficult to establish water solubility and other parameters used for environmental fate assessments.

TABLE 1
PHYSICOCHEMICAL DATA FOR MDI

Property	MDI	Reference
Molecular weight	250.3 g/mol	US EPA (1985)
Physical state	Ranging from dark amber viscous liquid to white waxy solid	EU (2005)
Melting point	2,4'-MDI: 34-38°C 4,4'-MDI: 39-43°C Polymeric MDI: 5°C	EU (2005)
Boiling point	> 300 °C	EU (2005)
Relative density	4,4'-MDI: 1.325 Polymeric MDI: 1.2381	EU (2005)
Vapour pressure (20°C)	2,4'-MDI: 0.0014 Pa 4,4'-MDI: 0.002 Pa Polymeric MDI: 0.005 Pa ------ "MDI": 0.0004 Pa	EU (2005) ------- ISOPA (http://www.isopa.org/isopa/uploads/docs/guidlines_af.pdf)
Vapour pressure (40°C) **Vapour pressure (80°C)**	"MDI": 0.006 Pa "MDI": 2 Pa	ISOPA (http://www.isopa.org/isopa/uploads/docs/guidlines_af.pdf)
Surface tension	NA, since substance will react with water	EU (2005)
Water solubility (mg/l)	Due to the high reactivity of the NCO group with water, current EC standard methods cannot be used. Based on calculations, a worst case value of 0.02 mg/l was used for the EU risk assessment.	EU (2005)
Log P (octanol/water)	Measured to 4.5, but considered irrelevant due to the transient existence of MDI in water	EU (2005)

TABLE 2
PHYSICOCHEMICAL DATA FOR TDI

Property	TDI	Reference
Molecular weight	174.17 g/mol	WHO (1987)
Physical state	Colourless liquids or crystals, turning pale yellow standing.	WHO (1987)
Melting point	2,4-TDI: 22 °C 2,6-TDI: 7.2 °C TDI 80:20 mix <15 °C TDI 65:35 mix < 8 °C	Health and Environment Canada (2008)
Boiling point	2,4-TDI: 252.5-254 °C 2,6-TDI: 247-248.5 °C Mixed TDI: 252 - 254 °C	Health and Environment Canada (2008)
Relative density	1.22	Health and Environment Canada (2008)
Vapour pressure (20°C)	2,4-TDI: 1.3 Pa 2,6-TDI: 1.6 Pa Mixed TDI: 1.4-1.5 Pa ---- "TDI": 1.0 Pa	Health and Environment Canada (2008) ----- ISOPA (http://www.isopa.org/isopa/uploads/docs/guidlines_af.pdf)
Vapour pressure (40°C) Vapour pressure (80°C)	"TDI": 6.2 Pa "TDI": 350 Pa	ISOPA (http://www.isopa.org/isopa/uploads/docs/guidlines_af.pdf)
Surface tension	NA, reacts with water	No ref, but same logic as for water solubility and Log P
Water solubility (mg/L)	NA, reacts with water	Health and Environment Canada (2008)
Log P (octanol/water)	Na, reacts with water	Health and Environment Canada (2008)

2. Regulatory framework

This chapter gives an overview of how MDI and TDI are addressed in existing and upcoming EU and Danish legislation, international agreements and also by eco-labelling criteria. The chapter focuses on legislation where monomeric MDI and/or TDI are addressed specifically, either as MDI/TDI monomers or as a member of the group of “isocyanates”. Legislation where the substances are implicitly addressed, e.g. non-presence on positive lists or their implied presence within the general scope of a regulation/directive (e.g. due to their classification), is not listed.

In Appendix 1: “Background information to chapter 2 on legal framework”, a brief overview of legal instruments in the EU and DK and how they are related may be found. The appendix also gives a brief introduction to the chemicals legislation, explains the lists referred to in Section 2.1.3 on REACH, and provides a brief introduction to international agreements and eco-labelling schemes addressed.

2.1 Legislation

This section first lists existing legislation addressing MDI and TDI and then gives an overview of ongoing activities, focusing on which substances are in the pipeline in relation to various REACH provisions.

2.1.1 Existing legislation

Table 3 provides an overview of existing legislation addressing MDI and TDI. For each area of legislation, the entries in the table first list the EU legislation (if applicable) and then possible transposition of this into Danish law and/or other national rules. The latter will only be elaborated upon in case of Danish rules differing from EU rules. At the end of the table, Danish legislation beyond EU legislation is listed.

The table shows that the 2005 MDI risk assessment (EU, 2005) resulted in a restriction related to consumer use of MDI-containing products and a Commission recommendation related to MDI used professionally. No general restriction for TDI exists. 2,4-TDI, 2,6-TDI, 2,4’-MDI and 4,4’-MDI are on the positive list of the plastic food contact material regulation with certain restrictions (as well as amine degradation products) and TDIs are explicitly prohibited in cosmetics. “Isocyanates” (including MDI and TDI) are specifically indicated to be within the scope of the IPPC (Integrated Pollution Prevention and Control) and PRTR (Pollutant Release and Transfer Register) directives. TDI is specifically mentioned in Annex 1, Part 2 of the Seveso Directive. Isocyanate waste is considered hazardous waste (nomenclature: “08 05 01 waste isocyanates”) in relation to EU waste legislation, including the EU implementation of the Basel Convention. Finally, a Commission recommendation states that Member States should address occupational diseases caused by isocyanates.

For the Danish situation, the table depicts an array of national legislation in place in relation to occupational handling of isocyanates, including the need for training, labelling, handling, security measures, limitations of spray applications and the establishment of Danish occupational exposure limits. Most of these requirements are also applicable off-shore and on ships.

Finally, it should be noted that there appears to be some ambiguity as to whether all TDI and/or MDI isomers are covered by a given instrument, as sometimes only some of the isomers/CAS-numbers are listed; it is not immediately apparent as to why other isomers/CAS-numbers are not. Furthermore, in a few cases, other forms than monomeric MDI and TDI are listed, in particular “prepolymers”, whereas polymeric forms are generally not listed. It is not clear whether other forms such as polymeric forms or modified/prepolymer forms were addressed when the legislation was drafted.

TABLE 3
EU AND DANISH LEGISLATION ADDRESSING ISOCYANATES

Legal instrument *1	EU/national	Substances	Requirements
Legislation addressing products			
General restrictions/limitations on use			
Annex XVII of REGULATION 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) **NB! This restriction was taken over by REACH from the previous restrictions directive (76/769/EEC) and is therefore placed in this table and not in the subsequent section on REACH**	EU	2,2'-MDI, 2,4'-MDI, 4,4'-MDI and mixes of MDI isomers (CAS-number 2536-05-2, 5873-54-1, 101-68-8 and 26447-40-5). Restriction originally only referred to CAS-number 26447-40-5, but COMMISSION REGULATION 126/2013 clarified that it relates to all MDI isomers in line with the EU risk assessment on which the restriction was originally based.	1. Shall not be placed on the market after 27 December 2010, as a constituent of mixtures in concentrations equal to or greater than 0,1 % by weight of MDI for supply to the general public, unless suppliers shall ensure before the placing on the market that the packaging: (a) contains protective gloves which comply with the requirements of Council Directive 89/686/EEC (**********); (b) is marked visibly, legibly and indelibly as follows, and without prejudice to other Community legislation concerning the classification, packaging and labelling of substances and mixtures: ‘— Persons already sensitised to diisocyanates may develop allergic reactions when using this product. — Persons suffering from asthma, eczema or skin problems should avoid contact, including dermal contact, with this product. — This product should not be used under conditions of poor ventilation unless a protective mask with an appropriate gas filter (i.e. type A1 according to standard EN 14387) is used.’ 2. By way of derogation, paragraph 1(a) shall not apply to hot melt adhesives.

Legal instrument *1	EU/national	Substances	Requirements
COMMISSION RECOMMENDATION 2008/98/EC of 6 December 2007 on risk reduction measures for the substances: Piperazine; Cyclohexane; Methylenediphenyl diisocyanate; But-2yne-1,4-diol; Methyloxirane; Aniline; 2-Ethylhexylacrylate; 1,4-Dichlorobenzene; 3,5-dinitro-2,6-dimethyl-4-tert-butylacetophenone; Di-(2-ethylhexyl)phthalate; Phenol; 5-tert-butyl-2,4,6-trinitro-m-xylene	EU	MDI (CAS-number 26447-40-5), which in the underlying risk assessment is assumed to address all MDI isomers.	"Employers using MDI for uses identified as a concern in the risk assessment should take note of any sector specific guidance developed at national level based on the practical non-binding guidance, to be published by and available from the Commission as foreseen under Article 12(2) of Council Directive 98/24/EC (3) (Chemical Agents Directive)." NB! Reference is made to the EU MDI risk assessment (EU, 2005).
Food legislation			
COMMISSION REGULATION (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food	EU	CAS-number: 91-08-7 (2,6-TDI), CAS-number: 584-84-9 (2,4-TDI) , CAS-number: 101-68-8 (4,4'-MDI) and CAS-number: 5873-54-1 (4,4'-MDI) TDI dimers and other isocyanates are listed as well Primary aromatic amines formed by hydrolysis of isocyanates (MDI and TDI can form primary aromatic di-amines)	It is required that isocyanate migration from plastic packaging should not be analytically detectable in the food, and that the content of isocyanates in the food plastic material must not exceed 1 mg/kg in the final product expressed as isocyanate moiety. This value applies to all isocyanates as part of a so-called “group restriction”. The regulation further specifies (Annex II, 2) that “Plastic materials and articles shall not release primary aromatic amines, ..., in a detectable quantity into food or food simulant. The detection limit is 0,01 mg of substance per kg of food or food simulant. The detection limit applies to the sum of primary aromatic amines released”.

Legal instrument *1	EU/national	Substances	Requirements
COMMISSION REGULATION (EU) No 284/2011 of 22 March 2011 laying down specific conditions and detailed procedures for the import of polyamide and melamine plastic kitchenware originating in or consigned from the People's Republic of China and Hong Kong Special Administrative Region, China	EU	Primary aromatic amines, which might result from content of MDI	Polyamide and melamine plastic kitchenware originating in or consigned from China and Hong Kong shall be imported into the Member States only if the importer submits to the competent authority for each consignment a declaration to the competent authority that the requirements regarding primary aromatic amines as set out in the Plastic Food Contact Material regulation are complied with. It is further specified that the national competent authority shall check the documentation within two working days of arrival and check in more detail (including analytical) 10% of the consignments.
***Executive order concerning import of certain plastic kitchenware originating in or consigned from the People's Republic of China and Hong Kong (Bekendtgørelse om indførsel af visse plastkøkkenartikler med oprindelse i eller afsendt fra Kina og Hongkong, BEK nr 345 af 18/04/2012)**	DK	Idem	Outlines specific and detailed conditions and procedures for import to Denmark in relation to the above regulation 284/2011, including upfront notification, places of control and application for further shipment.

Legal instrument *1	EU/national	Substances	Requirements
Cosmetics			
REGULATION (EC) No 1223/2009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 30 November 2009 on cosmetic products	EU	2,4-TDI, 2,6-TDI and mixes thereof (CAS-numbers: 584-84-9, 91-08-7 and 26471-62-5)	Included in Annex II (LIST OF SUBSTANCES PROHIBITED IN COSMETIC PRODUCTS)
*** Executive order on cosmetic products (Bekendtgørelse om kosmetiske produkter, BEK nr 422 af 04/05/2006). This will be repealed following the full transition of all provision from the old cosmetics directive to the cosmetics regulation 1223/2009**		idem	Idem
COMMISSION DECISION of 9 February 2006 amending Decision 96/335/EC establishing an inventory and a common nomenclature of ingredients employed in cosmetic products	EU	PPG-26/TDI COPOLYMER	"PPG-26/TDI COPOLYMER" listed in Annex I specifying between other nomenclature to be used for labelling. Function indicated: Film forming/plasticizer.
Occupational health legislation			
COMMISSION RECOMMENDATION of 19 September 2003 concerning the European schedule of occupational diseases	EU	Isocyanates	Recommends Member States to implement provisions for scientifically recognised occupational diseases liable for compensation and subject to preventive measures with reference to Annex I. Annex I, item 1 (Diseases caused by chemical agents) lists "Isocyanates".
*** Executive order on occupational health educations (Bekendtgørelse om arbejdsmiljøfaglige uddannelser, BEK nr. 1088 af 28/11/2011)**	DK	Isocyanates	Specifies that work with isocynates requires certificate from specific training. It is specified which skills must be obtained via this education and who can provide the training.

Legal instrument *1	EU/national	Substances	Requirements
*** Executive order on work with substances and materials (Bekendtgørelse om arbejde med stoffer og materialer, BEK nr 292 af 26/04/2001)**	DK	Products with ≥ 0.5w/w% monomeric or prepolymeric isocyanates, thus including monomeric and prepolymeric MDI and TDI	Annex III specifies requirements for work with isocyanates, including - Curing time must be specified in the occupational safety data sheet - Minimum safety precautions - Spraying is generally prohibited, but permission following a notification can be given for certain activities - Work is not allowed for persons with asthma, eczema, chronic lung disorders or allergies towards isocyanates - The need for education (specified in Executive order 1088/2011) - That designated/separate dressing rooms are available - That waste (packaging, spillage, residuals, used protective clothing) should be disposed of in waste containers clearly marked with the content - Requirements to first aid equipment
***Executive order on certain obligations for manufacturers, suppliers and importers of substances and materials (Bekendtgørelse om særlige pligter for fremstillere, leverandører og importører mv. af stoffer og materialer efter lov om arbejdsmiljø, BEK nr 559 af 04/07/2002)**	DK	Products with ≥ 0.5 w/w% monomeric or prepolymeric isocyanates. However, for MDI and TDI, the threshold is ≥ 0.1% given their hazard classification.	Professionally used products with ≥ 0.1 w/w% MDI or TDI intended for professional use should be registered with the Danish Product Registry. For isocyanates in general (including prepolymers), the registration threshold is ≥ 0.5 w/w%. Curing time must be specified in the occupational safety data sheet.
***Executive order on derivation of code numbers (Bekendtgørelse om fastsættelse af kodenumre, BEK nr 301 af 13/05/1993)**	DK	Products containing prepolymers, oligomers, polyisocyanates and monomeric isocyanates.	Specifies that residual monomers in polymers contribute to the calculation of the code number if present in concentrations above 0.1% or above 0.01% for volatile isocyanates (e.g. TDI, HDI and HMDI).
*** Executive order on classification, packaging, labelling, sale and storage of substances and mixtures (Bekendtgørelse om klassificering, emballering, mærkning, salg og opbevaring af stoffer og blandinger, BEK nr 1075 af 24/11/2011)**	DK	Products with monomeric, oligomeric and prepolymeric isocyanates. No lower concentration limit indicated.	General provision prohibiting sale to consumers of substances classified as toxic or very toxic, including substances/mixtures classified as acutely toxic in category 1, 2 or 3. Must be labelled: "Contains isocyanates. See manufacturer instructions" NB! It is uncertain how this provision will be continued once the executive order is eventually repealed by the CLP regulation.

Legal instrument *1	EU/national	Substances	Requirements
*** Executive order about use of substances and materials /chemical agents) on off-shore facilities (Bekendtgørelse om anvendelse af stoffer og materialer (kemiske agenser) på offshore-anlæg m.v., BEK nr 1502 af 15/12/2010)**	DK	Products with ≥ 0.5w/w% monomer or prepolymeric isocyanates, thus including monomeric and prepolymeric MDI and TDI.	List similar provisions for work with isocyanates offshore as those for work with isocyanates on-shore.
*** Executive order concerning working environment on ships (Bekendtgørelse om Meddelelser fra Søfartsstyrelsen A, teknisk forskrift om arbejdsmiljø i skibe, BEK nr 1246 af 11/12/2009)**	DK	Products with ≥ 0.1% 2,4-TDI, 2,6-TDI and mixes thereof (CAS-numbers: 584-84-9, 91-08-7 and 26471-62-5) (MDIs not specifically mentioned, but implicitly including when present in products >0.1% given their classification as carcinogenic cat.2)	List similar provisions for work with isocyanates on ships as those for work with isocyanates on-shore.
*** Executive order concerning occupational limit values for substances and materials (Bekendtgørelse om grænseværdier for stoffer og materialer, BEK nr 1134 af 01/12/2011)**	DK	CAS-number: 101-68-8 Diphenylmethan-4,4'-diisocyanat (4,4'-MDI) CAS-number: 584-84-9, 2,4-Toluendiisocyanat (2,4 TDI) CAS-number: 91-08-7, 2,6-Toluendiisocyanat (2,6 TDI)	0.005 ppm 0.05 mg/m^3 0.005 ppm 0.035 mg/m^3 0.005 ppm 0.035 mg/m^3

Legal instrument *1	EU/national	Substances	Requirements
*** Executive order concerning precautionary measures to prevent the cancer risk during work with substances and materials (Bekendtgørelse om foranstaltninger til forebyggelse af kræftrisikoen ved arbejde med stoffer og materialer, BEK nr 908 af 27/09/2005)**	DK	Products with ≥ 0.1% 2,4-TDI, 2,6-TDI and mixes thereof (CAS-numbers: 584-84-9, 91-08-7 and 26471-62-5) (MDIs not specifically mentioned, but implicitly including when present in products ≥ 1% given their classification as carcinogenic cat.2)	Specifies the labelling requirement: "Contains a substance regulated by the Danish occupational health regulations concerning cancer risk"
Legislation addressing waste			
Commission decision of 3 May 2000, establishing a list of wastes pursuant to article 1(a) of Council Directive 75/442/EC and council decision 94/904/EC	EU	Waste containing TDIs > 0.1% MDIs > 1% (limits based on classification)	08 05 01 waste isocyanates – listed as hazardous waste.
Waste Framework Directive 2008/98/EC	EU		Provides for requirements to hazardous waste listed according to Commission decision of 3 may 2000.
REGULATION (EC) No 1013/2006 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 14 June 2006 on shipments of waste	DK		This Regulation implements the Basel Convention in EU, establishing procedures and control regimes for the shipment of waste, depending on the origin, destination and route of the shipment, the type of waste shipped and the type of treatment to be applied to the waste at its destination. Isocyanates ("08 05 01* waste isocyanates") is listed in Annex V as waste subject to export prohibition to non-OECD countries.
*** Executive order no 1309 on waste (Bekendtgørelse om affald, BEK nr 1309 af 18/12/2012)**			Transposition of the waste framework directive into Danish law
Commission Recommendations of 27 June 1990 on the reduction of chlorofluorocarbons used by the Community's: - foam plastics industry - refrigeration industry	EU	Polyurethane foam sector (Using isocyanates)	Recommends foam plastics manufacturers and their association to reduce/eliminate the use of fully halogenated chlorofluorocarbons Relevance for this project is particularly related to disposal of PUR products as proper disposal addresses the presence of halogenated chlorofluorocarbons. See also Chapter 4.

Legal instrument *1	EU/national	Substances	Requirements
Legislation addressing emissions			
DIRECTIVE 2010/75/ on industrial emissions (integrated pollution prevention and control) (IPPC) **The IPPC Directive will be repealed with effect from 7 January 2014 by Directive 2010/75/EU on industrial emissions.**	EU	Isocyanates	Annex I specifies that the production of isocyanates is subject to the general provisions of this directive
REGULATION 166/2006 concerning the establishment of a European Pollutant Release and Transfer Register (PRTR)	EU	Isocyanates	Same Annex I entry as for above IPPC directive triggering that such production should be included in the European Pollutant Release and Transfer Register
DIRECTIVE 2012/18/EU on the control of major-accident hazards involving dangerous substances (SEVESO III). NB! This will replace the current Council Directive 96/82/EC (SEVESO II)	EU	2,4-TDI and 2,6-TDI (CAS-numbers: 584-84-9 and 91-08-7)	Listed as named dangerous substances in Annex I, Part 2.
*** Executive order on the control of risk from for major accidents with dangerous substances (SEVESO II) (Bekendtgørelse om kontrol med risikoen for større uheld med farlige stoffer, BEK nr 1666 af 14/12/2006)**	DK	idem	idem

* Unofficial translation of names of Danish legal instruments.

2.1.2 Classification and labelling

Table 4 shows that that all addressed (mixes of) monomeric TDI and MDI are subject to harmonised classification. Furthermore, it shows that MDI isomers and mixes thereof have the same harmonised classification. The same applies to TDI isomers and mixes thereof. The table shows that MDI, as well as TDI, are classified as suspected of causing cancer, as dermal and respiratory sensitisers, as well as eye, skin and respiratory irritants. For human health, classification differs in relation to acute toxicity, where MDI is harmful if inhaled; whereas TDI is fatal if inhaled, and in relation to toxicity after repeated exposure where only MDI is classified (potential to cause damage to liver and kidney).

The most notable difference between MDI and TDI is that only TDI is classified for environmental effects (Harmful to aquatic life with long lasting effects).

TABLE 4
HARMONISED CLASSIFICATION OF ISOCYANATES ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION)

Index No	International Chemical Identification	CAS No	Classification	
			Hazard Class and Category Code(s)	Hazard statement Code(s)
615-005-00-9	2,2'-methylenediphenyl diisocyanate (2,2'-MDI)	2536-05-2	Carc. 2 Acute Tox. 4 * STOT RE 2 * Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Resp. Sens. 1 Skin Sens. 1	H351 H332 H373** H319 H335 H315 H334 H317
615-005-00-9	o-(p-isocyanatobenzyl)phenyl isocyanate (2,4'-MDI)	5873-54-1	Carc. 2 Acute Tox. 4 * STOT RE 2 * Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Resp. Sens. 1 Skin Sens. 1	H351 H332 H373** H319 H335 H315 H334 H317
615-005-00-9	4,4'-methylenediphenyl diisocyanate (4,4'-MDI)	101-68-8	Carc. 2 Acute Tox. 4 * STOT RE 2 * Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Resp. Sens. 1 Skin Sens. 1	H351 H332 H373** H319 H335 H315 H334 H317
615-005-00-9	Methylenediphenyl diisocyanate (mix of MDI isomers)	26447-40-5	Carc. 2 Acute Tox. 4 * STOT RE 2 * Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Resp. Sens. 1 Skin Sens. 1	H351 H332 H373** H319 H335 H315 H334 H317
615-006-00-4	4-methyl-m-phenylene diisocyanate (2,4-TDI)	584-84-9	Carc. 2 Acute Tox. 2 * Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Resp. Sens. 1 Skin Sens. 1 Aquatic Chronic 3	H351 H330 H319 H335 H315 H334 H317 H412

Index No	International Chemical Identification	CAS No	Classification	
			Hazard Class and Category Code(s)	Hazard statement Code(s)
615-006-00-4	2-methyl-m-phenylene diisocyanate (2,6-TDI)	91-08-7	Carc. 2 Acute Tox. 2 * Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Resp. Sens. 1 Skin Sens. 1 Aquatic Chronic 3	H351 H330 H319 H335 H315 H334 H317 H412
615-006-00-4	m-tolylidene diisocyanate (mix of TDI isomers)	26471-62-5	Carc. 2 Acute Tox. 2 * Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Resp. Sens. 1 Skin Sens. 1 Aquatic Chronic 3	H351 H330 H319 H335 H315 H334 H317 H412

* Use of "*" in connection with a hazard category (e.g. Acute Tox. 4 *) implies that the category stated shall be considered as a minimum classification.

** Use of "**" in connection with a hazard statement code (e.g. H373**) implies that the route of exposure is not specified.

2.1.3 REACH

Authorisation List / REACH Annex XIV

As of March 2013, none of the isocyanates are included in REACH Annex XIV, which is a list of substances that require authorisation for continued use in the EU.

Community rolling action plan (CORAP)

Table 5 shows ongoing REACH substance evaluations for MDI and TDI that may lead to further community action, such as e.g. restriction or authorisation. For MDI, evaluation is indicated to be for the 4,4'-MDI isomer, which is the MDI registered in the highest volume (see Chapter 3). However, it is assumed that this evaluation will be valid for all MDI isomers given the similarities in properties. This approach is in line with the EU risk assessment in 2005 (EU, 2005) addressing all (mixes) of MDI. In this regard, it should be noted that the EU MDI risk assessment generally referred to the CAS-number for MDI mixes (26447-40-5), a number which for technical reasons has not been registered under REACH. The background for this technicality is given in Chapter 1.

For TDI, the evaluation addresses the registered mix of TDIs, being commercially of the most interest (see also Chapter 3); this is implicitly assumed also to address pure 2,4-TDI and 2,6-TDI, as these are the two constituents of this mix.

Interestingly, one of the triggers for evaluation listed is the suspected PBT properties of the hydrolysis degradation products (i.e. aromatic amines).

(Draft) substance evaluation reports are not yet publicly available.

TABLE 5
ISOCYANATES INCLUDED IN THE DRAFT COMMUNITY ROLLING ACTION PLAN, 2013-2015 UPDATE (ECHA, 2012)

CAS No	EC No	Substance Name	Year	Member State	Initial grounds for concern
101-68-8	202-966-0	4,4'-Methylenediphenyl diisocyanate (4,4'-MDI)	2013	Estonia	Human health/Sensitiser and CMR (hydrolysis product); Environment/Suspected PBT (hydrolysis product); Exposure/Wide dispersive use, high aggregated tonnage
26471-62-5	247-722-4	m-Tolylidene diisocyanate (mixed TDI)	2012	Poland	Human health/CMR and sensitiser; Environment/ Suspected PBT (hydrolysis products); Exposure/Wide dispersive use, high aggregated tonnage

It should be noted that in a parallel process, draft strategies for possible additional risk management of TDI and MDI are circulating among EU authorities. These draft strategies are also confidential.

Registry of Intentions

No registry of Intentions by ECHA and Member States' authorities for restriction proposals, proposals for harmonised classification and labelling, or proposals for identifying MDI and TDI as Substances of Very High Concern (SVHC) have been identified.

Candidate list

As of August 2013, MDI and TDI have not been included in the candidate list (ECHA, 2013b).

Annex XIV recommendations

MDI and TDI have not been recommended for Annex XIV inclusion (ECHA, 2013c). NB: Possible inclusion would first require uptake on the candidate list.

2.1.4 Other legislation/initiatives

To the best of our knowledge and as confirmed by the consulted Danish and EU trade organisations, no voluntary agreements are in place.

There are no standard conditions relating to isocyanates for Danish companies, facilities and activities listed in appendix 2 of Executive Order 1454/2012 (Godkendelsesbekendtgørelsen, BEK nr 1454 af 20/12/2012).

2.2 International agreements

Table 6 gives an overview of how MDI and TDI are addressed by various international agreements. As can be seen, isocyanates are generally not addressed in conventions relating to presence/transport in the environment, which is logical given their reactivity. Hazardous waste containing isocyanates is subject to the provisions of the Basel convention, and as a "parallel" to the Seveso directive, TDI is specifically addressed by the UNECE Convention on the Transboundary Effects of Industrial Accidents.

TABLE 6
INTERNATIONAL AGREEMENTS ADDRESSING ISOCYANATES

Agreement	Substances	How the isocyanates are addressed
OSPAR Convention	-	-
HELCOM (Helsinki Convention)	-	-
Rotterdam Convention (PIC Convention)	-	-
Stockholm Convention	-	-
Basel Convention	Isocyanate waste	Sets out control measures of the movements of hazardous waste (including isocyanate waste), and restricts transfer of hazardous waste from developed to less developed countries (LDCs; not adopted). The Convention also intends to minimize the amount and toxicity of wastes generated, to ensure their environmentally sound management as closely as possible to the source of generation, and to assist LDCs in environmentally sound management of the hazardous and other wastes they generate.
	Polyurethanes	Technical guidelines for the identification and environmentally sound management of plastic wastes and for their disposal: - "All polymers can successfully be recycled into second-life applications without significant impact on the environment. An overview of polymers and copolymers is given in Appendix 7A. Once the plastics have been cleaned and shredded, the process is much the same as for the production of plastics." Polyurethanes are listed in Appendix 7A.
Convention on Long-range Transboundary Air Pollution (CLRTAP)	-	-
UNECE Convention on the Transboundary Effects of Industrial Accidents	Toluene diisocyanate (individual TDI isomers not indicated)	Listed as a named substance (Annex I). Threshold quantity for identifying a hazardous activity: 100 tonnes.

2.3 Eco-labels

Table 7 gives an overview of how isocyanates are addressed by the EU and Nordic eco-labelling schemes, indicating that isocyanates are addressed in relation to chemical building products (Nordic Swan), Furniture and fitments (Nordic Swan) and Textiles (Nordic Swan and EU flower).

In addition, without having direct requirements as to isocyanates in the criteria themselves, several background documents to the Nordic Swan criteria (e.g. for outdoor furniture and playground equipment, disposables for food and floor coverings) mention isocyanates as a possible component in glues. The background documents discuss various issues such as:

- The fact that products with high content of isocyanates will be captured by criteria excluding products with certain hazard classifications and are thus implicitly out of scope of such criteria;
- The importance of complete curing, and
- Issues regarding formaldehyde based versus isocyanate based adhesives (both are potentially toxic; focus should therefore be on reducing emissions).

TABLE 7
ECO-LABELS TARGETING ISOCYANATES

Eco-label	Substances	Mixtures and articles + criteria	Document title
Nordic Swan	Isocyanates (except pre-reacted as stated in next column)	'In-going' chemical substances which must not form part of the product include: "Isocyanates – excepted from this are water based polyisocyanates with a chain length of more than 10 when the amount of impurities of isocyanates with a chain length of less than 10 is documented."	Nordic Ecolabelling of "Chemical building products" (Adhesives, Sealants, Fillers and Outdoor paints and varnishes)
	Isocyanates	For Polyurethanes (criterion R38) Blowing agents and isocyanate compounds: - CFC, HCFC, HFC, methylene chloride and halogenated organic compounds must not be used as blowing agents. - Isocyanate compounds must only be used in a closed process with the prescribed protective equipment and in accordance with regulatory requirements. Finally, it should be noted that an exemption from the general ban of carcinogenic substances is given for the use of isocyanate based adhesives classified with R40. (The criteria background document discusses the need for using adhesives based on isocyanates, formaldehyde and polyvinylacetate for laminating, recognising that this may be "undesirable in terms of health and the environment.")	Nordic Ecolabelling of Furniture and fitments

Eco-label	Substances	Mixtures and articles + criteria	Document title
	Aromatic diisocyanates (i.e. including MDI and TDI)	For production of Elastane: "Emissions to the air of aromatic diisocyanates during polymerisation and fibre production shall be less than 5 mg/kg produced fibre, expressed as an annual average."	Nordic Ecolabelling of Textiles, hides/skins and leather Includes products for apparel and furnishing
	Isocyanate compounds (i.e. including MDI and TDI)	Polyurethane foam: "Isocyanate compounds shall only be used in a closed process with the required protective equipment and in accordance with regulatory requirements."	
EU Flower	Aromatic diisocyanates (i.e. including MDI and TDI)	For production of "Elastane": " The emissions to air of aromatic diisocyanates during polymerisation and fibre production, measured at the process steps where they occur, including fugitive emissions as well expressed as an annual average, shall be less than 5 mg/kg of fibre produced. " In relation to "Coatings, laminates and membranes" it is specified that "Products made of polyurethane" shall comply with the same emission criterion as for production of elastane (see above)	COMMISSION DECISION of 9 July 2009 establishing the ecological criteria for the award of the Community Ecolabel for textile products

2.4 Summary and conclusions

The seven (mixes of) TDI and MDI within the scope of this project are subject to harmonised classification under the CLP regulation. They are all classified as suspected of causing cancer, as dermal and respiratory sensitisers, for acute toxicity following inhalation, as well as eye, skin and respiratory irritants. Furthermore, MDI is classified for potential to cause damage to liver and kidney following repeated exposure, whereas TDI is classified for environmental effects (harmful to aquatic life with long lasting effects).

MDI is subject to an EU restriction on the use of MDI-containing consumer products and a Commission recommendation related to MDIs used professionally. 2,4-TDI, 2,6-TDI, 2,4'-MDI and 4,4'-MDI are on the positive list of the plastic food contact material regulation with certain restrictions and TDIs are prohibited in cosmetics. "Isocyanates" (including MDI and TDI) are specifically indicated to be within the scope of the IPPC (Integrated Pollution Prevention and Control) and PRTR (Pollutant Release and Transfer Register) directives. TDI is specifically mentioned in Annex 1, Part 2 of the Seveso Directive. Isocyanate waste (nomenclature: "08 05 01 waste isocyanates") is regulated as hazardous waste. Finally, a Commission recommendation states that Member States should address occupational diseases caused by isocyanates.

For the Danish situation, an array of national legislation is in place in relation to occupational handling of isocyanates, including the need for training, labelling, handling, security measures, limitations of spray applications and the establishment of Danish Occupational Exposure Limits. Most of these requirements are also applicable off-shore and on ships.

MDI and TDI are generally not addressed in international agreements, except that TDI is specifically addressed by the UNECE Convention on the Transboundary Effects of Industrial Accidents (in parallel with being specifically addressed by the Seveso directive) and isocyanates waste, classified as hazardous waste, falls under the provisions of the Basel Convention.

Isocyanates are addressed by a few EU and Nordic eco-labelling criteria, in particular in relation to TDI in adhesives, furniture and textiles.

In general there is some ambiguity as to whether some or all TDI and MDI isomers are addressed by a given requirement and whether other forms, such as prepolymer and polymeric isocyanates, have been considered in relation to drafting the requirements. It should be noted that most of the specific Danish requirements are also applicable to prepolymers.

TDI and MDI are currently undergoing REACH substance evaluation and further risk management considerations in the EU, which might lead to further action at EU level. These activities are thus far subject to confidentiality, but the Danish EPA has direct access to the activities and the related documents.

3. Manufacture and uses

As set out in Chapter 1, the uses/applications of MDI/TDI are often considered under the following main categories of uses:

- Flexible PUR (e.g. for furniture upholstery and mattresses);
- Rigid (and non blown Solid) PUR (e.g. for insulation, district heating tubes, refrigeration, construction).

"C.A.S.E.":

- **C**oatings (surface treatment like paints and lacquers)[11]
- **A**dhesives;
- **S**ealants (e.g. fillers/joint fillers), and
- **E**lastomers (e.g. rubber and thermoplastic elastomers).

Flexible and rigid PUR, as well as elastomers (E) are typically supplied as already cured products, whereas for coatings (C), adhesives (A) and sealants (S), the curing itself forms part of the functionality of the products during/after use and the products therefore contain free isocyanate monomers.

Often an additional grouping is applied:

- Binders (used for binding particles together mainly for chipboards).

Although terminology/grouping is not always consistent among references, the above groupings are used to the extent possible in this chapter.

3.1 Manufacturing and overall import, export and consumption

3.1.1 Manufacturing processes

As manufacturing of MDI and TDI does not take place in Denmark, this paragraph will describe the manufacturing process of MDI and TDI briefly.

MDI

Based on correspondence with ISOPA (ISOPA, 2013), the following (steps of the) manufacturing process of MDI can be outlined:

Manufacturing of diaminodiphenylmethane (DADPM)

In the manufacturing of MDI, diaminodiphenylmethane (DADPM) is formed initially through the reaction of formaldehyde with aniline in the presence of a hydrochloric acid catalyst. The percentage distribution of isomers of DADPM formed during this step depends on the ratio of aniline to formaldehyde, the acid concentration, and the reaction conditions. After the reaction, the mixture is neutralised by adding caustic soda, and separates into an organic phase and an inorganic (aqueous) phase. The organic phase containing crude DADPM is washed. Excess aniline from washing is isolated by distillation for recycling in the first step of the reaction. The inorganic (aqueous) phase is purified from any residual organics and discharged for further treatment or recovery.

[11] "Coatings" in this context are normally considered to be industrial surface coatings, e.g. for coating metal and concrete constructions. However, isocyanate-based products are also used for other types of coating, e.g. coating of textiles. It is not clear under which of the main "C.A.S.E" categories, textiles coatings would fall. MDI/TDI volumes used for such applications are assessed to be inferior compared to e.g. industrial coatings and would thus not influence the figures presented in this chapter significantly. On the other hand, consumer use of such textile coatings could cause significant exposure.

Phosgenation of DADPM to crude MDI
During this stage phosgene is reacted with DADPM in an inert solvent to crude MDI (also sometimes termed oligomeric MDI) and a hydrogen chloride byproduct. Depending on the running of the process, polymeric MDI (PMDI) may also be the outcome of this manufacturing step.

Solvent Recovery and MDI Purification
Following phosgenation, when evolution of hydrogen chloride is complete and a homogeneous solution is obtained, the solvent is recovered by distillation.

Purified monomeric MDIs can be obtained by fractional distillation, crystallization or sublimation.
The remnants from these purification processes are PMDI.

Thus PMDI can be obtained directly from the phosgenation process or as remnants from subsequent purification.

Manufacturing of modified/prepolymer MDI
Purified monomeric MDI and/or PMDI can be used to further react with themselves, amino groups or glycols/polyether polyols to form modified MDIs, often called MDI prepolymers. Thus, modified/prepolymer MDIs are not produced directly, but are the result of further modification of monomeric or polymeric MDIs.

TDI
Toluene is nitrated to dinitrotoluene (DNT) producing an isomer mix that is catalytically hydrogenated to crude toluene diamine (TDA). This reaction product is purified by fractional distillation to remove the mixed 2,3 and 3,4 isomers. The purified TDA is then phosgenated to convert the amine groups to isocyanate groups. The isocyanate mixture is distilled to generate a liquid TDI product, typically 65:35 and 80:20 2,4:2,6 isomer mixes (Randal and Lee, 2003).

3.1.2 Manufacturing sites
The 2005 EU risk assessment of MDI notes that there are 13 EU production sites (all > 1000 tonnes/year): 5 in Germany, 2 in the Netherlands, 2 in Belgium, and one site in the UK, Spain, Italy and Portugal.

As of today (ISOPA, 2013), there are:
- 7 sites in the EU manufacturing MDI (2 in Germany and one in each of the following countries: Spain, Belgium, Portugal, The Netherlands and Hungary), and
- 5 sites in the EU manufacturing TDI (3 in Germany, one in France and one in Hungary).

3.1.3 Manufacturing, import, export and overall consumption volumes

Globally
Based on data provided by ISOPA (the European Diisocyanate and Polyol Producers Association), the global market amounts to about 5 million tonnes MDI/year and about 1.9 million tonnes TDI/year. In comparison, speciality/aliphatic isocyanates are indicated to have a global market volume of 285,000 tonnes/years. This means that MDI/TDI account for about 96% of the global isocyanate market volume (ISOPA, 2013).

The EU MDI risk assessment notes that the world production of MDI represented 1.2 million tonnes/year in 1991 and 2.5 million tonnes/year in 1996 (EU, 2005).

Thus, it appears that the world production and consumption of MDI and TDI is steadily increasing. This is supported by ISOPA, which indicates that the overall polyurethane (PUR) consumption increased from about 1 million tonnes/year in 1970 to about 14.1 million tonnes/year in 2012.

EU

Recent market data

Data for the EU MDI and TDI market has been acquired from IAL consultants (2013). In this context, it should be noted that the European trade organisation (ISOPA) also refers to IAL consultants for market data.

Table 8 provides aggregated EU (+Norway) MDI and TDI consumption data (i.e. MDI and TDI used for production in the EU) acquired from IAL consultants[12].

TABLE 8
YEARLY MDI AND TDI CONSUMPTION DATA FOR EU (PLUS NORWAY). SOURCE: IAL CONSULTANTS (2013). IAL CONSULTANTS ROUGHLY ESTIMATES THAT THE UNCERTAINTY ON THESE FIGURES IS ABOUT 5% (+/-)

Year	Monomeric MDI (tonnes/year)	Polymeric MDI (tonnes/year)	TDI (tonnes/year)	Total MDI and TDI (tonnes/year)	Speciality Isocyanates (tonnes/year)
2011	180,300	996,000	361,000	**1,537,300**	84,300
2016 (estimated trend)	195,800	1,145,900	411,000	**1,752,700**	91,800

Similarly to the global figures, these figures indicate that the increasing application trend is expected to continue for the European market.

The figures in the table represent the total consumption for production in the EU, i.e. manufactured plus imported minus exported MDI and TDI. Therefore, the figures do not capture import of MDI and TDI in mixtures/preparations such as coatings, adhesives and sealants.

As for the global market, speciality isocyanates account for a relatively low volume (about 5%) compared to the MDI and TDI consumption volumes.

It can also be seen that MDI (monomers and polymeric) are roughly used in quantities about 3 times that of TDI and that about 85% of the MDI use takes place as polymeric MDI. Assignment of “Monomeric MDI” or “Polymeric MDI” is based on the terminology used by the market actors interviewed in the market analysis. Thus, possible different understandings of e.g. Polymeric MDI among market actors may cause some inaccuracies behind the figures presented (IAL consultants, 2013).

[12] Text accompanying acquisition of the tables: “IAL is an independent consultancy with no commercial investments with any PU market player. IAL thus offers an unbiased view of the market and its forecasts are objective and trusted within the industry. IAL has been researching the polyurethane and PU precursors market since the 1980’s. The data is from IAL’s flagship EMEA report which is now in its ninth publication. Over the years IAL has refined the data each time, increasing the level of accuracy, by speaking to a large number of respondents including manufacturers, distributors, end-users and associations. IAL now holds a strong reputation in the industry due to the accuracy and depth of its reports and its reports have been well received. IAL has strong relationships with key Isocyanate producers and conducts many interviews about production and demand across many countries and regions. The data is also cross referenced with secondary statistics from PU end use markets, such as car production statistics, footwear production, new housing statistics and furniture production. Such methodology and triangulation of data sources has enabled IAL to produce the most robust analysis of the market possible."

EU MDI Risk Assessment

For MDI, the EU risk assessment (EU, 2005) estimated an EU production trend of:

- 1980: 267,000 tonnes/year;
- 1993: 540,000 tonnes/year, and
- 1996: 790,000 tonnes/year.

For the 1996 figures, the following mass-balance was made: Consumption = production (790,000 tonnes/year) + import (3,500 tonnes/year) - export (105,000 tonnes/year) = 689,000 tonnes/year.

Comparing this mass balance with Table 8 indicates that the total MDI consumption would be approximately doubled from 689,000 tonnes/year in 1996 to 1,341,700 (1,145,900 + 195,800) tonnes/year in 2016. This trend supports other figures showing steadily increasing demand for MDI.

The figures also indicate that in 1996 there was a net export of MDI, although the main amount of MDI manufactured was used for further processing within the EU.

For 1996, EU (2005) estimates that the 689 000 tonnes/year consumed can be divided into:

- 510,000 tonnes/year directly used of PUR production;
- 135,000 tonnes/year converted to prepolymer MDI and then used for PUR production, and
- 44,000 tonnes/year converted to prepolymer MDI and then used in "speciality MDI" products.

REACH

Given that MDI and TDI are manufactured in high volumes by a few EU manufacturers and that a relatively small amount is imported (see the below Eurostat figures), it must be assumed that the majority of the MDI and TDI volume was registered by the first and second REACH registration deadlines (December 2010 and June 2013).

Registered monomeric MDIs as well as oligomeric MDI are presented in Table 9.

TABLE 9
IDENTIFIED PREREGISTERED MDI AND TDI SUBSTANCES WITH INDICATION OF THE ACCUMULATED REGISTERED TONNAGE AS OF AUGUST 2013 (ECHA, 2013A)

CAS No	EC No	Substance name *1	Registered, tonnage band , t/y *2
MDIs			
2536-05-2	219-799-4	2,2'-methylenediphenyl diisocyanate (2,2'-MDI)	1,000-10,000
5873-54-1	227-534-9	o-(p-isocyanatobenzyl)phenyl isocyanate (2,4'-MDI)	10,000-100,000
101-68-8	202-966-0	4,4'-methylenediphenyl diisocyanate (4,4'-MDI)	100,000-1,000,000
26447-40-5	247-714-0	Methylenediphenyl diisocyanate (mix of MDI isomers)	Not registered
N.A. (but could have been 26447-40-5)	905-806-4	Reaction mass of 4,4'-methylenediphenyl diisocyanate and o-(p-isocyanatobenzyl)phenyl isocyanate (mix of MDI monomers)	10,000 - 100,000
32055-14-4	500-079-6	Oligomeric MDI; crude MDI reaction product, containing monomeric (>50%) and polymeric MDI	1,000,000 - 10,000,000
TDIs			
584-84-9	209-544-5	4-methyl-m-phenylene diisocyanate (2,4-TDI)	100,000-1,000,000
91-08-7	202-039-0	2-methyl-m-phenylene diisocyanate (2,6-TDI)	Not registered
26471-62-5	247-722-4	m-tolylidene diisocyanate (mix of TDI isomers)	100,000-1,000,000

The registration figures account for manufacturing of pure MDI, for import of pure MDI and TDI and for MDI and TDI imported as substances in mixtures. The latter differs from e.g. market data from IAL consultants and Eurostat figures presented elsewhere in this chapter. The REACH registration figures are not corrected for export, which however appears to be insignificant based on other statistics in this chapter.

In any case, the oligomeric MDI (crude MDI coming out of manufacturing) is registered in a tonnage range accommodating the total IAL MDI figures of above 1 million tonnes MDI/year.

Further refinement of oligomeric MDI yields monomeric and polymeric MDI (PMDI), of which monomeric MDIs are registered and PMDIs not (see Chapter 1).

For Monomeric MDI the three "pure" isomers are registered, but the mix of MDIs apparently is not. However, as set out in Chapter 1, these amounts could be covered by the other registrations (either under 4,4’-MDI if this isomer constitutes above 80%, or in the case where MDI monomers are combined to form what would be considered a mixture under REACH). For technical reasons it may also be registered as other substances, e.g. under EC-number 905-806-4, included in Table 9. As per Table 9, this EC-number is however registered in relatively low amounts. 4,4'-MDI logically dominates the registrations in terms of volume, being the most prevalent isomer coming out of the MDI manufacturing process.

It should be noted that the EU 2005 MDI risk assessment (EU, 2005) generally used the MDI mix CAS-number (26447-40-5), but as indicated previously, the risk assessment stated that this number was assumed to address all isomers. As can be seen in chapter 2, this issue has also recently been clarified in relation to the EU restriction which followed from that risk assessment: it was clarified that all MDI monomers are covered by the restriction.

TDIs have been registered in a total volume above 200,000 tonnes/year and below 2,000,000 tonnes/year. Although the REACH registration data (also addressing mixtures and not export) are not directly comparable to the IAL data provided in Table 8, the REACH registration ranges are sufficiently wide to accommodate the IAL data.

For TDI, the 2,4-TDI isomer and the CAS-number for mixes of TDI monomers are registered, whereas the 2,6-TDI is not registered. This is logical in light of the general findings in literature stating that 2,4-TDI and particularly the TDI-80:20 and 65:35 mixes, are commercially the most relevant, whereas the 2,6-TDI monomer is more rare and difficult to isolate.

In relation to modified/prepolymer MDI, ISOPA (ISOPA, 2013) has clarified that these have been registered as "No Longer Polymers". Registration status for the most common modified/prepolymer MDIs is outlined in Table 10.

TABLE 10
IDENTIFY OF REGISTERED MODIFIED/PREPOLYMER MDI AS OF AUGUST 2013 (ECHA, 2013A)

CAS No	EC No	Substance name *1	Registered, tonnage band , t/y *2
25686-28-6	500-040-3	4,4'-MDI homopolymer	10,000-100,000
109331-54-6	500-297-1	2,4'-MDI/4,4'-MDI homopolymer	100-1,000
59952-43-1	500-142-8	4,4'-MDI/DPG	Not registered
88288-99-7	500-270-4	2,4'/4,4'-MDI/DPG	10,000-100,000
52747-01-0	500-119-2	4,4'-MDI/TPG	Not registered
75880-28-3	500-262-0	2,4'/4,4'-MDI/TPG	1,000-10,000
NA	500-312-1	MDI/1,3-BD/TPG/PG	1,000-10,000
NA	500-313-7	MDI/MDI homopolymer/1,3-BD/TPG/PG	Tonnage Data Confidential

PG: Propylene Glycol, DPG: Dipropylene Glycol, TPG: Tripropylene Glycol, PPP: Poly Propylene Glycol

As described under MDI manufacturing, modified/prepolymer MDIs are manufactured from further reaction of monomeric or polymeric MDIs. Considering the figures in the table, only a fraction is converted to modified/prepolymer MDI. However, given the wide tonnage ranges available, it is difficult to generate a more precise estimate of the percentage of monomeric and polymeric MDI converted.

Eurostat
Statistics on EU external trade and EU production of isocyanates on their own in tonnes/year from EUROSTAT statistics are shown in Table 11 and Table 12.

TABLE 11
EU27 EXTERNAL IMPORT AND EXPORT OF ISOCYANATES (EUROSTAT, 2013A)

CN code	Text	Import, t/y		Export, t/y	
		Average 2006-2010	2011	Average 2006-2010	2011
2929.1000	Isocyanates	28,842	23,403	282,719	294,442

TABLE 12
EU27 PRODUCTION OF ISOCYANATES (EUROSTAT, 2013B)

PRODCOM Code	Text	Production, t/y	
		Average 2006-2010	2011
2014.4450	Isocyanates	1,759,211	1,801,423

The nomenclature used for the two statistics differs, but "isocyanates" with no further breakdown by type are included in specific commodity codes in both statistics. Thus, the data covers other types of isocyanates than MDI and TDI addressed in this report. However, as shown previously for the EU and global markets, MDI and TDI must be assumed to be the main contributors to these figures (about 95%).

The total EU consumption should be production plus import minus export. Based on the statistics in Table 11 and Table 12, this gives a total consumption of 1,503,384 tonnes/year in 2011, close to the IAL estimate for 2011 of 1,537,300 tonnes/year.

In line with previous findings, these figures appear to confirm that most of the isocyanates used in the EU are actually manufactured in EU (little import) and that EU is a net exporter, although the figures indicate that by far the main amount manufactured in EU is used within EU.

Finally, the figures support other findings in indicating a positive trend in the amount of isocyanate manufactured and used.

The Nordic Market

Data for Nordic consumption for production (i.e. production plus import minus export of pure MDI and TDI – not including import/export of MDI and TDI in mixtures/preparations) has been acquired from IAL consultants (see footnote on page 52). The aggregated figures are shown in Table 13.

TABLE 13
YEARLY MDI AND TDI CONSUMPTION DATA FOR THE NORDIC COUNTREIS (DENMARK, NORWAY, SWEDEN AND FINLAND). SOURCE: IAL CONSULTANTS. IAL CONSULTANTS ROUGHLY ESTIMATES THAT THE UNCERTAINTY ON THESE FIGURES IS ABOUT 5% (+/-)

Year	Monomeric MDI (tonnes/year)	Polymeric MDI (tonnes/year)	TDI (tonnes/year)	Total MDI and TDI (tonnes/year)	Speciality Isocyanates (tonnes/year)
2011	2,450	48,435	16,859	67,743	2,883
2016 (estimated trend)	2,699	53,875	19,179	75,753	3,130

In terms of distribution between MDI and TDI, a similar picture as that seen for the European market is observed: i.e. about 3 times more MDI (monomeric and polymeric) compared to TDI. On the other hand, when comparing to EU an even higher percentage of the MDI is estimated to be polymeric MDI: about 95% where the EU figures indicated the figure to be about 85%.

It can also be seen that the speciality isocyanates are assumed to constitute a minor amount (about 4%) of the total isocyanate volumes, generally in line with EU and global figures.

Finally, a similar increasing trend as for the European and global market is assumed for the Nordic market.

Denmark

Various sources provide information on import, export and/or overall consumption of isocyanates in Denmark.

Statistics Denmark

Statistics on production, import and export of isocyanates retrieved from Statistics Denmark are shown in Table 14. Statistics Denmark uses the Combined Nomenclature (CN) for the import/export statistics as well as for the production statistics. As for EU/Eurostat statistics, the indicated quantities refer to all isocyanates, including MDI and TDI. As for the global market, it must be assumed that MDI and TDI account for the vast majority of the isocyanate volume.

To our knowledge, manufacture of isocyanates does not take place in Denmark, so the small amount of isocyanate production indicated must be due to incorrect registration.

The data indicates a significant increase in import of isocyanates to Denmark, which contradicts the trend observed by the Danish Plastics Federation (see below).

Export is insignificant, which is logical as these statistics only address pure MDI and TDI (not in mixtures/preparations). As is shown below, the data retrieved from the Danish Product Registry (also addressing isocyanates in formulations/mixtures) indicate a significant export.

TABLE 14
DANISH PRODUCTION, IMPORT AND EXPORT OF ISOCYANATES (STATISTICS DENMARK, 2013)

CN8 code	Text	Import, t/y		Export, t/y		Production, t/y	
		Average 2007-2011	2012	Average 2007-2011	2012	Average 2007-2011	2012
2929.1000 *1	Isocyanates	4,937	8,773	72	320	114	87

*1 For the period 2007-2008 the commodity code was separated into two codes

Danish Product Registry

The Danish Product Registry requires registration of import/manufacture of all occupationally used substances and mixtures which contain at least one substance classified as dangerous in a concentration of at least 0.1% to 1% (depending on the classification of the substance).

For substances included in mixtures used for formulation of other mixtures in Denmark (e.g. those included in raw materials used for production of paint), the quantities may be double-counted as both the raw material and the final mixture may be registered.

MDI and TDI are classified as dangerous and the MDI and TDI used for PUR production are used industrially.

Uses for coatings, adhesives and sealants are largely industrial/professional, but consumer products also exist. However, the Danish Coatings and Adhesives Association assumes that the products used by consumers could also be used by professionals, thus assuming that the Product Registry data would cover the total amount of MDI and TDI applications in Denmark. Based on this assumption, the Product Registry data should largely address the total Danish MDI and TDI import on their own and in mixtures.

Extracts from the Danish Product Registry have been provided (April 2013) to the project confidentially. Only aggregated data can be provided in this reporting; i.e. it should not be possible to identify individual companies. To ensure this, data on applications or consumptions provided in the report should pertain to more than 3 importers/manufacturers/products.

Extracts were provided for the seven MDI and TDI (mixes of) monomers addressed in this project (see Chapter 1), as well as for a range of modified/prepolymer MDIs. Proposals for relevant CAS-numbers for the latter were provided by the Danish Plastics Federation at the beginning of the project. For confidentiality reasons, the identity of these substances/CAS-numbers cannot be revealed, as the searches showed few registrations for these CAS-numbers. Overall, however, the total amount for these modified/prepolymer MDI CAS- numbers was insignificant. The conclusion must be one or more of the following:

- Very low amounts of modified/prepolymer MDIs are imported;
- Modified/prepolymer MDIs imported/used are registered under the CAS-numbers of the monomeric CAS-numbers, and/or
- Modified/prepolymer MDIs are registered under CAS-numbers other than those suggested by the Danish Plastics Federation.

The average aggregated MDI and TDI figures for the Danish market are shown in Table 15.

TABLE 15
AGGREGATED MDI AND TDI FIGURES FOR THE DANISH MARKET AS EXTRACTED FROM THE DANISH PRODUCT REGISTRY

Substance	Production/Import (average estimate) (Tonnes/year)	Export (average estimate) (Tonnes/year)
MDI		
2,2'-MDI	20-30	0-2
2,4'-MDI	800-1,400	50-250
4,4'-MDI	2,500-4,900	900-1,700
MDI mix	100-200	20-50
MDI-tot	3,400-6,500	950-2,000
TDI		
2,4-TDI	2,700-2,800	1-2
2,6 TDI	1,000-1,100	0
TDI mix	1,500-3,300	2
TDI-tot	5,300-7,200	3-4
Total		
Total	**8,700-13,700**	**950-2,000**

Variations in the figures derive from the fact that double counting may occur. This possibility has provided the project with varying figures, depending on whether extracts have been done according to function or branch categories. As well, the figures provided to the project are associated with ranges of content in the registered products. As these ranges are generally rather wide, there are significant variations in the overall figures. Given the possibility for double counting, the overall figures are likely to be closer to the lower ranges indicated in the table.

As there is no isocyanate production in Denmark, the production/import figures must be assumed to indicate the imported amount. The total amount appears to be in the same range, possibly slightly higher than what is indicated in the 2011 figure from Statistics Denmark (Isocyanates: 8,773 tonnes/years), assuming that “Isocyanates” mainly address MDI and TDI. A higher tonnage would appear logical as the Danish Product Registry figures include import of MDI and TDI in mixtures/preparations, which the Danish Statistics figures do not.

The figures indicate that MDIs and TDIs are used in approximately equal amounts on the Danish market. This deviates from findings for the Nordic, EU and the global markets, where MDIs are used in amounts approx. three times higher than TDI. This could be explained by the fact that polymeric MDIs have not been registered under the CAS-numbers examined.

It could also be supposed that the Danish situation differs from the EU and Nordic situation. Estimates from The Danish Plastics Federation indicate that the total MDI and TDI volumes could be about equal given that the largely MDI-based rigid PUR production has declined in recent years. This situation would result in a relatively higher production of TDI-based flexible PUR (data is presented below under “Estimates from Danish trade organisations”).

In relation to individual monomers, it is logical that 4,4’-MDI is imported/used in the highest quantity when comparing to the REACH registration figures. 2,4’-MDI is imported/used in an amount approx. an order of magnitude less than 2,4’-MDI. This mirrors the distribution of EU registration volumes for these substances.

For TDI, the relative distribution of isomers on the Danish market seems to differ significantly from those at the EU level. In particular, it appears that 2,6-TDI (which is not registered under REACH) is imported in an amount of approx. 1,000 tonnes/year. Given the limited availability of this isomer (difficult to isolate), this must be considered a reporting inaccuracy.

There appears to be a significant export of MDI isomers, whereas the export of TDI seems insignificant. These export figures must be assumed to stem from export of MDI in not yet reacted preparations, e.g. coatings, adhesives and paints. For PUR products, the MDI/TDI monomers would be reacted and no longer be present. In theory, the export figures could also represent rebranding/repackaging of MDI in Denmark, but the authors are not aware of such activities. For confidentiality reasons, this issue cannot be further elaborated upon based on the Product Registry data provided to the project. However, comparing the export figures with those from Statistics Denmark indicates a significant difference. This is likely explained by Statistics Denmark operating at product level (i.e. export of mixtures with isocyanates would not be captured), whereas the Product Registry operates at constituent level. This fact further supports the above assumption that the Danish Product Registry export figures are for export as constituents in mixtures (coatings, adhesives, sealants and the like).

Given the uncertainties related to registered amounts, possible incorrect assignment of CAS-numbers, concentration ranges available to the project and confidentiality issues, it is difficult to draw firm conclusions based on the Danish Product Registry data provided.

Estimates from Danish trade organisations
Regarding the consumption (import minus export) of MDI and TDI for PUR production in Denmark, the PUR section of the Danish Plastics Federation (Brønnum, 2013) refers to the Report "Mapping of waste products with content of polyurethanes" (Danish EPA, 2005a) with the below assessment about the market trend.

The amount of production of flexible PUR and PUR elastomers today is about the same as those listed for flexible PUR in the report, i.e. about 22,000 tonnes/year. The amount of isocyanate used for manufacturing flexible polyurethane is about 30% of the PUR mass, thus about 6,600 tonnes/year. Mainly TDI (about 90%) is used for this type of polyurethane, but also increasingly modified types of MDI. This gives about 6,000 tonnes TDI/year and 600-700 tonnes MDI/year for these applications.

On the other hand, the use of MDI for production of rigid PUR foam is assessed to have decreased since 2004/2005, largely due to shift of production to Eastern Europe of polyurethane products used for cooling applications. The PUR section of the Danish Plastics Federation assesses that the total amount today would account to maximum 8,000 tonnes PUR/year. About 65% of the mass of rigid polyurethane origins from isocyanate, which is solely MDI. Thus, the estimated MDI volume for production of rigid PUR in Denmark is 5,200 tonnes/year.

The Danish Coatings and Adhesives Association has been contacted in relation to MDI and TDI volumes applied for coatings, adhesives, sealants and similar products. The association does not have aggregated volume data and refers to figures in the Danish Product Registry. As shown in the previous sections and further discussed below, those figures unfortunately cannot clarify the MDI and TDI amounts used for these applications.

The above estimates from the Danish Plastics Federation indicate that about 6,000 tonnes MDI/year and 6,000 tonnes TDI/year are used for production of flexible and rigid PUR products, as well as elastomers. Roughly considering (in line with EU data) that MDI and TDI in coatings, adhesives and sealants would account for 10% of the total volume would give approximately a further 1,000 tonnes MDI and TDI/year on the Danish market.

Considering associated uncertainties, these figures seem to be in line with the figure from Danish Statistics of approximately 9,000 tonnes isocyanates/year and the Danish Product Registry 9,000-14,000 tonnes/year (which cover import of and uses for coatings, adhesives and sealants, but also likely represent some double counting).

3.2 Uses and applications of MDI and TDI

3.2.1 EU level

Table 16 subdivides the 2011 MDI and TDI consumption for production volumes on the EU market (EU27+Norway) into main application categories.

TABLE 16

YEARLY MDI AND TDI CONSUMPTION DATA FOR EU (PLUS NORWAY) SUBDIVIDED INTO MAIN APPLICATION AREAS. SOURCE: IAL CONSULTANTS (2013). IAL CONSULTANTS ROUGHLY ESTIMATES THAT THE UNCERTAINTY ON THESE FIGURES IS ABOUT 5% (+/-)

EU27+Norway (2011)	Polymeric MDI (t/year)	Monomeric MDI (t/year)	TDI (t/year)	Total MDI and TDI (t/year)	Speciality Isocyanates (t/year)
Adhesives	17,900	28,500	18,300	64,700 (4%)	11,600
Coatings	35,500	10,900	30,100	76,500 (5%)	66,800
Elastomers	0	101,500	2,500	104,000 (7%)	5,300
Sealants	5,300	6,700	4,400	16,400 (1%)	600
Binders	145,900	0	500	146,400 (10%)	0
Flexible Foam	83,400	32,700	305,200	421,300 (27%)	0
Rigid Foam	708,000	0	0	708,000 (46%)	0
Total	996,000	180,300	361,000	1,537,300	84,300

The table clearly shows that the main applications of MDI and TDI are for production of PUR products (flexible and rigid foam, as well as elastomers) accounting for about 80%.

Of the remaining volumes, binders account for about 10% and coatings, adhesives and sealants for the remaining 10%.

As with other data from IAL, the figures do not address import/export of MDI and TDI in mixtures/preparations, but it might be assumed that import/export level out and that the figures therefore represent the consumption of MDI/TDI containing coatings, adhesives and sealants on the EU market.

3.2.2 Nordic Level

Table 17 provides an overview of MDI/TDI consumption for production on the Nordic Market in main application categories.

TABLE 17
YEARLY MDI AND TDI CONSUMPTION FOR PRODUCTION DATA FOR THE NORDIC MARKET SUBDIVIDED IN MAIN APPLICATION AREAS. SOURCE: IAL CONSULTANTS. IAL CONSULTANTS ROUGHLY ESTIMATES THAT THE UNCERTAINTY ON THESE FIGURES IS ABOUT 5% (+/-)

Nordic market (2011)	Polymeric MDI (t/year)	Monomeric MDI (t/year)	TDI (t/year)	Total MDI and TDI (t/year)
Adhesives	120	80	56	256 (0.4%)
Coatings	2,228	528	1,053	3,808 (5.6%)
Elastomers	0	420	10	430 (0.6%)
Sealants	0	0	0	0 (0%)
Binders	7,580	0	0	7,580 (11%)
Flexible Foam	3,185	1,422	15,741	20,347 (30%)
Rigid Foam	35,322	0	0	35,322 (52%)
Total	48,435	2,450	16,859	67,743

The table shows a similar pattern as compared to the EU market, although with little or no production/formulation of sealants, adhesives and elastomers.

The main categories listed in the tables are further subdivided in applications. The following outlines the most significant sub-categories:

- Adhesives: "Construction" (100% of the amount);
- Coatings: "Transport" - Marine and vehicle (37%), "Construction" (33%), "Industrial coatings" (15%), "Textile, Leather, Wood and furniture coatings" (12%);
- Elastomers: "Footwear" (44%), "RIM/RRIM" ((Reinforced) Reaction Injection Moulding) (37%), "CAST" (19%);
- Flexible foam: "Slabstock" (manufacturing in blocks) (86%), "Transport" (including seating and carpet backing) (6-7%), "Furniture components" (6-7%);
- Rigid foam: "Pipe-in-pipe" insulation (32%), "Refrigeration" (25%), "Rigid-faced Panels" (23%), and
- Binders: "Forest products" (88%)[13], "Foundry core" (6%), "Rubber crumb" (6%).

As for other IAL data, these figures indicate production using MDIs and TDIs and not which MDI- and TDI-based products are actually used on the Nordic market.

[13] Given the huge forest sectors in Norway, Sweden and Finland, most of this is likely to be used and possibly also produced in Nordic countries other than Denmark.

3.2.3 Denmark

Data from the Danish Product Registry
In addition to the total figures presented in Table 15, subdivisions into function groups (UC62 codes) and into branch codes (NACE) have been provided to the project. As noted previously, data pertaining to less than four applications/companies cannot be revealed for confidentiality reasons. As noted below, this places significant limits on what can be presented in this report.

As indicated in Table 15, the data from the Product Registry are variable/uncertain. The same is true for the underlying function and branch data, which add up to different total amounts. In the following, best estimates on the basis of the available data are provided.

Application of TDIs
As noted in relation to Table 15, the significant import of about 1000 tonnes/year of the 2,6-TDI isomer was surprising. Unfortunately, the subdivided data into functions and/or branches cannot be shared because of the low number of companies having registered this monomer.

Insight can only be provided when considering all TDIs together. This indicates that about 55-60% of the volume (about 4,000 of 7,000 tonnes/year) is used in paints, lacquers, and similar surface treatment products, inks and fillers/sealants. The remaining TDI amount cannot be further subdivided due to confidentiality.

Comparing the amount of about 4,000 tonnes TDI/year for paints, lacquers etc. with other evidence, doubt is cast on the figure. The IAL figures for the entire Nordic market (although not accounting for import of mixtures) indicate TDI consumption for non-PUR products of about 1,000 tonnes/year. Furthermore, the estimate from the Danish Plastics Federation that about 6,000 tonnes TDI/year is used for flexible PUR production cannot be accommodated given the above. In conclusion, it appears highly unlikely that the correct branch code has been assigned for these TDI registrations.

Application of MDIs
For MDI as well, little insight can be provided due to confidentiality. What can be extracted is that about 50% of the 4,4'-MDI amount and about 80% of the 2,4'-MDI may be associated with PUR production. The data do not allow splitting this amount into what likely goes toward rigid PUR and flexible PUR.

Concentration ranges
As the project has not been provided with original data entries, but rather with aggregated registration data (often indicating very wide ranges, e.g. 0.1-32% and 12-77%), and for confidentiality reasons, no exact data about the concentration in products can be provided.

Information from Danish trade organisations
The PUR section of the Danish Plastics Federation has provided an overview on the main producers of PUR products in Denmark:
- Rigid PUR: 9 companies;
- Flexible PUR: 2 companies, and
- PUR elastomer: 3 companies.

It was noted in a previous section that:
- about 5,200 tonnes MDI/year are used for rigid PUR – isocyanates constituting about 65% of the PUR product mass, and
- about 6,000 tonnes TDI/year and 600-700 tonnes MDI/year are used for flexible PUR and elastomers – isocyanates constituting about 30% of the PUR product mass.

To the knowledge of the Danish Plastics Federation, no board production using MDI-binders is taking place in Denmark.

As follow up to dialogue with the Danish Coatings and Adhesives Association, four Danish importers/producers of coatings, adhesives and sealants[14] were interviewed and asked to fill in the table presented in Appendix 2. Although this survey cannot be considered fully representative, it provides a reasonable indication of types of coatings, adhesives and sealants on the Danish marked:

Coatings/paints:

- Heavy duty one component paints for cements floors and the like, 10-30 % (w/w) MDI, professional use, applied with brush or roller;
- Two-component coating systems for applications on concrete and metal, 25-50% (w/w) MDI in the hardener, professional use, applied with spatula, and
- Protective paints for civil infrastructures and wind mills, 0-0.02 % (w/w) TDI and 2 - 3.5 % (w/w) MDI, professional use, spray/brush.

Adhesives/sealants:

- One component foam sealants (general applications), 10-25% (w/w) MDI, mainly professional use, but also consumer use, aerosol cans;
- Two component foam sealants (panel bonding, windmill adhesive), >90% (w/w) MDI in hardener, professional use, putty knife/spraying;
- One component moisture stable adhesives, 40-60% MDI (w/w), professional and consumer use, pouring;
- Joint sealants, < 0.1% (w/w) MDI, professional use, cartridge application;
- Joint sealants, 0,01-0,6% (w/w) MDI and 0,01-0,04 % (w/w) TDI, professional/industrial and consumer use, cartridge/spatula, and
- Yacht wood sealer, 0.5 % (w/w) TDI, professional and consumer use, brush.

It can be seen that adhesives/sealants (even in aerosol cans) are expected to be available to the consumer. Coatings/paints are generally not expected to be available to the consumer, although as revealed via correspondence with the branch and as also pointed out in e.g. US EPA (2011a, 2011b), it cannot be excluded that consumers can get access to MDI and TDI products not intended for consumer use via the Internet or in DIY markets.

It is also noted that joint sealants and yacht wood sealers that are directly available to consumers contain TDI. TDI, although considerably more volatile and toxic via inhalation than MDI, is not subject to an EU restriction for consumers as the one in place for MDI (see Chapter 2).

Based on this survey and contact with The Danish Coatings and Adhesives Association, it appears that all MDI/TDI based adhesives and sealants are imported, whereas some coatings/paints are produced in Denmark and some are imported.

Appendix 2 gives some indications of total amount of MDIs and TDIs for such products, but given the number of companies interviewed and data gaps in the tables, it is not possible to provide a good indication of total MDI and TDI amounts used for coatings, adhesives and sealant based on this survey.

Finally, it is noted that in Danish EPA consumer product projects, TDI was found analytically in textile paints (Danish EPA, 2005c) and spray paints (Danish EPA, 2004a), and MDI was found in sealants (Danish EPA, 2004b).

PUR consumer products on the Danish market

The main consumer exposure is assumed to be related to application of the above discussed coatings, adhesives and sealants containing free MDI/TDI monomers.

[14] These four companies prefer to remain anonymous.

As discussed in Section 1.4, some ambiguity exists as to the presence and concentration of MDI/TDI in PUR-based products or products in which PUR has been used to coat or glue together other components. Thus, consumers might be exposed to MDI/TDI as residual monomers or degradation products during use of such products. It has not been possible to quantify the number/volume of such products on the Danish market. However, based on information obtained in other parts of this project, including the EU MDI risk assessment (EU, 2005) and the Danish EPA projects reviewed as part of Section 1.4, a non-exhaustive list showing the widespread use of PUR-products is compiled:

- Foam in automotive seats
- Foam in mattresses
- Foam in furniture
- Mats
- Textile fibres; e.g. used for swimsuits and underwear
- Textile coating
- Zipper straps
- Mittens/gloves
- Artificial leather
- Protective cloths for work place protection
- Shoes/shoe soles
- Ski booths
- Roller skate booths
- Cable sheathing
- Hoses
- Foamed facecloths
- Carpet backing
- Foam for packaging
- Food contact materials (laminates)
- Conveyor belts (also for food)
- Tents
- Briefcases
- Security glass.

3.3 Historical trends in use

As described in previous sections, the use of isocyanates is steadily increasing for the global market, where polyurethane consumption has increased from about 1 million tonnes/year in 1970 to about 14 million tonnes/year in 2012. Data from Eurostat and IAL consultants indicate that an increasing trend is also taking place in EU and the Nordic market, where IAL consultants forecast a yearly growth of about 2% from 2011 to 2016.

For the Danish situation, the figures are uncertain. The PUR section of Danish Plastics Federation estimates that use of MDI and TDI for the production of flexible PUR and elastomers is rather stable, whereas production of rigid PUR products has decreased because production of PUR for cooling applications has largely moved to countries with lower production costs. However, in line with the general global and EU trend, it must be assumed that the consumption of PUR based products is increasing. No trend data for the use of MDI and TDI in coatings, adhesives and sealants in Denmark have been identified.

3.4 Summary

Manufacture
MDI and TDI are manufactured on a large scale in a few EU facilities not located in Denmark.

Overall volumes and trends

Volume-wise, MDI and TDI account for about 95% of the use of isocyanates with an estimated:

- EU consumption of about 1.5 million tonnes/year;
- Nordic market consumption of about 67,000 tonnes/year, and
- Danish consumption of about 9,000 – 14,000 tonnes/year.

As shown in Section 3.3, the global, EU and Nordic consumption is steadily increasing. A similar trend is expected for Denmark.

The Danish volume is indicated as a range because of variations in estimates from different sources. On the other hand, all sources (Statistics Denmark, the Danish Product Registry and Danish trade associations/branches) fall within the range indicated.

Applications and split between MDIs and TDIs

Main applications of TDIs and MDIs are:

- Flexible PUR (e.g. for furniture upholstery and mattresses) (largely TDI-based, but about 10% MDI), and
- Rigid PUR (e.g. for insulation, district heating tubes, refrigeration, construction) (purely polymeric MDI-based).

"C.A.S.E.":

- **C**oatings (surface treatment such as paints and lacquers) (Nordic data indicate that about 70% of these are MDI-based, the rest TDI-based);
- **A**dhesives (Nordic data indicate that about 80% of these are MDI-based, the rest TDI-based);
- **S**ealants (e.g. fillers/joint fillers/foam sealants) (largely MDI-based), and
- **E**lastomers (e.g. rubber and thermoplastic elastomers) (almost purely MDI-based).

In addition:

- Binders (used for binding particles together mainly for chipboards) (purely MDI based).

Flexible and rigid PUR, as well as elastomers (E) are typically supplied as already cured products, whereas for coatings (C), adhesives (A), sealants (S) and binders, the curing itself forms part of the functionality of the products during/after use.

In the EU and Nordic market, 80% and 83%, respectively, of TDI and MDI consumption for production are applied for PUR production (rigid, flexible and elastomer). Binders for the production of chipboards account for 10% of the EU market and 11% of the Nordic market. This leaves about 10% (EU) and 6% (Nordic) for production of coatings, adhesives and sealants.

Please note that these figures represent the MDI and TDI 'consumption for production' and not the consumption of PUR products or consumption of products containing MDI/TDI (such as coatings, adhesives and sealants), as the latter are affected by import/export.

For the Danish market, it has not been possible to obtain precise data on the distribution of the MDI/TDI volumes among the main application groups. However, it is assumed that the majority of MDI and TDI are used for PUR production; the Danish Plastics Federation estimates that about 6,000 tonnes TDI/year and 6,000 tonnes MDI/year are used for production of flexible, rigid and elastomeric products. The Danish Plastics Federation notes that Danish production of rigid PUR has decreased in recent years, leaving a relatively high production of flexible PUR, which is largely TDI-based.

To our knowledge no board production using MDI binders is taken place in Denmark.

Although no exact data have been found, but considering data collected for EU and the Nordic market, it is estimated that about 10% overall of the Danish MDI and TDI volume is accounted for in coatings, adhesives and sealants, corresponding to approx. 1000 tonnes/year. However, it should be stressed that this is an estimate made with a high level of uncertainty.

Adhesives and sealants are supplied to consumers, including MDI in aerosol cans and products containing TDI (e.g. joint sealants and yacht wood sealers). It should be noted that no EU consumer restriction is in place for TDI-based products similar to the one applicable for MDI-based products. Finally, it is also speculated whether it is possible for consumers to get access to more professional grades of products, such as e.g. coatings and paints.

A range of PUR-based consumer products are available on the Danish market. As discussed in Section 1.4, ambiguity exists as to the possible content of residual MDI/TDI monomers and/or degradation products.

Production in Denmark

Dialogue with Danish trade organisations has provided the following figures for Danish productions facilities using MDI and TDI:

- Rigid PUR production: 9 companies;
- Flexible PUR production: 2 companies;
- PUR elastmer production: 3 companies;
- Coatings/paints: A few companies;
- Adhesives/Sealants: None, and
- Chipboards using MDI based binders: None (assumed).

Terminology

Whereas TDI seems to be used mainly in its monomeric form(s), MDIs are supplied in range of forms and unfortunately, the associated terminology applied among various actors is not always straightforward. This creates some ambiguity, which was already discussed in Chapter 1.

ISOPA has clarified that oligomeric (the crude reaction product) and monomeric MDIs have been registered (see Table 9), whereas polymeric MDIs have not been registered (they are considered polymers). However, "polymeric" seems to be a term used with different meanings by different stakeholders.

Modified/Prepolymer MDIs are obtained via further reaction of monomeric or polymeric MDIs and some of these have been registered (see Table 10).

In general, care should be taken when interpreting MDI statistics, as there seems to be significant ambiguity in use of terminology.

Which CAS-numbers are used?

In addition to the terminology ambiguity, it is not always straightforward what a given MDI/TDI CAS-number refers to. As outlined, the "scientific" CAS-number 26447-40-5 for mixed MDIs is because of REACH rules not registered, but for technical reasons these are implicitly included under the pure isomer MDI CAS-numbers as well as under a new EC-number (see Chapter 1). As indicated in other places in this report, this CAS-number (26447-40-5) was used by the EU 2005 MDI risk assessment, and in that report it was assumed to cover all MDIs (including the pure monomers). The non-registration of this CAS-number causes some confusion.

Further, it may sometimes appear that CAS-numbers are randomly chosen. For example, data from the Danish Product Registry show that an amount of about 1000 tonnes 2,6-TDI is used annually in Denmark. This appears to be misreporting, considering that 2,6-TDI has not been registered under REACH and is a monomer, which is technically very difficult to isolate.

3.5 Conclusions

- TDIs and MDIs are used in large and increasing amounts; about 1.5 million tonnes/year in EU and 9 000-14 000 tonnes/year in Denmark.
- About 80-90% of the volume is used for PUR production (flexible, rigid and elastomers) at relatively few facilities, where it must be assumed that exposure can be systemically and continuously controlled.
- A minor amount in terms of share (estimated at approx. 10%), but still significant in terms of tonnage (EU: Approx. 150 000 tonnes/year; Denmark: Approx. 1000 tonnes/year), is used in adhesives, coatings and sealants. In particular the estimate for the Danish situation is uncertain. However, use of these products is widespread among professionals and consumers and must therefore be assumed to have the potential to be less controlled than production of PUR products.
- MDI and TDI containing adhesives and sealants are also supplied to consumers, whereby an EU restriction (warnings and provisions of gloves) applies for monomeric MDI, but the same restriction is not explicit for polymeric and modified/prepolymeric MDIs, nor for TDI. MDI containing aerosol cans and TDI-based adhesives/sealants are supplied to consumers.
- It is speculated that consumers might get access to MDI- and TDI-based products (e.g. coatings/paints) intended for professional use only.
- Oligomeric (crude reaction product) and Monomeric MDIs have been registered under REACH. Polymeric MDIs have not been registered, whereas modified/prepolymer MDIs, considered "no longer polymers", have been registered under various CAS-numbers.
- There is ambiguity about the use of CAS-numbers for monomers, mixes of monomers and the terminology related to polymeric MDI, modified/prepolymer MDI etc. Therefore, there seems to be a need to oversee this issue in relation to possible further investigations and to possible recasting existing or drafting new guidance and legislation, a finding also supported by observations in Chapters 1 and 2.
- Overall, no detailed overview exists of the use of MDI/TDI-containing coatings, adhesives and sealants on the Danish market and in particular the accessibility for consumers (e.g. via the Internet) to these products, including those originally intended for professional use.

4. Waste management

This chapter will address:

1. Waste containing free MDI and TDI monomers, possibly originating from:
- Production of PUR products (residual starting MDI and TDI monomers);
- Production of coatings, adhesives, sealants and paints, and/or
- Industrial, professional and consumer use of coatings/paints, adhesives and sealants.

2. Disposal of PUR waste, which originates from:
- PUR production, and
- PUR products (also addressing disposal of contained blowing agents).

It is judged that MDI and TDI will not be present in end-of-life building parts (paints, sealants or PUR insulation) in significant amounts, as it must be foreseen that a possible content of uncured MDI and TDI would largely have reacted because of high reactivity.

4.1 Waste from manufacture of MDI and TDI

There is no manufacture of MDI and TDI in Denmark and therefore no associated waste streams.

4.2 Waste containing MDI and TDI monomers

4.2.1 Disposal of MDI and TDI containing waste from production of flexible and rigid PUR and elastomers

Logstor A/S (2013) and Gram Commercial A/S (2013) have advised that there is no disposal of isocyanates raw materials from production. The chemicals are delivered in tank lorries and pumped into the storage tanks in the factories. Stability is guaranteed for 6 months but can be stored for 1 year with no problem (Logstor A/S, 2013).

It is judged that the same is valid for other factories producing rigid and flexible PUR products and elastomers, and therefore, based on these statements, no waste containing free MDI and TDI monomers is expected from PUR production.

However, Logstor A/S has advised that from trials in research and development, there may be a few drums with MDI residues. These are sent to Nord (former Kommunekemi) as hazardous waste.

4.2.2 Disposal of MDI and TDI containing waste from production and professional use of coatings, adhesives and sealants

As outlined in Chapter 3, there are a limited number of Danish facilities producing MDI- and TDI-containing coating/paints, but seemingly no Danish facilities producing adhesives and sealants. The coating/paint companies interviewed (see Appendix 2) indicate that MDI and TDI-containing production waste is disposed of as hazardous waste “Isocyanate”. It must be assumed that this waste is disposed of under legally required controlled collection conditions (waste code: 08 05 01 waste isocyanates, see Chapter 2).

Waste (e.g. unused products and waste packaging) from professional and industrial use of coatings, adhesives and sealants containing MDI and TDI should be disposed of as hazardous isocyanate waste. This necessity is confirmed by the recommendations given in Safety Data Sheets (SDSs) by interviewed Danish suppliers of these products (SDS wording reproduced in table in appendix 2). Some of these specifically indicate the EAK: 08 05

01 code, whereas this must be implicitly inferred for the wording related to other products. However, for a sealant supplied in aerosol cans the EAK: 16 05 04 ("gases in pressure containers (including halons) containing dangerous substances") is rightly recommended to the users of such products.

No data have been identified in relation to the extent to which professional and industrial users of these products are actually disposing of waste according to these guidelines.

The Danish EPA has provided extracts for EAK code 08 05 01 for 2012 " Waste from production, formulation, distribution and use of paint, lacquer and ceramic enamel, adhesives, sealants and print colours (isocyanate waste)". From these statistics, the following volumes and methods of disposal can be extracted:

- Incineration 99 % (224 tonnes)
- Recycling < 1% (1.3 tonnes).

Typically, organic substances will degrade at temperatures higher than 600°C, because the thermal energy at this temperature is so high that the covalent chemical bonds will be broken. The incineration temperature for Danish incineration plants is typically 850° C, far higher than 600 °C. Thus, isocyanates will degrade during incineration.

4.2.3 Disposal of MDI and TDI containing waste from consumer use of coatings, adhesives and sealants

No statistics/information on consumer disposal of MDI and TDI based coatings, adhesives and sealants have been identified. One would hope that most MDI and TDI containing consumer products are correctly delivered to the recycling stations as dangerous chemicals, which would then undergo controlled disposal. However, it is judged that minor items may end up in household waste (e.g. glue residues in small tubes, repair coating residues in small containers) and larger items may end up in the fraction "small combustible waste" at the recycling stations (e.g. sealant residues in sealant PE tubes/containers). PE sealant tubes/containers may also end up in the plastics fraction.

Given that this type of waste is disposed of within packaging, it is in any case judged that consumer as well as waste handler exposure to MDI and TDI monomers would be low.

4.3 PUR waste from production and use of PUR products

As set out in Chapter 3, the largest amount of MDI and TDI is used for production of thermoset PUR (flexible and rigid) in construction (insulating panels, doors), flexible furniture foams, as sandwich insulating foamed layers for refrigerators, freezers, isolating district heating pipes, etc.

In these products, MDI and TDI monomers are reacted to form polyurethanes (see Section 1.2).

For a number of years, PUR foam has been blown by cyclopentane or by reaction of an excess of the diisocyanates, which in the presence of a small amount of water produces CO_2 gas. Formerly, the foam was blown with Freon and later with HCFCs, still constituting an issue in relation to disposal of older products.

At the first reference group meeting of the project, it was agreed to use the Danish EPA report "Mapping of waste products with content of polyurethanes" (Danish EPA, 2005a), which was considered to give a good background. This section is therefore largely based on that report, supplemented with recent knowledge obtained from contact with trade organisations and companies.

4.3.1 Summary of the 2005 Danish PUR waste project

This section will provide a brief summary of the Danish EPA PUR waste project (Danish EPA, 2005a). The project focussed on:

- A description of valid legal rules in Denmark and within the EU;
- A description of expected new legal rules in Denmark and within the EU;

- Mapping of production waste from the manufacturing of products based on PUR or containing PUR in Denmark;
- Mapping of end-of-life products based on PUR alone or with content of PUR in Denmark;
- Estimate of the costs for Danish enterprises when handling PUR-based waste, and
- Mapping of existing utilization and recycling technologies for production waste and end-of- life products based on PUR or containing PUR.

In total, 12 companies were interviewed in the mapping exercise, corresponding to nearly 70% of the annual consumption of PUR raw materials. The production waste corresponds to 15% of the PUR volume and the production waste from the producers of flexible PUR foam is high (23%) due to the cutting process. For district heating pipes, the production waste was only 5%.

The total annual Danish PUR production was estimated at 43,000 tonnes/year; flexible foam accounted for 22,200 tonnes, district heating pipes and producers of freezers both accounted for 6,500 tonnes and other uses for 7,800 tonnes.

The amount of annual waste from freezers was estimated at 782 tonnes in 2003, for district heating it was estimated at 1,250 tonnes in 2012 and from cars at 3,500 tonnes in 2004. Textiles and furniture account for approx. 1% in the fraction of "small combustible waste" and from <0.1% to 15% in samples from "large combustible waste".

It is stated that the amount of flexible PUR foam which ends up in the waste is difficult to estimate from the statistical data available, but it is foreseen that the amount would be high.

Different recycling technologies are described in the Danish EPA report. At a European level, rebounded flexible foam is estimated at 120,000 tonnes/year and energy recovery in incineration plants is estimated at 110,000 tonnes/year. Other recycling methods comprise use of granulates from flexible foam (e.g. for carpet backing), glue pressing of rigid foam, use of granulate from rigid foam as oil spill absorber and for mortar, use of powder made from rigid or flexible PUR in new PUR products as additive in an amount of 10 – 15 %, and compression injection moulding of elastomer integral foam.

4.3.2 General changes in PUR amounts since 2005

PUR Production

In table 5 in Danish EPA (2005a), the total amount of rigid PUR is estimated at 17,400 tons PUR/year, corresponding to 11,310 tons MDI/year.

As the amount used for insulated pipes according to Logstor A/S is unchanged, the amount of MDI for this application is assumed to be unchanged, at approx. 4,225 tons MDI/year.

As the Danish Plastics Federation estimates that the estimated MDI volume for production of rigid PUR in Denmark today is 5,200 tons /year (see Chapter 3), the amount used for cooling applications must be assumed to be reduced to about 975 tons/year from 7,085 tons/year. If this is a correct assumption, which we believe, the amount for production of rigid PUR for cooling applications has been reduced to less than 15% since 2005.

For flexible PUR, the production is considered approximately equal to 2005 (see Chapter 3) and therefore, the amount of PUR production waste may be considered approximately the same.

PUR products

Given the generally increasing global and EU trend in use of polyurethane, it must be assumed that for the Danish situation as well, the consumption and thereby waste from flexible and rigid PUR products is increasing. This might be partly reversed through longer service-life of the products because of increased quality (Logstor A/S, for example, notes that insulating pipes are of a higher quality today than in 2005).

As the PUR foam for cooling applications currently uses pentane as blowing agent, it must be foreseen that the CFC and HCFC foamed PUR originating from refrigerators and freezers would be reduced compared to 2005 and will keep on declining in the coming years.

It is considered unlikely that significant amounts of free diisocyanates (MDI and TDI) are present in PUR products at end-of-life due to the high reactivity of the diisocyanates and the fact that depolymerisation of PUR generally demands high temperatures (> 200 °C or fire), see also Section 1.4.

4.3.3 Status on present treatment of PUR waste in Denmark

WEEE cooling furnitures

Product waste

Disposal of PUR from refrigerators and freezers is at present regulated by the EU directive 2012/19/EU. The directive demands that all PUR containing CFCs, HCFCs and pentane as blowing agents from WEEE waste has to be processed so the blowing agent does not escape to the environment.

Producer responsibility (WEEE) for refrigerators and freezers indicates that the producers must:

i) co-finance the collection and waste treatment of end-of-life freezers;
ii) make product declarations with information on treatment;
iii) in the design phase make waste treatment easier, and
iv) promote recovery of end-of-life freezers.

At the site of the H.J. Hansen's recycling company in Odense, discarded refrigerators and freezers etc. are recycled. The PUR foam is blown into Fynsvaerket for thermal recovery. In this process, CFCs and other blowing agents are destroyed so they will not harm the environment. The same will be the case for PUR and possible residual isocyanates, which will also be completely destroyed by controlled high temperature incineration. Typically, non-halogenated organic substances will degrade at temperatures higher than 600°C because the thermal energy at this temperature is so high that the covalent chemical bonds will be broken. The incineration temperature for Danish incineration plants is typically 850° C, far higher than 600 °C.

H.J. Hansen, one of the biggest recyclers in Denmark of end-of-life refrigerators and freezers, informed the project that the company treats about 18,000 tons PUR from refrigerators and freezers, and that about 65–70 % contain CFCs or HCFCs (H.J. Hansen, 2013). The use of these blowing agents was terminated in the beginning of the 2000s.

The treatment is separation of the PUR foam, which is then incinerated for energy recovery. The PUR foam from the new generation of refrigerators and freezers (cyclopentane-blown) is treated in the same way.

The present requirements for waste recovery from WEEE cooling furniture is 75%, plus 5% for energy recovery. In 2015 the requirements will be 80% and 5% respectively for energy recovery. These figures relate to the entire cooling furniture of which PUR typically accounts for about 15%. H.J. Hansen at present recycles 82 % (mainly metal and the compressor unit) without taking into account the PUR energy recovery.

FEHA (2013) has advised that in 2012 the amount of cooling furniture sold to consumers in Denmark was in total 261,010 units, distributed as:

- Refrigerators: 94,072;
- Freezers and refrigerators combined: 111,692;
- Upright/Cabinet freezers: 39,236 ("fryseskabe" in Danish), and
- Chest freezers: 16,010.

FEHA (2013) expects that the freezing units are discarded and end up as waste after a period of around 8 – 10 years.

Production waste
As the production of cooling furniture is assumed to have dropped to below 15 % of the amount in 2005, it is judged that the amount of production waste is small and not of real concern.

District heating PUR insulated pipes

Product waste
District heating pipes have formerly been blown with CFCs and HCFCs. The outer part of the pipe is currently made of polyethylene (PE) but PVC has formerly also been used. The old district heating pipes will still end up as waste for a number of years, as the expected service lifetime should be 50 years (Aarhus AffaldVarme, 2013).

Aarhus AffaldVarme advises at the same time that the district heating pipes produced from late 1970s to the beginning of the 1980s were of inferior quality due to poorly made outer plastic covers. Aarhus AffaldVarme replaces around 25 km of district heating pipes per year at present, but expects that this amount will increase to 35 km/year for the next 3-4 years.

Many of the out-of-service district heating pipes are left in the ground. This statement is supported by Danish EPA (2006), in which Odense Municipality estimates that only 30% of end-of-life district heating PUR insulated pipes are removed, and the remaining 70 % remain in the ground side by side with the new district heating pipes.

According to Danish EPA (2006), H.J. Hansen cuts the district heating pipes into smaller pieces before shredding. After shredding the waste is separated into plastics (PVC or HDPE), metal and PUR foam. The metal is recycled but the plastic and PUR is deposited to landfill. Other waste companies in Denmark also shred the district heating pipes; they also recycle the metal and either incinerate the plastic and PUR or deposit it to landfill (Danish EPA, 2006). The only law regulating the handling of end-of-life district heating pipes is the circular regarding municipality regulations for waste suitable for incineration of June 21, 1995 (Cirkulære om kommunale regulativer om forbrændingsegnet affald af 21. juni 1995). In this circular it is banned to landfill waste which can be incinerated.

The waste treatment/management is therefore the responsibility of the customers, e.g. municipalities.

Production waste
Only PMDI is used for the production of pre-insulated pipes. The amount of PMDI for production corresponds well with the amount reported in Danish EPA (2005a) of 6,500 t for 2012. The amount of internal production waste has dropped to 3%. The internal production waste is still recycled by the glycolysis process established in 1998. The formed recycling polyol is used for new foamed PUR in the factory. All recycled PUR is used for new PUR, so the recovery in the process is 100 %. The polyethylene waste in the factory is recycled by the company Vestergaard Larsen, which granulates and adjusts the additives.

For district heating pipes at present, only cyclo-pentane is used for blowing the foam, but for the oil/gas sector, CO_2 blown systems are used as high densities are needed for these applications. However, liquid CO_2 is not used.

Building Waste
PUR containing end-of-life building waste is either incinerated or deposited to landfill depending on which type of material it is laminated to (Danish EPA, 2006). If laminated to a material which benefits energy recovery, it is incinerated, or otherwise deposited to landfill.

Flexible PUR

Product waste
It is judged that flexible PUR products are either collected at the recycling stations, companies and institutions or from the household waste streams. The products are ultimately incinerated with energy recovery. End-of-life vehicles are shredded, e.g. at the site of H.J. Hansen in Odense. The shredding waste fraction is focus in the recently updated Danish national implementation plan for the Stockholm Convention, among others because PUR foam in older cars may contain the brominated flame retardant PentaDBE (Pentabromodiphenyl ether) (Danish EPA, 2013). The implementation plan states that PUR foam from shredding will end up in the light fraction and by-and-large be disposed of by landfill. Further, the plan conservatively estimates that the average concentration of pentaBDE in this waste fraction is 6 mg/kg for Danish conditions (compared to an estimated average EU concentration of 70 mg/kg). On the other hand, as the Danish car park is relatively old, it is assumed that pentaBDE will remain longer in this waste fraction in Denmark than in the EU, where it is estimated that pentaBDE containing vehicles will have been disposed of by 2016.

Production waste
Information from one company confirms that the amount of flexible foam production is at the same level as in the 2005 report. The amount of internal production waste is also unchanged (on the order of 23%). The internal production waste is exported to the United States for recycling as carpet backing on a cost-neutral basis. The company has made efforts to reduce the amount of TDI by using MDI or prepolymeric isocyanates. Around 50% of the products are exported in the form of mattresses and pillows. The foam system uses liquid CO_2 as the blowing source for the process in addition to CO2 formed by hydrolysis of TDI/MDI by water.

Elastomeric solid PUR

Production waste
Elastomeric solid PUR TPEs (thermoplastic elastomers) can be reused by melting as they are not cross-linked. To what extend this occurs is not known, but the amounts must be low as little production takes places in Denmark.

Example of recycling of internal PUR production waste and external rubber waste
For PUR-based cross-linked elastomeric rubbers, recycling by melting is not possible due to the cross-linking, but the rubber can be granulated. Some years ago, Danish Technological Institute carried out a project whereby PUR waste was crushed and mixed with rubber powder from used tyres (GENAN DK) to produce materials with noise and vibration damping properties.

Consumer PUR product waste (other than cooling furniture)
Recycling of PUR products from consumers' waste is foreseen to be difficult as the diverse group of PUR products would have to be sorted from the mixed plastic waste streams. Another problem is that PUR is often glued or laminated to other materials (plastics, metals etc.), which makes recycling a challenge. In general, consumer PUR products are therefore assumed to be incinerated.

Further information on PUR recycling
A highly detailed description of the different recycling technologies for PUR products is given by Rasshofer (1994). More recent literature on PUR waste and recycling technologies is found in Saechtling (2007). The descriptions of PUR recycling in the two cited books provide further information on recycling possibilities, but not with regard to the economy of recycling post-consumer and end-of-life PUR waste. To our knowledge, recycling of end-of-life PUR products in Denmark does not take place.

4.4 Presence and release of MDI and TDI and degradation products from waste disposal

As discussed in Section 1.4, MDI and TDI monomers (as residual monomers or from degradation) may be present in PUR products, as may amines, as degradation products. Given the discussion in Section 1.4, there is no consensus in relation to whether these substances may be present in PUR products in significant amounts as their reactivity with other substances and the environment is swift. Given the high reactivity of MDI/TDI, possible presence of such monomers must be assumed to be further lowered when products reach the waste stage.

No references addressing possible problems with free monomers or amine degradation products in the waste stage have been identified within the scope of this project.

As set out in Section 1.4, clarification/consensus on this issue is considered a data gap.

4.5 Summary and conclusions

Waste from manufacture of MDI and TDI
There is no manufacturing in Denmark of MDI and TDI and, therefore, no production waste.

Waste fraction containing free MDI and TDI monomers
According to interviews with a number of producers, there is no MDI and TDI waste from the production of rigid and flexible PUR. From trials in research and development, small amounts of MDI/TDI might end up as waste. This is send to Nord (former Kommunekemi).

From production and professional use of coatings, adhesives and sealants, interviews with coating/paint companies indicate that the waste is disposed of as hazardous waste “Isocyanate”, waste code :08 05 01. From the Danish EPA waste statistics, data regarding waste code 08 05 01 has been extracted for 2012. According to this extract, 244 tonnes (99%) are incinerated and less than 1 % recycled. Isocyanates will degrade completely during combustion.

Waste from use of coatings, adhesives and sealants by consumers should ideally be collected as hazardous waste, but may end up in household waste or in various fractions at the recycling stations. It is assumed that it is minor items and that they will go to incineration, where the isocyantes will be degraded.

PUR production waste amounts and treatments
Recycling of production waste from the production of district heating insulated pipes (rigid PUR) is done by glycolysis (100 % recovery as new regenerated polyol for production). The Danish producer of such pipes in Denmark confirms that the amount of PMDI used for production is unchanged (2012) from the amount in Danish EPA (2005a): 6,500 tonnes, but the amount of internal waste has decreased to 3%, which is recycled in the above mentioned glycolysis process.

Production waste of flexible PUR products is used for new applications after milling (carpet backing), according to information provided by producers. This is an important recycling process for flexible PUR as there is a high amount of production waste (23 %) in the cutting process.

Recycling possibilities for flexible PUR are continuously improved, requiring higher demands regarding the purity of the raw materials. The amount of production of flexible foam products in Denmark is judged to be unchanged from the amount in Danish EPA (2005a): 22,200 tonnes.

Product waste amounts and treatments
Waste treatment is strictly regulated by Danish law as well as at the European level with regard to PUR WEEE. The PUR waste from end-of-life cooling furniture is not recycled, but rather incinerated with energy recovery, thereby also removing previous (CFCs, HCFCs) and current (cyclo-pentane) blowing agents. End-of-life PUR products from other sources (cars, furniture, building insulating foams, etc.) is, to our knowledge, incinerated

with energy recovery or deposited to landfill; it is not recycled. One issue with PUR, which makes recycling difficult is that PUR is often laminated to other materials (e.g. in sandwich panels), thus complicating separation. The amount of PUR products which end up in the waste stream is unknown, except for cooling furniture (H.J. Hansen treats about 18,000 tonnes of PUR from this source annually).

Incineration

Isocyanates and polyurethanes will degrade completely during incineration at municipality waste incineration plants.

5. Environmental effects and exposure

As outlined in Chapter 2, MDI and TDI are subject to substance evaluations under REACH. The (draft) TDI substance evaluation has been finalised and a report is available. The MDI substance evaluation is ongoing. It is still uncertain whether these substance evaluations will be made publicly available or remain confidential. As also outlined in Chapter 2, some confidential investigations regarding possible additional EU risk management activities are ongoing. The latter summarises what is known about exposure to isocyanates, building on the confidential parts of REACH registrations as well as other sources.

The Danish EPA has access to REACH substance evaluations and EU risk management activities and reports, and will thus have direct access to agreed-upon evaluations of hazards, as well as the most recent exposure information at EU level.

As a consequence, this chapter will not make a detailed hazard investigation nor a detailed summary of EU exposure data.

5.1 Environmental hazard

5.1.1 Classification

As outlined in Chapter 2, MDI and TDI are subject to harmonised classification. The harmonised classification for environmental endpoints is reproduced in Table 18, showing that MDI has not been classified, whereas TDI is classified for environmental effects as H412: Harmful to aquatic life with long lasting effects.

TABLE 18
HARMONISED CLASSIFICATION FOR ENVIRONMENTAL EFFECTS OF MDI AND TDI ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION)

Index No	International Chemical Identification	CAS No	Classification	
			Hazard Class and Category Code(s)	Hazard statement Code(s)
615-005-00-9	2,2'-methylenediphenyl diisocyanate (2,2'-MDI)	2536-05-2	NA	NA
615-005-00-9	o-(p-isocyanatobenzyl)phenyl isocyanate (2,4'-MDI)	5873-54-1	NA	NA
615-005-00-9	4,4'-methylenediphenyl diisocyanate (4,4'-MDI)	101-68-8	NA	NA
615-005-00-9	Methylenediphenyl diisocyanate (mix of MDI isomers)	26447-40-5	NA	NA

Index No	International Chemical Identification	CAS No	Classification	
			Hazard Class and Category Code(s)	Hazard statement Code(s)
615-006-00-4	4-methyl-m-phenylene diisocyanate (2,4-TDI)	584-84-9	Aquatic Chronic 3	H412
615-006-00-4	2-methyl-m-phenylene diisocyanate (2,6-TDI)	91-08-7	Aquatic Chronic 3	H412
615-006-00-4	m-tolylidene diisocyanate (mix of TDI isomers)	26471-62-5	Aquatic Chronic 3	H412

5.1.2 Hazards assessment

The EU MDI risk assessment (EU, 2005) points out the difficulty of testing MDI because interfering solvents are needed as MDI reacts readily with water. Despite this, a range of tests, typically indicating that LC/EC values are above a higher limit are available, indicating low inherent toxicity to environment species.

The Canadian TDI Screening assessment (Health and Environment Canada, 2008) notes that it is unlikely that TDI will cause toxicity because of its expected transient appearance in the environment. A number of ecotoxicological studies for TDI and its degradation products indicate low to moderate toxicity to water flea, fish, shrimp and algae (LC_{50}> 1 mg/l) and low toxicity towards terrestrial biota (NOECs, EC_{50} and LC_{50} > 100 mg/l) and birds (LC_{50} > 100 mg/l).

5.2 Environmental fate

When released to water, the NCO groups of MDI and TDI react readily with the OH groups of water to form *inter alia* amines, which will readily react with more MDI/TDI to generate inert urea (EU, 2005; Health and Environment Canada, 2008).

In air, MDI and TDI undergo photocatalytic degradation with estimated half-lives of 1.33 for MDI (EU, 2005) and 1.4-1.7 (measured and estimated) for TDI (Health and Environment Canada, 2008).

Health and Environment Canada (2008) concludes that TDI is not meeting the Canadian criteria for P (persistence criteria: half-life air > 2 days, half-life in soil and waste > 265 days) or B (criterion BCF, BAF > 5000).

One of the triggers for EU substance evaluations of TDI and MDI was the possible PBT properties associated with MDI and TDI degradation products following hydrolysis (amines). The currently confidential conclusions from these evaluations are, or will be, available to the Danish EPA.

The environmental fate of PUR/PUR-products is not addressed in any detail in available authoritative assessments of MDI and TDI. However, please refer to Section 1.4 regarding PUR degradation mechanisms.

5.3 Environmental exposure

5.3.1 Sources of release

There is no MDI/TDI production in Denmark; therefore, releases to the Danish environment may occur in the following situations:

- During production of flexible and rigid PUR products, although emissions are considered low given the tight control of MDI and TDI in these facilities;
- During production of PUR coatings/paints in a few facilities in Denmark;
- During industrial/professional/consumer use of coatings, adhesives and sealants, and

- Release from waste/waste treatment related to the above activities. See Chapter 4 for more details. Waste should be collected as hazardous waste, which is predominantly incinerated; thus, consumer products in particular might end up elsewhere in the waste streams.

No emission data for the Danish situation have been identified.

5.3.2 Monitoring data

No biomonitoring data for MDI/TDI have been encountered, which is logical given the reactivity of MDI/TDI with water. Furthermore, no biomonitoring data of amine degradation products have been identified within the project.

The Canadian TDI Screening assessment (Health and Environment Canada, 2008) states the following: "Measured concentrations of toluene diisocyanate in environmental media and dietary sources in Canada were not located."

5.4 Environmental impact

The 2005 MDI EU risk assessment (EU, 2005) concludes that all risk characterisation ratios for MDI and the primary aromatic amine degradation product (MDA) are well below 1, indicating that MDI does not seem to cause any risk to the environment.

The Canadian TDI Screening assessment (Health and Environment Canada, 2008) concludes the following: "Based on the available information, it is concluded that TDI is not entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity, or that constitute or may constitute a danger to the environment on which life depends."

In a recent study supporting the Dutch authorities in relation to possible further risk management for isocyanates, RPS (2012) likewise concludes that for MDI and TDI, no risks for the environment are expected.

5.5 Summary and conclusions

Based on existing risk assessments from authoritative bodies, MDI and TDI do not seem to constitute any risk to the environment, although TDI is classified as harmful for the environment.

Ongoing REACH substance evaluations re-examine this issue, including possible PBT properties of MDI and TDI hydrolysis products (amines).

The Danish EPA has access to the confidential substance evaluations and can use the outcomes to evaluate whether further action in relation to MDI/TDI and the environment is appropriate.

6. Human health effects

As outlined in Chapter 2, MDI and TDI are subject to substance evaluations under REACH. The (draft) TDI substance evaluation is available. The MDI substance evaluation is ongoing. It is still uncertain whether these substance evaluations will be made publicly available or remain confidential. As also outlined in Chapter 2, some confidential investigations regarding possible additional EU risk management activities are ongoing. The latter summarises what is known about exposure to isocyanates, building on the confidential parts of REACH registrations and other sources.

The Danish EPA has access to REACH substance evaluation and EU risk management activities and reports, and will thus have direct access to agreed-upon evaluations of hazards, as well as the most recent exposure information at EU level.

As a consequence, this chapter will not make a detailed hazard investigation nor a detailed summary of EU exposure data. Rather, main issues investigated will be indicated.

Focus will be on the Danish situation to the extent that data could be obtained within the framework of this project.

6.1 Human health hazard

6.1.1 Classification

Table 19 shows that that all addressed (mixes of) monomeric TDI and MDI are subject to harmonised classification. It shows that MDI isomers, and mixes thereof, have the same harmonised classification. The same applies to TDI isomers and mixes thereof. The table shows that MDI and TDI are classified as suspected of causing cancer, as dermal and respiratory sensitisers, as well as eye, skin and respiratory irritants. Classification differs in relation to acute toxicity, where MDI is harmful if inhaled, whereas TDI is fatal if inhaled; and in relation to toxicity after repeated exposure, where only MDI is classified (potential to cause damage to liver and kidney).

TABLE 19
HARMONISED HUMAN HEALTH CLASSIFICATION OF MDI AND TDI ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION)

Index No	International Chemical Identification	CAS No	Classification	
			Hazard Class and Category Code(s)	Hazard statement Code(s)
615-005-00-9	2,2'-methylenediphenyl diisocyanate (2,2'-MDI)	2536-05-2	Carc. 2 Acute Tox. 4 * STOT RE 2 * Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Resp. Sens. 1 Skin Sens. 1	H351 H332 H373** H319 H335 H315 H334 H317

Index No	International Chemical Identification	CAS No	Classification	
			Hazard Class and Category Code(s)	Hazard statement Code(s)
615-005-00-9	o-(p-isocyanatobenzyl)phenyl isocyanate (2,4'-MDI)	5873-54-1	Carc. 2 Acute Tox. 4 * STOT RE 2 * Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Resp. Sens. 1 Skin Sens. 1	H351 H332 H373** H319 H335 H315 H334 H317
615-005-00-9	4,4'-methylenediphenyl diisocyanate (4,4'-MDI)	101-68-8	Carc. 2 Acute Tox. 4 * STOT RE 2 * Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Resp. Sens. 1 Skin Sens. 1	H351 H332 H373** H319 H335 H315 H334 H317
615-005-00-9	Methylenediphenyl diiso-cyanate (mix of MDI isomers)	26447-40-5	Carc. 2 Acute Tox. 4 * STOT RE 2 * Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Resp. Sens. 1 Skin Sens. 1	H351 H332 H373** H319 H335 H315 H334 H317
615-006-00-4	4-methyl-m-phenylene diisocyanate (2,4-TDI)	584-84-9	Carc. 2 Acute Tox. 2 * Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Resp. Sens. 1 Skin Sens. 1	H351 H330 H319 H335 H315 H334 H317
615-006-00-4	2-methyl-m-phenylene diisocyanate (2,6-TDI)	91-08-7	Carc. 2 Acute Tox. 2 * Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Resp. Sens. 1 Skin Sens. 1	H351 H330 H319 H335 H315 H334 H317
615-006-00-4	m-tolylidene diisocyanate (mix of TDI isomers)	26471-62-5	Carc. 2 Acute Tox. 2 * Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Resp. Sens. 1 Skin Sens. 1	H351 H330 H319 H335 H315 H334 H317

The corresponding classification according to the dangerous substance directive (67/548/EEC):

- MDIs: Carc3; R40 Xn; R20-48/20 Xi; R36/37/38 R42/43
- TDIs: Carc3; R40 Tx; R26 Xi; R36/37/38 R42/43

6.1.2 Hazards assessment

As shown in Table 19, TDIs and MDIs are subject to agreed harmonised classifications for a range of endpoints. The properties/classification of highest concern are carcinogenicity, the sensitising properties (dermal and in particular respiratory) and for TDI, the high acute toxicity by inhalation (potentiated by the volatility of TDI having a vapour pressure about three orders of magnitude higher than MDI). Regarding possible toxicity for fertility, the EU 2005 risk assessment for MDI (EU, 2005) concludes that "*No fertility or multigenerational studies are available for MDI. Data from (sub)chronic toxicity studies did not reveal clear substance related and/or significant impairment of organs of the reproductive system of the male and female. However, the test protocols of the available (sub)chronic studies present gaps and weaknesses (e.g. not all sex organs were included and systematically examined; lack of control and historical data to put the obtained results into context). In conclusion, the studies are considered too limited to allow a determination of a NOAEL for fertility. As the current database does not adequately cover the toxicity for fertility for MDI, a conclusion (i) is reached with regard to fertility*"[15]. A possible motivation behind this conclusion were some findings in reproductive organs (e.g. increased testes weight) found in the (sub)chronic toxicity studies, although considered by the authors of those studies to be chance findings or normal background related to aging[16]. EU (2005) also indicates toxicokinetics data gaps, including presence of amines as metabolites.

Considering that one of the criteria for prioritising MDI and TDI for REACH substance evaluation was possible CMR properties (also of the hydrolysis products, i.e. amines), it must be assumed that the REACH substance evaluations will closely investigate and conclude on the above issues. Therefore, only a few additional notes will be made in the current report.

The International Agency for Research on Cancer (IARC) has assessed TDI (2,4-TDI, 2,6-TDI as well as commercial mixtures) and concludes the evaluation by assigning TDI to Group 2B - *possibly carcinogenic to humans* (IARC, 1999).

The Danish Working Environment Authority has provided extracts from statistics for reported occupational diseases in Denmark (Høyer, 2013). Reported diseases where isocyanates have been part of the cause of the disease are reproduced in Table 20. As workers are exposed to various agents, the statistics provide the possibility to suggest more than one cause of a reported disease. Analysing the comments from medical doctors to the reported diseases reveals that there can be some bias, in particular with workers exposed to epoxy products and workers exposed to e.g. grinding dust, which could be dust from isocyanate painted subjects, but also dust from other sources. However, for most of the cases reported, it is assessed that exposure to isocyanate has had an influence on the disease reported.

The statistics do not distinguish between MDI, TDI and other isocyanates. However, given the volume of MDI and TDI compared to other isocyanates (see Chapter 3), it appears likely that most of the diseases reported are associated with MDI and TDI exposure.

It should also be noted that the statistics only capture reported disease cases.

[15] A "Conclusion (i)" requires further information collection

[16] ISOPA (European Diisocyanate & Polyol Prodcuers Asociation) has been addressed specifically in relation to providing information about any new information generated in response to the 2005 EU MDI risk assessment request for more information on fertility. In response, ISOPA has referred to the ECHA dissemination tool. Search in the ECHA dissemination tool (http://echa.europa.eu/information-on-chemicals/registered-substances) indicate that no recent studies have been conducted in relation to reproductive toxicity of MDI. However, supporting evidence not summarised on the ECHA dissemination website may be present in the confidential IUCLID files.

TABLE 20
REPORTED WORKING RELATED DISEASES INVOLVING EXPOSRE TO ISOCYANATES IN DENMARK

Diagnosis - grouped	Year registered						
	2007	2008	2009	2010	2011	2012	Total
Other	3			1		2	6
Skin disorders		2	2		3	3	10
Cancer				1			1
Airway diseases	10	7	4	9	11	9	50
Muscle skeletal diseases	1						1
Nervous system					1		1
Total	14	9	6	11	15	14	69

The table shows the following:
- In particular, airway and to some extent, skin disorders are reported. This appears logical given the classification of isocyanates as irritants and sensitisers via these routes. The comments from medical doctors associated with the reported diseases are generally too unspecific to distinguish between irritation and sensitisation.
- Given the nature and magnitude of the figures, it is difficult to indicate any trend with high significance. However, the reported diseases seem to be at a relatively stable level, possibly slightly increasing over the last 2-3 years.

The Danish Working Environment Authority (Høyer, 2013) indicates that these numbers are relatively low compared to other chemical agent related diseases in Denmark. On the other hand, it should be considered that as a starting point, Danish workers are not allowed to work with isocyanates if they suffer from asthma or eczema, have recorded chronic pulmonary diseases or recorded skin or respiratory allergy to isocyanates. In addition, persons with excessive perspiration of the hands (hyperhidrosis manuum) are also not allowed to work with isocyanates.

The underlying comments from the medical doctors sometimes provide the opportunity to identify in which types of working environment the workers have been exposed. Analysing the medical doctor comments for the 50 reported airway diseases reveal that about 19 may be attributed to work with coatings, adhesives and sealants, 3 to production of PUR products and 2 to laboratory work with isocyanates. The remaining comments are too unspecific. For the 10 reported skin diseases, 6 can be attributed to work with coatings, adhesives and sealants. Although the data material is highly uncertain (e.g. due to the differing nature of the medical doctors' comments), it seems clear that professional/industrial work with coatings, adhesives and sealants are the occupational settings with the highest risk for exposure and effects following exposure to isocyanates. This supports the considerations provided in the summary section of Chapter 3, that the widespread use of coatings, adhesives and sealants, e.g. in the construction sector, are likely less controlled than at facilities producing PUR products under controlled conditions.

Statistics on consumer diseases related to isocyanates exposure have not been identified.

6.1.3 No-effect levels

Occupational exposure limit values
Occupational Exposure Limits (OELs) from a range of EU and non-EU countries have been reproduced in Table 21 and Table 22. The OELs are indicated to be valid for the 2,4-TDI and 2,6-TDI isomers, but as the mixed TDI consists of these two isomers, the values are assumed to be relevant for mixed TDI as well. A search for the

mixed TDI CAS-number (26471-62-5) in the same data source, however, only explicitly supports this for Belgium, Poland and Sweden. For MDI, only values for the 4,4'-MDI CAS-number are listed. However, as above, these values are assumed to be relevant for all (mixes) of MDI monomers.

The Danish values are in line with most of the OELs indicated for other countries. Sweden and Poland (for MDI) have slightly lower/stricter values, whereas France and Italy (for MDI) have slightly higher values.

As shown in Chapter 2, there is no established EU OEL.

TABLE 21
NATIONAL LIMIT VALUES FOR 2,4-TDI AND 2,6 TDI (IFA, 2013)

Substance	Toluene diisocyanate; 2,4-TDI; 2,6-TDI			
CAS No.	584-84-9			
	91-08-7			
	Limit value - Eight hours		**Limit value - Short term**	
Unit	ppm	mg/m³	ppm	mg/m³
Austria	0,005	0,035	0,02	0,17
Belgium	0,005	0,037	0,02	0,14
Canada – Ontario	0,005		0,02 (1)	
Denmark	0,005	0,035	0,01	0,07
France	0,01	0,08	0,02	0,16
Germany (AGS)	0,005	0,035	0,005 (1) 0,02 (2)	0,035 (1) 0,14 (2)
Hungary				0,035
Italy	0,02	0,16		0,01
Japan	0,005			
Latvia		0,05		
Poland		0,007		0,021
Singapore	0,005	0,036	0,02	0,14
South Korea	0,005	0,04	0,02	0,15
Spain	0,005	0,036	0,02	0,14
Sweden	0,002	0,014	(0,005)	(0,04)
USA - OSHA			0,02	0,14

Canada – Ontario: (1) ceiling limit value
Germany (AGS): (1) 15 minutes average value (2) Ceiling limit value

TABLE 22:
NATIONAL LIMIT VALUES FOR MDI (IFA, 2013)

Substance	Methylene bisphenyl isocyanate (MDI)			
CAS No.	101-68-8			
	Limit value - Eight hours		Limit value - Short term	
Unit	ppm	mg/m³	ppm	mg/m³
Austria	0,005	0,05	0,01	0,1
Belgium	0,005	0,052		
Canada - Ontario	0,005		0,02 (1)	
Canada - Québec	0,005	0,051		
Denmark	0,005	0,05	0,01	0,1
France	0,01	0,1	0,02	0,2
Germany (AGS)		0,05		0,05 (1)
				0,1 (2)
Germany (DFG)		0,05 inhalable aerosol		
			0,05 inhalable aerosol (1)(2)	
Hungary				
Poland		0,05		0,05
Singapore		0,05		0,2 (1)
South Korea	0,005	0,051		
Spain	0,005	0,055		
Sweden	0,005	0,052		
USA - NIOSH	0,002	0,03	0,005 (1)	0,05 (1)
USA - OSHA	0,005	0,05	0,02 (1)	0,2 (1)

Canada – Ontario: (1) ceiling limit value
Germany (AGS): (1) 15 minutes average value (2) Ceiling limit value
Germany (DFG): (1) STV 15 minutes average value (2) A momentary value of 0,1 mg/m³ should not be exceeded.
Poland: (1) ceiling value
Sweden: (1) ceiling limit value
USA – NIOSH: (1) ceiling limit value (10 min)

Food

As outlined in Chapter 2, TDI and MDI are allowed in plastic food contact materials under certain restrictions (see details in Chapter 2). The underlying scientific opinion dates back to 1986 and specifies that it is not possible to establish a reference value (neither acceptable nor tolerable daily intakes) due to lack of data and therefore recommends that migration into food should be "not detectable by an agreed sensitive method" (SCF, 1986).

REACH Registrations (DNELs)

Derived no-effect levels (DNELs) for registered MDIs and TDIs are provided in Table 23 and Table 24. These have been obtained from the ECHA dissemination website (http://echa.europa.eu/web/guest/information-on-chemicals/registered-substances). The dissemination website does not reproduce the full justification around these values from the confidential registration dossiers and it is therefore not possible to comment on the derived DNELs in a fair manner.

It is assumed that the REACH substance evaluations will carefully evaluate the derived DNELs and the surrounding justifications.

Notable observations from the tables are that no DNELs are provided for dermal worker exposure to TDI and no DNELs (neither inhalation nor dermal) are provided for consumer exposure to TDI. It is not clear whether these values are lacking in the REACH registrations, or simply have not been transferred to the dissemination tool.

Although inhalation must indeed be assumed to be a key exposure route for the volatile TDI, it appears strange that no dermal DNEL is in place, as TDI generally has the same properties as MDI, for which dermal DNELs exist.

A possible explanation as to why no consumer DNELs for TDIs are derived could be an assumption that TDI is not present in consumer products. However, as already discussed in Chapter 3, it appears that TDI containing products are indeed commercially available to consumers, and that it is likely that consumers can get access to these products. This possibility is discussed further in the below exposure section.

TABLE 23
DERIVED NO EFFECT LEVELS (DNELS) FOR MDI

Population - route		Value	Sensitive end-point	Comment
Workers - inhalation	Long term exposure - systemic	0.05 mg/m³	irritation (respiratory tract)	German MAK value
	Long term - local	0.05 mg/m³	irritation (respiratory tract)	German MAK value
	Acute/short term exposure - systemic	0.1 mg/m³	irritation (respiratory tract)	German MAK value
	Acute/short term exposure - local	0.1 mg/m³	irritation (respiratory tract)	German MAK value
Workers - dermal	Acute/short term - systemic	50 mg/kg bw/day	Acute toxicity	NOAEL: 2500 mg/kg bw/day (species not indicated)

Population - route		Value	Sensitive end-point	Comment
	Acute/short term - local	28.7 mg/cm^2	Acute toxicity	Based on NOAEL, but value not indicated
Workers - eyes	Local	"Medium hazard"		No threshold derived
General population/ consumers - inhalation	Long term exposure- systemic	0.025 mg/m^3	irritation (respiratory tract)	50% of worker (50% of German MAK)
	Long term - local	0.025 mg/m^3	Irritation (respiratory tract)	50% of worker (50% of German MAK)
	Acute/short term exposure - systemic	0.05 mg/m^3	irritation (respiratory tract)	50% of worker (50% of German MAK)
	Acute/short term exposure - local	0.05 mg/m132	Irritation (respiratory tract)	50% of worker (50% of German MAK)
General population/ consumers - dermal	Acute/short term - systemic	50 mg/kg bw/day	Acute toxicity	50% of worker
	Acute/short term - local	17.2 mg/cm^2	Acute toxicity	Based on NOAEL, but value not indicated
General population/ consumers - oral	Systemic	20 mg/kg bw/day	Not indicated	Based on NOAEL: 2000 mg/kg bw/day (species not indicated)
General population/ consumers - eyes	Local	"Medium hazard"		No threshold derived

TABLE 24
DERIVED NO EFFECT LEVELS (DNELS) FOR TDI

Population - route		Value	Sensitive endpoint	Comment
Workers - inhalation	Long term exposure - systemic	0.035 mg/m^3	Irritation (respiratory tract)	No further indication
	Long term exposure - local	0.035 mg/m^3	Irritation (respiratory tract)	German MAK value
	Acute/short term exposure - systemic	0.14 mg/m^3	Irritation (respiratory tract)	German MAK value

	Acute/short term exposure - local	0.14 mg/m³	Irritation (respiratory tract)	German MAK value

6.2 Human exposure

6.2.1 Direct exposure

Consumers

MDI in coatings, adhesives and sealants
The EU MDI risk assessment (EU, 2005) identified consumer exposure as a possible concern and thus as a need for risk reduction. As a consequence, an EU restriction addressing MDI containing consumer products was introduced in 2009. This requires that products containing more than 0.1% MDI shall not be placed on the marked for the general public, unless the packaging contains appropriate protective gloves and is clearly marked with text indicating the potential for allergic reactions, specific risks for vulnerable groups and additional risk management in case of poor ventilation (see details in Chapter 2). It should be noted that the restriction does not explicitly address polymeric MDI or MDI prepolymers considered as toxic as monomeric MDI by industry (see Chapter 1). Danish suppliers of MDI-based products indicate that the restriction is followed for monomeric as well as polymeric/modified/prepolymer MDI-containing consumer products supplied on the Danish market.

The US EPA in its recent action plan for MDI (US EPA, 2011a) takes note of the EU restriction and a rapid increase in consumer and DIY products with free MDI on the US market, including sprays, foams and adhesives (16 products in 2004 and 43 products in 2010). In addition, it is noted that "professional grade" products are accessible to consumers in home improvement stores and via the Internet. It is noted that consumers are not trained in using these products and do not have access to appropriate protective measures.

It is also noted that, when using high pressure sprays, chemical migration may occur between floors in a building, causing unprotected consumers (including children) on other floors to be exposed. It is noted that asthmatic children may be particularly vulnerable as they are more susceptible to inflammatory narrowing of the airways.

US EPA (2011a) notes that limited consumer exposure data are available and that a number of "next steps" are considered, including monitoring programs of consumer exposure to products with uncured MDI and development of regulations related to consumer products and/or commercial uses of uncured MDI products where the general population could be exposed.

The survey of coatings, adhesives and sealants on the Danish market conducted in this project (See appendix 2) shows that MDI is present in a range of consumer products, including aerosols. Thus, even if MDI is not very volatile, it could lead to consumer inhalation exposure via such applications. Specific exposure data for Danish consumer exposure have not been identified. In a Danish EPA (2004b) consumer product project, MDI was found in sealants in concentrations of about 1% (w/w).

A Danish EPA study investigated emissions from a range of products, which were considered to possibly/likely contain MDI: car window adhesive, mattresses, one component adhesives and sealers, polyurethane raincoats, floor adhesives, and a hair conditioner (which might contain MDI-based co-polymers) (Danish EPA, 2007). No MDI emissions to air for these products were detected using two analytical methods. This might not be surprising considering that MDI has a relatively low vapour pressure. It is notable from the report that when analysing using HPLC on a C8 column, a peak close to MDI was identified. Although not discussed in the report, this peak could have been caused by other more volatile isocyanates, such as TDI or aliphatic isocyanates.

TDI in coatings, adhesives and sealants
As outlined under “no-effect levels” (Section 6.1.3), no DNELs for consumer exposure to TDI are available via the REACH dissemination tool and it is speculated whether this lack derives from the fact that TDI has not been registered for consumer use.

The US EPA action plan for TDI (US EPA, 2011b) notes that “some members of the industry have stated that uncured TDI is not used in consumer products.”

However, although noting that it is “unclear how many products containing uncured TDI are available for consumer purchase”, the US EPA action plan concludes that such products are available on the US market. The survey of coatings, adhesives and sealants on the Danish market conducted in this project (See appendix 2) also indicates that consumer products containing free TDI are available on the Danish market. Some previous surveys of Danish consumer products have found TDI in textile paints (Danish EPA, 2005c) and spray paints (Danish EPA, 2004a). In addition to this is possible consumer access, e.g. via the Internet, to products originally intended for professionals. This is considered plausible by US EPA (2011b) and supported by some of the persons interviewed among Danish suppliers of such products.

Consumer access to products containing free TDI is of particular concern for the following reasons:

- TDI is volatile and thereby inherently likely to lead to inhalation and thereby respiratory sensitisation (vapour pressure is about three orders of magnitude higher than for MDI), and
- TDI is not subject to a consumer product EU restriction such as for MDI; therefore, there are not the same requirements for providing gloves and instructions for using these inherently more potent products.

In conclusion, information concerning how and in which quantities consumers have or can get access to coatings, adhesives and sealants with free TDI, is limited.

TDI/MDI monomers and degradation products in PUR products
In PUR products, MDI and TDI monomers are largely/completely reacted to polyurethane, eliminating the MDI and TDI monomer toxicity.

However, possible content of MDI/TDI monomers (as residual monomers or from degradation), as well as possible amine degradation products, may be present. Section 1.4 provided a long discussion on this topic, illustrating conflicting evidence based on monitoring results and theoretical (chemistry and thermodynamic) considerations. Free monomers had e.g. been found in baby mattresses and in textiles. One of the issues discussed is the possibility that some analytical techniques might generate free monomers when interfering with the PUR material, and in this case, the analytically determined monomers would be an artefact. No firm conclusion was reached within the scope of this project.

In any case, considering chemistry and the fact that free monomers would have to migrate out of the PUR material would indicate that consumer exposure is likely to be low. On the other hand, consumers (including infants) are in contact with such products, sometimes over long periods (e.g. mattresses). Amines can be generated via degradation/hydrolysis of isocyanates. In particular, the primary aromatic amines deriving from free monomers are a cause for concern. The magnitude of primary aromatic amines is therefore closely related to the presence of free monomers.

Overall, it is necessary to look further into all arguments provided on the issue of free monomers and degradation products in PUR products, in particular those to which consumers are exposed. As set out elsewhere in this report, consensus on the issue of residual monomers and degradation products in PUR products must be considered an important knowledge gap.

As discussed in Section 1.4, heating of PUR products or PUR coated surfaces may cause liberation of free isocyanates, amines and other degradation products, e.g. during ironing of clothes containing PUR fibres, a fact that might not be known among consumer users of PUR products.

Occupational exposure

As outlined in Chapter 2, an array of national Danish legislation is in place in relation to handling isocyanates (including MDI and TDI) in occupational settings. Nevertheless, as indicated previously in this chapter, a steady number of occupational diseases caused by isocyanates is reported every year.

Direct occupational exposure to free MDI and TDI may generally take place in the following situations:

- During production of PUR products and production of coatings, adhesives and sealants, and
- During industrial/professional use of coatings, adhesives and sealants.

In terms of potential for exposure and thereby hazards and risks, it is assumed that the application of MDI and TDI for PUR production (flexible, rigid and elastomers) takes place in standardised productions facilities, enabling systematic and continuous control of the handling of MDI and TDI. In particular in Denmark, where a suite of national occupational legislation related to professional/industrial use of isocyanates is in place (see Chapter 2), requiring education, training and tight control, this must be assumed. In Denmark, these PUR production activities take place in about 14 Danish facilities (see Chapter 3). Some industry interviews support that there is focus on compliance with the Danish Occupational rules in these facilities (See Appendix 3). A similar pattern must be assumed for MDI-based binders used for production of chipboards, although there is no indication that such production takes place in Denmark.

A Swedish study from 2003 measuring air concentration/exposure of isocyanates in 13 facilities handling free isocyanates (including foaming, casting, (flame) lamination and production of consumer products) found in 260 samples, average daily concentrations of <0.0001 to 0.038 mg isocyanate/m^3, which at that time were below the OELs (0.04 mg/m^3 for TDI and 0.04 mg/m^3 for MDI). No peak values are reported. The highest average daily values were identified for flame lamination with TDI. These values would be above the current Swedish OEL for TDI (0.014 mg/m^3, see Table 21). Actually, the study may have triggered this lowering as clinical investigations showed a certain increase in eye irritation, nose-bleeding, couching attacks and lowering of lung function among exposed workers compared to controls (Littorin et al., 2003).

On the other hand, adhesives and sealants and to some extent coatings are used for a range of activities in less standardised settings, not the least in the construction sector. Whereas such applications should adhere to the strict Danish occupational rules, it is likely less standardised than for PUR production, and application of the MDI/TDI products might occur as only one of many tasks of a professional. In particular products applied by spraying applications and as aerosols could cause significant exposure[17]. Furthermore, the statistics on occupational diseases confirm that the majority of cases can be related to occupational use of coatings, adhesives and sealants.

6.2.2 Indirect exposure

Secondary exposure from thermal degradation products

As set out in Section 1.4, heating of PUR products or PUR coated surfaces might take place in a range of branches, e.g. when welding or grinding PUR coated surfaces and PUR products cause liberation of free isocyanates, amines and other degradation products. This risk might not be known among professional users of PUR products. No review identifying such exposure and risk management in place to minimise exposure has been identified.

Air, soil and drinking water

No data on exposure of the general population to MDI and TDI via air, drinking water or soil/plants have been identified. This appears logical given the reactivity of isocyanates with e.g. water. Furthermore, no data on general population exposure via these exposure routes to MDI and TDI degradation products (amines) have been identified.

[17] It should be noted that specific Danish legislation requires notifications of spraying applications (see Chapter 2).

Food/food contact materials
Laminates/laminating adhesives based on isocyanate technology are to a great extent used when different food packaging materials have to be combined, e.g. when attaching information labels. Specific concern is related to the primary aromatic amines that may be generated by degradation of free MDI and TDI monomers (see e.g. TemaNord, 2002).

In 2001, the Danish Food Directorate conducted a pilot campaign (Trier and Petersen, 2001) and in 2002, a control campaign (Trier and Petersen, 2002) addressing migration of amines from laminated food plastics materials was carried out. In the pilot study, food packed in plastic packaging materials were bought and 10 of these packages - analytically determined to contain polyurethane based on aromatic isocyanates - were analysed for primary aromatic amine migration. No measurable migration was found even with a very low detection limit (Trier and Petersen, 2001). In the control study, plastic laminate samples were already taken in the storage area of laminate producing companies in order to capture material at an early stage. Of 33 samples, two samples showed primary aromatic amines at or above the detection limit (1 and 1.7 µg primary aromatic amines/kg food simulant). A further 8 of the 33 samples showed traces of primary aromatic amines. The report concluded that there did not seem to be significant problems, as the levels found were well below the EU migration limit of 20 µg primary aromatic amines/kg food simulant. This conclusion was further supported by the argument that laminate samples were taken even before the laminates were used for food packaging, thus constituting the worst case in terms of content of uncured/free isocyanates. It should be noted that the EU migration limit has currently been lowered 10 µg primary aromatic amines/kg food simulant (see Chapter 2), but still the detected worst case values are well below this limit.

More concern might pertain to food contact material which is heated. As discussed in Section 1.4, Trier et al. (2010) found 4,4´-methylenedianiline (MDA) in a large number of food contact materials, especially black kitchen utensils imported to Denmark from China. The samples were analysed by HPLC-MS_MS by an accredited test method for contact with aquatic food simulants; the risk assessment concluded the findings to be of major concern. As noted in Section 1.4, MDI might be the source of the formation of MDA, although that was not concluded in the study. As a follow-up to these findings, the Commission Regulation (284/2011) concerning import of such products from China and Hong Kong has been put in place, as well as a Danish executive order further specifying procedures when importing such plastic utensils to Denmark. See Chapter 2 for details.

Indoor climate
No data identified. However, if the findings of free TDI monomers in PUR products are not false positives generated by the analytical methods, TDI could possibly be liberated to the indoor environment from such products.

6.3 Bio-monitoring data
In a commentary, Cocker (2011) summarises how biomonitoring is used to assess exposure to isocyanates. The following discussion is based on that reference. Isocyanate–protein adducts in urine and blood are used for monitoring exposure to a range of isocyanates, including TDI and MDI. This is based on analysis of their corresponding primary amines - TDA (toluene diamine) and MDA (methylenediamine) - released after hydrolysis of the isocyanate–protein adducts in urine or blood. A good correlation is obtained between biomonitoring results and inhalation exposure. Association between biomonitoring results and dermal exposure has also been shown, although with inferior correlation than what was found for inhalation. The “German Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area” has established a Biologischer Leit-Wert (BLW) value for MDI of 10 µg MDA/l (approx. 4 µmol MDA per mol creatinine) based on the levels likely to be found in urine after inhalation exposure to 50 µg MDI/m^3. In 2005, the UK Health and Safety Executive (HSE) published a biological monitoring guidance value (BMGVs) of 1 µmol of isocyanate-derived diamine per mol creatinine in urine samples collected at the end of exposure. It is noted that these values are not health-based, but are rather triggers for further action, including examination of control measures and work practices in place.

6.4 Human health impact

It must be expected that the ongoing REACH substance evaluations will perform up-to-date risk/safety assessments of exposure to MDI and TDI at the European level.

For the Danish situation, no risk assessments have been identified, but as summarised previously, about 10-15 occupationally related diseases (mainly airway diseases, but also skin disorders) likely attributable to isocyanate exposure are reported per year.

6.5 Summary and conclusions

MDI and TDI are classified as suspected of causing cancer, as dermal and respiratory sensitisers, as toxic following inhalation and as eye, skin and respiratory irritants. In particular, their ability to cause respiratory sensitisation is of concern. Inherently, TDI, having a vapour pressure about three orders of magnitude above that of MDI, is more likely to cause inhalation exposure and TDI exerts higher inhalation toxicity. However, MDI applications using aerosols and spraying also take place. Possible toxicity to fertility has been highlighted as an issue, e.g. in the 2005 MDI risk assessment (EU, 2005) and CMR properties of MDI/TDI and their degradation products (primary aromatic amines) is one of the reasons why both substances are subject to REACH substance evaluations. In parallel, a number of investigations regarding possible implementation of further risk management are ongoing at EU level. These activities are in the process of summarising hazards and the situation regarding exposure at the EU level. These activities are ongoing and/or confidential and can therefore not be summarised here. However, the Danish EPA has full access to all activities and documentation and can use that material as background for possible further action on these substances. Therefore, the main focus in this project is on the Danish situation, as a supplement to the EU activities.

Occupational exposure limits for MDI and TDI are in place in an array of EU and non-EU countries and the Danish values are similar to those in most other countries. In terms of exposure measurement and control, biomonitoring methods exist to measure the corresponding primary aromatic amines (MDA for MDI and TDA for TDI) following hydrolysis of isocyanate-protein adducts in urine and blood. A good correlation is found between inhalation exposure and this type of biomonitoring. Germany and the UK have established biological monitoring guidance values to assist in control of occupational exposure.

In terms of exposure, and thereby risk, most attention should probably be paid to professional and consumer use of coatings, adhesives and sealants.

Extracts from Danish statistics over occupational diseases show a constant level of 10-15 registrations per year related to isocyanate exposure. Most of these are related to use of coatings, adhesives and sealants; the majority are related to airway diseases and a lower number to skin disorders.

This survey has shown that MDI- and TDI-containing adhesives and sealants are marketed for Danish consumers, with some MDI products marketed as aerosols. Furthermore, as e.g. also speculated by recent US EPA action plans on MDI and TDI, it cannot be excluded that consumers can get access to products intended for the professional market, e.g. via the Internet.

Consumer use of TDI-based products seems to be a cause for concern, as TDI is not subject to an EU restriction (as is MDI) requiring that products are provided with gloves and extended safety information. This is triggered by the fact that TDI is both more volatile than MDI and exerts higher inhalation toxicity.

MDI-containing products in aerosol cans might also be a cause for concern, as consumers would likely not use such products with appropriate ventilation and risk management controls.

Altogether, there seems to be a knowledge gap in relation to coatings, adhesives and sealants marketed and/or accessible to Danish consumers, including TDI-based products and MDI-based products involving spraying/aerosol generation.

MDI and TDI monomers (as residual monomers and/or degradation products) have been detected in a number of PUR consumer products, including e.g. baby mattresses. Their presence seems to conflict with chemical and thermodynamic arguments, which, according to the understanding of European isocyanate and PUR products trade organisations, show that analytically determined MDI and TDI in such products must be artefacts related to the analytical techniques.

It is generally acknowledged that liberation of MDI, TDI, amines and other degradation products might appear as a result of thermal degradation. Such degradation might take place e.g. during ironing and during a range of heat generating processes such as grinding and welding in a range of branches. No overview has been identified quantifying such emissions and related risk management measures put in place to reduce exposure.

Isocyanate-containing laminates/adhesives are used in plastic food contact materials. The risk for formation of primary aromatic amines from uncured isocyanate monomers, which could migrate to the food, is a subject of attention and an EU migration level has been established. A control campaign conducted by the Danish Food Directorate in 2001/2002, however, showed that even for laminates taken directly from the stores (with a higher expected content of uncured isocyanates), only two samples out of 33 showed primary aromatic amines above the detection level, but still considerably below the EU migration level at that time, as well as that in place today.

MDA (the primary aromatic amine generated from MDI hydrolysis) has been found at high levels in plastic kitchen utensils imported from China and Hong Kong. These levels could stem from degradation of MDI in the products. As set out in Chapter 2, regulation has been put in place to monitor and control the level of primary aromatic amines in such products.

7. Information on alternatives

7.1 Introduction

According to Figovsky et al. (2012), the PUR market today amounts to about 5% of the total polymer market and the worldwide consumption of PUR is increasing steadily as shown in Chapter 3.

The amount of TDI and MDI used for coatings, adhesives and sealants is relatively small compared to the amounts of TDI and MDI used in flexible and rigid PUR products. However, as is shown below, the possibility of using alternatives for TDI and MDI for coating, adhesives and sealants is more promising than for the flexible and rigid foamed PUR products.

With a view to ensuring protection of consumers and professionals towards exposure to free diisocyanates, this might be good news as the exposure and risks are assumed to be highest for these products (see Chapter 6). On the other hand, the toxicity and risks associated with some of these alternatives might not be significantly superior to MDI and TDI based products.

Isocyanates can be processed to have many different product characteristics:

- As solid thermoset PUR
- As cellular plastics, rigid, semi rigid and flexible PUR
- As thermoplastic PUR with rubberlike properties and as PUR rubbers
- As adhesives
- As sealants
- As coatings
- As elastic fibres.

If polyurethanes are going to be replaced with other substances and materials, it is important to compare the properties of the possible substitutes with the present specification for the PUR applications.

7.2 Information search and method

Information collection on alternatives has been based on the following:

- Technical literature
- Internet search
- Contacts to trade organisations.

Regarding alternatives, the following grouping has been made:

- Alternative isocyanates to MDI and TDI
- NIPU = Non Isocyanate-based PolyUrethane
- Other alternative materials than NIPU PUR.

Furthermore, the chapter is organised to the extent possible according to the groups:

- Rigid and flexible PUR foams
- Coatings, adhesives and sealants.

As noted earlier, MDI and TDI are cured into polyurethane in PUR products, whereas the free MDI and TDI monomers form part of the functionality in coatings, adhesives and sealants, sold as uncured products.

Information has been identified from the following information sources:

- The technical literature including books on PUR chemistry and processing and books on recycling of PUR, as well as environmental aspects;
- The recent US EPA action plans for MDI and TDI (US EPA, 2011 a, 2011b) considered the most recent "state-of-the-art" literature;
- Internet searches on substitution, replacement and alternatives to polyurethanes, and not the least - inspired by US EPA (2011a, 2011b) - searches on NIPU, and
- Contact to trade organisations and companies.

Regarding contact with trade organisations and companies the following were contacted:

- The PUR section of the Danish Plastics Federation
- Danish Coatings and Adhesives Association
- ISOPA
- PU EUROPE
- EuroPUR
- Carpenter A/S
- Logstor A/S
- Gram Commercial A/S
- Affald Varme, Aarhus Kommune
- A range of importers/producers of coatings, adhesives and sealants (company identity confidential). See appendix 2.

7.3 Substitution of high volatile TDI to low volatile MDI or prepolymers

Several sources (e.g. Health and Environment Canada, 2008) indicate that TDI is increasingly being substituted with the less volatile MDI. Further, free/pure MDIs are increasingly substituted with modified/prepolymer MDI, often having a lower vapour pressure than monomeric MDI.

Several suppliers of modified/prepolymer isocyanates have been identified:

- BASF
- Bayer
- Dow Chemical
- Du Pont
- Evonik
- Huntsman
- Incorez.

Modified/prepolymer MDIs are more expensive than monomeric MDI but, as noted, they generally have a lower volatility which means that the exposure to MDI is reduced. They still might contain small amounts of free MDI unless they have been thin film distilled. However, the difference in vapour pressure between monomeric MDI and modifided/prepolymer MDI is, in any case, considerably lower than the three orders of magnitude difference between TDI and MDI. As noted earlier, prepolymer MDI is monomeric or polymeric MDI which has partly reacted with di- or polyfunctional alcohols.

As an example, the brochure from Bayer "Polyisocyanates and prepolymers: Products and applications" states that typical areas of application for the modified/prepolymer MDIs are wood coatings, corrosion protection, floor coatings, elastic adhesives in transportation, parquet adhesives, engineered wood constructions, flexible film lamination and sealants (Bayer, 2013).

Bayer claims that modified/prepolymer MDI with a low fraction of non-polymer bound components open up formulation options for the production of reactive polyurethane adhesives and sealants that are not subject to labelling requirements. This, however, seems to conflict with the statements received from ISOPA companies indicating that all forms of MDIs are labelled in line with the classification of the monomeric MDI (see Chapter 1).

The Bayer product range includes modified/prepolymer products based on aromatic and aliphatic NCO-terminated isocyanates, as well as silane terminated products.

Bayer's range of "polyisocyanates" comprises a broad range of products for 1 or 2 component polyurethane systems for a number of applications. The products are used by automotive original equipment manufacturers (OEM) for refinishing and the coating of transportation vehicles, wood, industrial goods and plastics. They are also used in reactive adhesives, textile coatings and anti-corrosion coatings.

Generally, it is judged that the use of modified/prepolymer isocyanates is an available and practised technology to reduce the exposure to free isocyanates from manufacturing of elastomeric PUR products, as well as from coatings, sealants and adhesives.

From an interview with Carpenter A/S (the major Danish producer of flexible PUR foam), it is known that modified/prepolymeric MDI as well as monomeric MDI have partly replaced TDI for the production of flexible foam for furniture (Carpenter, 2013). This is done to reduce the volatility of the isocyanate formulation. However, for low density foams, substitution of TDI with MDI is difficult because the foam quality becomes inferior.

7.4 Blocking of the isocyanate groups of MDI and TDI

It is also possible to modify the isocyanates by blocking with other chemical agents which are loosely bound to the isocyanate as it is liberated at higher temperature. Examples are blocking with oxims, phenols, caprolactam, malonester and triazoles (Oertel, 1983). Such modifications will reduce the exposure to the free isocyanates.

According to ISOPA, this masking/blocking of the isocyanate group is only possible with isocyanates used for textiles, fibres and coatings (ISOPA, 2013). For the main application areas of PUR (rigid and flexible), the high reactivity of MDI/PMDI and TDI is needed.

Encapsulation, in which the reactive isocyanates are encapsulated with a coat, is another possibility to reduce exposure to the isocyanates and to improve "pot life" of the product. This is foreseen to be used for some adhesives and sealants applications (US Patent Application, 2006).

7.5 Alternative isocyanates to MDI and TDI

Commercial isocyanates other than MDI and TDI are available, mostly for special purpose urethane applications. An aromatic type is naphtalen-1,5-diisocyanate (NDI), which is used for elastomeric polyurethane moulding. Hexamethylene diisocyanate (HDI) and 1-(isocyanatomethyl)-3,5,5-trimethyl-cyclohexan (IPDI) are used for coatings and lacquers in particular.

It is likely possible to reduce the amount of MDI and TDI in formularies for coatings and lacquers with more aliphatic isocyanate, but the aliphatic isocyanates are more expensive and less reactive, making curing time longer.

7.6 Non isocyanate based PUR (NIPU)

In the summary of chapter IV "Uses and Substitutes" in the US EPA MDI and TDI action plans (US EPA, 2011a; 20011b), it is stated that "Replacement of diisocyanates in an environmentally and economical friendly manner presents a significant challenge".

It is mentioned that two research groups have reported that it is possible to make "isocyanates-free" expanding foam products and a faster curing "isocyanates-free" flexible food packaging adhesive, which prevents potential migration of isocyanates into food.

It is our understanding that these examples might be "emerging technologies" but they are not significant to the huge market for polyurethane based products which are currently produced by isocyanate based PUR chemistry where the main chemicals still involve MDI and TDI reaction chemistry with various polyols.

In the US EPA report, it is stated that "*while research and development of appropriate alternatives is underway with a goal of direct product substitutions, it is important to focus on the safe use of existing polyurethane products through hazard communication and education of product users*."

PUR can be produced without making use of isocyanates. The alternative route is based on the reaction between cyclic carbonates and aliphatic and cycloaliphatic amines. This route to PUR has been known for the last 50 years, but this way of synthesizing non isocyanate based PUR (NIPU) has not been practised industrially for different reasons: low reactivity and decreased crosslinking density.

Recent research has overcome the slow reaction time, e.g. by using multifunctional cyclocarbonates and aliphatic di- or tri-amines, resulting in polyhydroxyurethanes (Figovsky et al., 2012). According to Figovsky et al., a great problem of the NIPU technologies is the absence of commercially available multifunctional cyclic carbonates. Another possible problem is that NIPU might have insufficient water resistance as the PUR formed is a polyhydroxyurethane polymer; however, it is claimed that it is possible by proper formulation to make the NIPUs resistant to water (Figovsky et al. 2012).

Javni and Petrovic (2008) has prepared a series of polyurethanes by reacting vegetable oil based cyclic polycarbonates with ethylene diamine, butylene diamine and hexamethylene and studied the effect of amine structure on mechanical and physical properties of the polyurethanes. All amines produced transparent elastomeric polyurethanes with glass transitions between 0° C and 40° C and hardness between 40 and 90 Shore A.

Based on the above challenges, it is judged that NIPUs in most applications still constitute an emerging technology, including the associated processing technologies.

The patent situation supports this judgement, as patents regarding NIPU have recently been applied for:

- Cyclic carbonate monomers and polymers prepared therefrom (US Patent Application, 2013), and
- US Patent Application (2012) describes the synthesis of NIPU from renewable resources. Cyclic polycarbonates can be obtained by reacting polyepoxides with carbon dioxide. A series of polyurethanes were prepared by reacting vegetable oil based cyclic polycarbonates with ethylene diamine, buthylene amin and hexamethylene amine. All amines produced transparent elastomeric polyurethanes with glass transition at 0 -40 ◦ C and hardness between 40 and 90 shore A.

It should be mentioned that the NIPUs are produced with reactive cyclic polycarbonates and the toxicity, exposure and risks of these have to be considered. However, the references on NIPU do not address this issue and no CAS-number has been found in these references.

7.7 Other alternative materials than NIPU PUR

As most polyurethane is used for foamed products for insulation/construction and furniture, it should be considered to what extent polyurethane can be substituted by other foamed plastics/rubber for these purposes:

- Polystyrene foams
- Polyolefin foams
- Epoxy foams
- Silicone foams
- Latex foams.

It may be that the substitutes have inferior mechanical/insulating properties, comfort or are less resistant to fire.

Other insulation materials should also constitute options, e.g. inorganic glass fibre, stone wool, and insulating materials based on natural fibres. These materials compete with PUR insulating foams especially for simple constructions and easy-to-mount applications.

But PUR insulation has advantages in many applications (e.g. high insulating capacity, requiring less space) that in many cases makes PUR the first choice – although it is more expensive.

Therefore, the use of PUR, although generally more expensive, may be preferred because of better mechanical properties, better adhesion to other materials (metals), better fire class (at least compared to other foamed plastics), good insulating properties and very good resistance to wear and weathering. It has to be mentioned that brominated polyols can be used for improving the fire resistance of PUR without using the banned brominated flame retardants.

Overall, the performance/price relationship regulates the market share between MDI/PMDI/TDI-based PUR materials and alternative materials, including mineral and glass wool for insulation applications. Mineral and glass wool are both manufactured in Denmark, which might influence the market share for insulation in Denmark to the benefit of mineral and glass wool compared to PUR-based insulation.

7.8 Alternative processes and materials for foams, coatings, adhesives and sealants by using NIPU Technology

Alternative process technology has been developed and commercialised for NIPU PUR. Exposure to isocyanates is eliminated as they are not used in these processes. However, as already mentioned, NIPUs are in many cases based on reactive chemicals as well.

One example found is the use of hybrid chemistry, by reacting aminoalkoxysilanes with cyclic carbonate-epoxy resins. Curing can take place at 10 C - 30 ◦C and results in adhesion to several substrates, and good resistance to weathering, abrasion and solvents (Figovsky 20129).

Foams
Formulations for spray foam that is based on NIPU exist. Wacker (2013) claims that NIPU GENIOSIL can replace polyurethane-based installation foams. GENIOSIL is based on silicone chemistry and on alpha silanes.

An isocyanate – free polyurethane (US Patent Application, 2013) based on the reaction of divinylbenzene dicyclic carbonate with triethylenetriamine combined with a blowing agent is claimed to be a new approach to make poly(hydroxyurethane) foams (http://purpatents.com).

Soudal (Soadafoam) claims to be the first company in the world to offer isocyanate free one component fixing foam. It has good adhesion to most substrates (e.g. wood, concrete, stone) (Soudafoam, 2013). It can be bought on the Internet at the address www.dolphinsealants.co.uk/shop/soudafoam-smx.html.

Coatings
HMG Paints (2011) has marketed a new non-isocyanate acrylic two component coating (top coat) with the same technical performance as a two component PUR finisher. The NIPU top coat developed is applied by conventional, HVLP or electrostatic spray and touch dries within 15 minutes, hard dries in 4 hours and attains fully cured properties in 7 days.

HMG Paints claims that the company is the largest independent paint manufacturer in the UK.

PPRC (2011) gives a short update on alternatives to PUR-based coating products indicating that mainly polysiloxane-based but also HNIPUR (hybrid non-isocyanate polyurethane)-based systems are used.

Adhesives
Henkel (2011) has developed the first laminating adhesive, which according to their claim contains no free isocyanate, under the trade name Liofol Fast One LA 1640-21. It is a one-component PUR laminating adhesive with fast cure compared to conventional adhesives, with low migration values. It is stated that it is safer for converters as well as consumers as the formation of primary aromatic amines is avoided. See Gierlings et al. (2012) for further details.

Wacker (2013) claims to exploit the benefits of alpha silanes by developing innovative general purpose adhesives and sealants to replace numerous polyurethane counterparts in the construction industry. The new products are claimed to offer the same or even better properties and to have no known harmful effects.

Sealants
For sealants, it may be possible to replace polyurethane with an MS polymer based (silane terminated polyol), which has good flexible and weathering properties.

As mentioned under adhesives, Wacker is developing a number of alpha silane based products to substitute polyurethanes in applications such as sealants.

7.9 Mini survey aiming at identification MDI and TDI containing coatings, adhesives and sealants at the Danish market and possible alternatives

A mini survey has been carried out with the aim of identification of MDI and TDI containing coatings, adhesives and sealants on the Danish market (see appendix 2).

The products identified covered paint for cement, paint for concrete floor, hardener for two-component PUR coating, protective coats for civil infrastructure, protective paints for on- and offshore applications, foam sealants and wood adhesives. The companies interviewed are kept anonymous for confidential reasons. The companies were asked for alternatives to MDI/TDI based products and associated pros and cons.

For concrete paint based on prepolymeric MDI, epoxy was suggested, but it was questioned whether epoxy would be less toxic. The epoxy solutions would likely have better adhesion and chemical resistance properties, but a drawback would be that the user would have to handle a 2-pack (need for mixing and stirring). For foam sealants, silane/STP (Silane Terminated Polymer) based products were suggested as alternatives to isocyanate based products, and even Rockwool. Silane/STP based products, however, do not have the same “fill effect” and would therefore be about 8-9 times more expensive per volume filled. Rockwool would be cheaper, but would not have the same fill-effect as MDI based sealants. For joint sealants and wood adhesives, MS/SMP (Silylated Polyether /Silyl Modified Polymers) based products were indicated as possible alternatives. For joint sealants, the alternatives are not more expensive, but barriers for substitution are lower chemical resistance of alternatives and tradition. For the wood adhesive, it was pointed out that the MS/SMP solution would be 3-4 times more expensive and that tradition is a barrier for substitution. For several of the interviewed companies there were no suggested alternatives to MDI/TDI based products.

7.10 Toxicity of alternative substances/materials

Toxicity of alternatives is rather complex as generally “systems” (“silan-based” or “polycyclic carbonate-based”) are described as alternatives. Assessments comparing the health and safety aspects of such alternatives to those based on isocyanate chemistry in a systematic way have not been identified.

As already noted, US EPA (2011a; 2011b) generically states that “Replacement of diisocyanates in an environmentally and economical friendly manner presents a significant challenge”.

As noted in Section 7.5, the aromatic naphtalen-1,5-diisocyanate (NDI) can be used for elastomeric polyurethane moulding and Hexamethylene diisocyanate (HDI) and 1-(isocyanatomethyl)-3,5,5-trimethyl-cyclohexan (IPDI) could be used for coatings and lacquers. However, as shown in Table 25, these alternative isocyanates are classified for several of the same hazardous properties as MDI and TDI, including as respiratory sensitisers. Thus, these substances cannot be considered preferred alternatives from a health and safety perspective.

TABLE 25
HARMONISED CLASSIFICATONS OF CERTAIN ISOCYANATE ALTERNATIVES ACCORDING TO ANNEX VII OF REGULATION (EC) NO 1272/2008 (CLP REGULATION)

International Chemical Identification	CAS No	Classification	
		Hazard Class and Category Code(s)	Hazard statement Code(s)
Naphtalen-1,5-diisocyanate (NDI)	3173-72-6	Skin Irrit. 2 Eye Irrit. 2 Acute Tox. 4 Resp. Sens. 1 STOT SE 3 Aquatic Chronic 3	H315 H319 H332 H334 H335 H412
Hexamethylene diisocyanate (HDI)	822-06-0	Skin Irrit. 2 Skin sens. 1 Eye Irrit. 2 Acute Tox. 3 Resp. Sens. 1 STOT SE 3	H315 H317 H319 H331 H334 H335
1-(Isocyanatomethyl)-3,5,5-trimethyl-cyclohexan (IPDI)	4098-71-9	Skin Irrit. 2 Skin sens. 1 Eye Irrit. 2 Acute Tox. 3 Resp. Sens. 1 STOT SE 3 Aquatic Chronic 2	H315 H317 H319 H331 H334 H335 H411

7.11 Historical and future trends

As polyurethane can be produced with a number of important technical functions, the market for PUR is huge and growing, see Chapter 3. It is foreseen that the largest increase will be in the construction of rigid PUR foam. The growth from 2009-2014 in the construction sector is estimated at 4.2% (IAL, 2012).

It is foreseen that the efforts to reduce exposure to free TDI and MDI will continue.

In the shorter term, the research in NIPU (non isocyanate-based polyurethanes) is expected to speed up to reduce the exposure of MDI and TDI especially for coatings, adhesives and sealants. Some commercial products for these applications are already marketed.

In the longer term, given the development of higher performing NIPU-based polyurethane chemistry, even larger markets are sure to open. According to Special Chem (2009), potential areas where NIPU can be useful are:

- Automobile applications (interior compartment and applications exposed to humidity and chemicals);
- Construction applications (concrete adhesives, coatings , floor coverings, roof tops);
- Marine applications (sealants, bridge decks, coatings and paint), and
- Consumer products (footwear, furniture, toys).

For semi-rigid and rigid PUR products, it is foreseen that they will largely be based on TDI and MDI, PMDI and modified/prepolymer MDIs for a long time.

The tendency to replace TDI with the less volatile MDI and modified/prepolymer MDI in flexible foam is foreseen to continue for the more dense foams. There will also be a trend towards using more polyols derived from renewable resources.

7.12 Summary and conclusions

Substitution of the volatile TDI with less volatile MDI, including modified/prepolymer MDI, has been undertaken and continues to take place, but may have reached a limit for technical reasons.

Blocking and encapsulation technologies "masking" the isocyanate groups to avoid/reduce exposure are being developed. To restore reactivity, this masking/blocking will disappear when the products are heated during processing.

Some alternative isocyanates substances, like naphtalen-1,5-diisocyanate (NDI), Hexamethylene diisocyanate (HDI) and 1-(isocyanatomethyl)-3,5,5-trimethyl-cyclohexan (IPDI) are available for some applications. They possess some of the same hazardous properties as MDI and TDI, not the least of which is respiratory sensitising properties.

For the larger application areas of MDI and TDI for PUR products (flexible foam for furniture, rigid foam for district heating pipes, board stock, sprayed foam, one-component foam, etc.), given the need for high reactivity, it is foreseen that the products will largely continue to be based on the free isocyanates MDI/PMDI and TDI. When possible, they may be supplemented with modified/prepolymeric MDI according to best available technology (BAT) processes with focus on protection of the workers against exposure to the free isocyanates.

From the identified literature, it is foreseen that non isocyanate-based polyurethane (NIPU) will primarily find a market in the coating/paint, adhesive and sealant segments in the short term, the segment to which consumers also have access to products with monomeric MDI/TDI. Promising NIPUs are based on the reaction between polycyclic carbonate oligomers and aliphatic or cycloaliphatic polyamines with primary amino groups. Innovation in relation to using NIPU is ongoing, as supported by several identified patent applications.

The availability of alternatives for coatings, adhesives and sealants has partially been confirmed by contact with a number of Danish importers/producers of coatings, adhesives and sealants, although quality, price and tradition might limit the use of alternatives. For example, it has been stated that isocyanate free foam on a silane/STP (Silane Terminated Polymer) basis is about 8-9 times more expensive than the PUR based foam.

Toxicity of alternatives is rather complex to judge as generally "systems" ("silan-based" or "polycyclic carbonate-based") are described as isocyanate free products, but without information on the toxic evaluation of the alternatives. Assessments comparing health and safety aspects of alternatives with those based on isocyanate chemistry in a systematic way have not been identified, but e.g. US EPA in their recent MDI and TDI action plans note that environmentally friendly substitution seems difficult.

Overall, to reduce exposure and risk, it seems advisable to:

- continue the search for substituting TDI with the three orders of magnitude less volatile MDI, including modified/prepolymer MDIs. The potential for further substitution in this vein is, however, uncertain;
- further exploit the use of blocked and encapsulated MDIs/TDIs, as well as NIPU technology, and
- focus on process substitution/optimisation (and education) with the aim of minimising consumer and worker exposure. This focus would apply to MDI/TDI as well as any substitute chemistry, which is generally based on highly reactive and therefore potentially toxic chemistry in order to fulfil the required technical function.

8. Abbreviations and acronyms

ADI	Acceptable daily intake
BAT	Best Available Technology
BCF	Bioconcentration factor
BLW	Biologischer Leit-Wert
BMGV	Biological Monitoring Guidance Value
C.A.S.E	Coatings, Adhesives, Sealants, Elastomers
CEFIC	European Chemical Industry Council
CFC	Chloro-Fluoro-Carbon
CLP	Classification, Labelling and Packaging (Regulation)
DNEL	Derived no-effect level
DPG	Dipropylene Glycol
ECB	European Chemicals Bureau
ECHA	European Chemicals Agency
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency
E-PRTR	European Pollutant Release and Transfer Register
EQC	Equivalent level of concern
EU	European Union
EuroPUR	European Association of Flexible Polyurethane Foam Blocks Manufacturers
FEHA	Danish federation for dealers and importers of Electronic household equipment (Brancheforeningen for forhandlere og importører af elektriske husholdningsartikler).
FSO	Fugebranchen, Danish trade organisation of the sealant industry
HCFC	Hydro-Chloro-Fluoro-Carbon
HELCOM	The Baltic Marine Environment Protection Commission (Helsinki Commission)
HNIPUR	Hybrid Non-Isocyanate Polyurethane
HSE	Health and Safety Executive
IARC	The International Agency for Research on Cancer
IPCS	International Programme on Chemical Safety
ISOPA	The European Diisocyanate and Polyol producers Association
Kow	Octanol/water partitioning coefficient
LOUS	List of Undesirable Substances (of the Danish EPA)
MDA	Methylenedianiline
MDI	Methylene diphenyl diisocyanate
MS	Silylated Polyether
MSWI	Municipal solid waste incinerators
MWWTP	Municipal waste water treatment plant
NIPU	Non Isocyanate-based PolyUrethane (reaction)
NOAEL	No observable adverse effect level
NOVANA	Danish national monitoring and assessment programme
OECD	Organisation for Economic Co-operation and Development
OEL	Occupational Exposure Limit
OEM	Original Equipment Manufacturer

OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic
PEC	Predicted environmental concentration
pentaDBE	Pentabromodiphenyl ether
PG	Propylene Glycol
PMDI	Polymeric MDI
PPG	Poly Propylene Glycol
PU/PUR	Polyurethane
PU Europe	European trade associations representing the polyurethane insulation industry
QSAR	Quantitative Structure and Activity Relationship
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SCF	Scientific Committee for Food
SMP	Silyl Modified Polymers
SPT	Association of Danish Cosmetics, Toiletries, Soap and Detergent Industries
STP	Silane Terminated Polymer
SVHC	Substance of Very High Concern
TDA	Thiodianiline
TDI	Toluene diisocyanate (or Tolerable Daily Intake)
TPE	Thermoplastic elastomer
TPG	Tripropylene Glycol
WEEE	Waste Electrical and Electronic Equipment
WHO	World Health Organization

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Appendix 1: Background information to chapter 2 on legal framework

The following annex provides some background information on subjects addressed in Chapter 3. The intention is that the reader less familiar with the legal context may read this concurrently with chapter 3.

EU and Danish legislation
Chemicals are regulated via EU and national legislations, the latter often being a national transposition of EU directives.

There are four main EU legal instruments:

- Regulations (DK: Forordninger) are binding in their entirety and directly applicable in all EU Member States.
- Directives (DK: Direktiver) are binding for the EU Member States as to the results to be achieved. Directives have to be transposed (DK: gennemført) into the national legal framework within a given time frame. Directives leave margin for manoeuvering as to the form and means of implementation. However, there are great differences in the space for manoeuvering between directives. For example, several directives regulating chemicals previously were rather specific and often transposed more or less word-by-word into national legislation. Consequently and to further strengthen a level playing field within the internal market, the new chemicals policy (REACH) and the new legislation for classification and labelling (CLP) were implemented as Regulations. In Denmark, Directives are most frequently transposed as laws (DK: love) and statutory orders (DK: bekendtgørelser).

The European Commission has the right and the duty to suggest new legislation in the form of regulations and directives. New or recast directives and regulations often have transitional periods for the various provisions setout in the legal text. In Chapter 2, we generally list the latest piece of EU legal text, even if the provisions identified are not yet fully implemented. On the other hand, we would e.g. include currently valid Danish legislation, e.g. the implementation of the cosmetics directive even if this is being replaced with the new Cosmetic Regulation.

- Decisions are fully binding on those to whom they are addressed. Decisions are EU laws relating to specific cases. They can come from the EU Council (sometimes jointly with the European Parliament) or the European Commission. In relation to EU chemicals policy, decisions are e.g. used in relation to inclusion of substances in REACH Annex XVII (restrictions). This takes place via a so-called comitology procedure involving Member State representatives. Decisions are also used under the EU ecolabelling Regulation in relation to establishing ecolabelling criteria for specific product groups.
- Recommendations and opinions are non-binding, declaratory instruments.

In conformity with the transposed EU directives, Danish legislation regulates to some extent chemicals via various general or sector specific legislation, most frequently via statutory orders (DK: bekendtgørelser).

Chemicals legislation
REACH and CLP
The REACH Regulation[18] and the CLP Regulation[19] are the overarching pieces of EU chemicals legislation regulating industrial chemicals. The below will briefly summarise the REACH and CLP provisions and give an overview of 'pipeline' procedures, i.e. procedures which may (or may not) result in an eventual inclusion under one of the REACH procedures.

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[18] Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

[19] Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures

(Pre-)Registration
All manufacturers and importers of chemical substance > 1 tonne/year have to register their chemicals with the European Chemicals Agency (ECHA). Pre-registered chemicals benefit from tonnage and property dependent staggered deadlines:

- 30 November 2010: Registration of substances manufactured or imported at 1000 tonnes or more/year, carcinogenic, mutagenic or toxic to reproduction substances above 1 tonne/ year, and substances dangerous to aquatic organisms or the environment above 100 tonnes/year.
- 31 May 2013: Registration of substances manufactured or imported at 100-1000 tonnes/year.
- 31 May 2018: Registration of substances manufactured or imported at 1-100 tonnes/year.

Evaluation
A selected number of registrations will be evaluated by ECHA and the EU Member States. Evaluation covers assessment of the compliance of individual dossiers (dossier evaluation) and substance evaluations involving information from all registrations of a given substance to see if further EU action is needed on that substance, for example as a restriction (substance evaluation).

Authorisation
Authorisation aims at substituting or limiting the manufacturing, import and use of substances of very high concern (SVHC). For substances included in REACH annex XIV, industry has to cease use of those substances within a given deadline (sunset date) or apply for authorisation for certain specified uses within an application date.

Restriction
If the authorities assess that that there is a risk to be addressed at the EU level, limitations of the manufacturing and use of a chemical substance (or substance group) may be implemented. Restrictions are listed in REACH annex XVII, which has also taken over the restrictions from the previous legislation (Directive 76/769/EEC).

Classification and Labelling
The CLP Regulation implements the United Nations Global Harmonised System (GHS) for classification and labelling of substances and mixtures of substances into EU legislation. It further specifies rules for packaging of chemicals.

Two classification and labelling provisions are:

1. **Harmonised classification and labelling** for a number of chemical substances. These classifications are agreed at the EU level and can be found in CLP Annex VI. In addition to newly agreed harmonised classifications, the annex has taken over the harmonised classifications in Annex I of the previous Dangerous Substances Directive (67/548/EEC); classifications which have been 'translated' according to the new classification rules.

2. **Classification and labelling inventory**. All manufacturers and importers of chemicals substances are obliged to classify and label their substances. If no harmonised classification is available, a self-classification shall be done based on available information according to the classification criteria in the CLP regulation. As a new requirement, these self-classifications should be notified to ECHA, which in turn publish the classification and labelling inventory based on all notifications received. There is no tonnage trigger for this obligation. For the purpose of this report, self-classifications are summarised in Appendix 2 to the main report.

Ongoing activities - pipeline
In addition to listing substances already addressed by the provisions of REACH (pre-registrations, registrations, substances included in various annexes of REACH and CLP, etc.), the ECHA web-site also provides the opportunity for searching for substances in the pipeline in relation to certain REACH and CLP provisions. These will be briefly summarised below:

Community Rolling Action Plan (CoRAP)
The EU Member States have the right and duty to conduct REACH substance evaluations. In order to coordinate this work among Member States and inform the relevant stakeholders of upcoming substance evaluations, a Community Rolling Action Plan (CoRAP) has been developed and published, indicating when and by whom a given substance is expected to be evaluated (ECHA, 2012).

Authorisation process; candidate list, Authorisation list, Annex XIV
Before a substance is included in REACH Annex XIV and thus subject to Authorisation, it has to go through the following steps:

1. It has to be identified as a SVHC leading to inclusion in the candidate list[20]
2. It has to be prioritised and recommended for inclusion in ANNEX XIV (these can be found as Annex XIV recommendation lists on the ECHA web-site)
3. It has to be included in REACH Annex XIV following a comitology procedure decision (substances on Annex XIV appear on the Authorisation list on the ECHA web-site).

The candidate list (substances agreed to possess SVHC properties) and the Authorisation list are published on the ECHA website.

Registry of intentions
When EU Member States and ECHA (when required by the European Commission) prepare a proposal for:

- harmonised classification and labelling,
- an identification of a substance as SVHC, or
- a restriction.

This is done as a REACH Annex XV proposal.

The 'registry of intentions' gives an overview of intentions in relation to Annex XV dossiers divided into:

- current intentions for submitting an Annex XV dossier,
- dossiers submitted, and
- withdrawn intentions and withdrawn submissions

for the three types of Annex XV dossiers.

International agreements

OSPAR Convention
OSPAR is the mechanism by which fifteen Governments of the western coasts and catchments of Europe, together with the European Community, cooperate to protect the marine environment of the North-East Atlantic.

Work to implement the OSPAR Convention and its strategies is taken forward through the adoption of decisions, which are legally binding on the Contracting Parties, recommendations and other agreements. Decisions and recommendations set out actions to be taken by the Contracting Parties. These measures are complemented by other agreements setting out:

- issues of importance;
- agreed programmes of monitoring, information collection or other work which the Contracting Parties commit to carry out;
- guidelines or guidance setting out the way that any programme or measure should be implemented, and
- actions to be taken by the OSPAR Commission on behalf of the Contracting Parties.

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[20] It should be noted that the candidate list is also used in relation to articles imported to, produced in or distributed in the EU. Certain supply chain information is triggered if the articles contain more than 0.1% (w/w) (REACH Article 7.2 ff).

HELCOM - Helsinki Convention

The Helsinki Commission, or HELCOM, works to protect the marine environment of the Baltic Sea from all sources of pollution through intergovernmental co-operation between Denmark, Estonia, the European Community, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden. HELCOM is the governing body of the "Convention on the Protection of the Marine Environment of the Baltic Sea Area" - more usually known as the Helsinki Convention.

In pursuing this objective and vision, the countries have jointly pooled their efforts in HELCOM, which is works as:

- an environmental policy maker for the Baltic Sea area by developing common environmental objectives and actions;
- an environmental focal point providing information about (i) the state of/trends in the marine environment; (ii) the efficiency of measures to protect it and (iii) common initiatives and positions which can form the basis for decision-making in other international fora;
- a body for developing, according to the specific needs of the Baltic Sea, Recommendations of its own and Recommendations supplementary to measures imposed by other international organisations;
- a supervisory body dedicated to ensuring that HELCOM environmental standards are fully implemented by all parties throughout the Baltic Sea and its catchment area; and
- a co-ordinating body, ascertaining multilateral response in case of major maritime incidents.

Stockholm Convention on Persistent Organic Pollutants (POPs)

The Stockholm Convention on Persistent Organic Pollutants is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have adverse effects to human health or to the environment. The Convention is administered by the United Nations Environment Programme and is based in Geneva, Switzerland.

Rotterdam Convention

The objectives of the Rotterdam Convention are:

- to promote shared responsibility and cooperative efforts among Parties in the international trade of certain hazardous chemicals in order to protect human health and the environment from potential harm;
- to contribute to the environmentally sound use of those hazardous chemicals, by facilitating information exchange about their characteristics, by providing for a national decision-making process on their import and export and by disseminating these decisions to Parties.
- The Convention creates legally binding obligations for the implementation of the Prior Informed Consent (PIC) procedure. It built on the voluntary PIC procedure, initiated by UNEP and FAO in 1989 and ceased on 24 February 2006.

The Convention covers pesticides and industrial chemicals that have been banned or severely restricted for health or environmental reasons by Parties and which have been notified by Parties for inclusion in the PIC procedure. One notification from each of two specified regions triggers consideration of addition of a chemical to Annex III of the Convention. Severely hazardous pesticide formulations that present a risk under conditions of use in developing countries or countries with economies in transition may also be proposed for inclusion in Annex III.

Basel Convention

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal was adopted on 22 March 1989 by the Conference of Plenipotentiaries in Basel, Switzerland, in response to a public outcry following the discovery, in the 1980s, in Africa and other parts of the developing world of deposits of toxic wastes imported from abroad.

The overarching objective of the Basel Convention is to protect human health and the environment against the adverse effects of hazardous wastes. Its scope of application covers a wide range of wastes defined as "hazardous wastes" based on their origin and/or composition and their characteristics, as well as two types of wastes defined as "other wastes" - household waste and incinerator ash.

The provisions of the Convention centre around the following principal aims:

- the reduction of hazardous waste generation and the promotion of environmentally sound management of hazardous wastes, wherever the place of disposal;
- the restriction of transboundary movements of hazardous wastes except where it is perceived to be in accordance with the principles of environmentally sound management; and
- a regulatory system applying to cases where transboundary movements are permissible.

Convention on Long-range Transboundary Air Pollution, CLRTAP

Since 1979 the Convention on Long-range Transboundary Air Pollution (CLRTAP) has addressed some of the major environmental problems of the UNECE (United Nations Economic Commission for Europe) region through scientific collaboration and policy negotiation.

The aim of the Convention is that Parties shall endeavour to limit and, as far as possible, gradually reduce and prevent air pollution including long-range transboundary air pollution. Parties develop policies and strategies to combat the discharge of air pollutants through exchanges of information, consultation, research and monitoring.

The Convention has been extended by eight protocols that identify specific measures to be taken by Parties to cut their emissions of air pollutants. Three of the protocols specifically address the emission of hazardous substances of which some are included in LOUS:

- The 1998 Protocol on Persistent Organic Pollutants (POPs); 33 Parties. Entered into force on 23 October 2003.
- The 1998 Protocol on Heavy Metals; 33 Parties. Entered into force on 29 December 2003.
- The 1991 Protocol concerning the Control of Emissions of Volatile Organic Compounds or their Transboundary Fluxes; 24 Parties. Entered into force 29 September 1997.

Eco-labels

Eco-label schemes are voluntary schemes where industry can apply for the right to use the eco-label on their products if these fulfil the ecolabelling criteria for that type of product. An EU scheme (the flower) and various national/regional schemes exist. In this project we have focused on the three most common schemes encountered on Danish products.

EU flower

The EU ecolabelling Regulation lays out the general rules and conditions for the EU ecolabel; the flower. Criteria for new product groups are gradually added to the scheme via 'decisions'; e.g. the Commission Decision of 21 June 2007 establishing the ecological criteria for the award of the Community eco-label to soaps, shampoos and hair conditioners.

Nordic Swan

The Nordic Swan is a cooperation between Denmark, Iceland, Norway, Sweden and Finland. The Nordic Ecolabelling Board consists of members from each national Ecolabelling Board and decides on Nordic criteria requirements for products and services. In Denmark, the practical implementation of the rules, applications and approval process related to the EU flower and Nordic Swan is hosted by Ecolabelling Denmark "Miljømærkning Danmark" *(http://www.ecolabel.dk/). New criteria are applicable in Denmark when they are published on the Ecolabelling Denmark's website (according to Statutory Order no. 447 of 23/04/2010).*

Appendix 2: Results of a mini survey aiming at identifying MDI and TDI containing coatings, adhesives and sealants on the Danish market

COATINGS

Product type Generic name	% MDI in product % TDI in product	Production (P) or import (I)	Application area (outdoor/ indoor, cement, wood, metal,..)	Application method (spray, brush, cartridge...)	% industrial/ % professional/ % consumer use %I / %P / %C	Typical size of packaging	WASTE		Alternatives Indicated chemistry as well as pros and cons (e.g. price, weather resistance, other quality parameters...)	*__Estimated total__* Danish market volume (interviewee's best guess) and market *__trends__* (increasing, decreasing, stable)
							Production – how disposed?	Recommendations for users		
Paint for concrete floor	5-10% MDI 10-25% Prepolymer MDI	P	Indoor, cement	Brush or roller	100 % Professional	5-20 L	Chemical waste- isocyanate	Chemical waste isocyanate – group Z	Water based 2 component epoxy. Pros: Better adhesion and chemical resistance. Cons: 2-pack (customer needs to mix and stir more failure happens thereby). Equal: Not necessarily better from a toxicology point of view.	"We don´t know what the total market volume is". "We can see that our production volume has increased, but we don´t know if our actual market volume has decreased."

Product type Generic name	% MDI in product % TDI in product	Production (P) or import (I)	Application area (outdoor/ indoor, cement, wood, metal,..)	Application method (spray, brush, cartridge...)	% industrial/ % professional/ % consumer use %I / %P / %C	Typical size of packaging	WASTE		Alternatives Indicated chemistry as well as pros and cons (e.g. price, weather resistance, other quality parameters...)	*Estimated total* Danish market volume (interviewee's best guess) and market *trends* (increasing, decreasing, stable)
							Production – how disposed?	Recommendations for users		
Paint for concrete floor	20-25% prepolymer MDI	P	Indoor, cement	Brush or roller	100 % Professional	5-20 L	Chemical waste- isocyanate	Chemical waste isocyanate – group Z	Water based 2 component epoxy. Pros: Better adhesion and chemical resistance. Cons: 2-pack (customer needs to mix and stir more failure happens thereby). Equal: Not necessarily better from a toxicology point of view.	"We don´t know what the total market volume is". "We can see that our production volume has increased, but we don´t know if our actual market volume has decreased."
Hardener for 2-component PUR coating	25-50% prepolymer MDI	P	Outdoor, indoor, cement, metal	Spatula	100 % Professional	2-20 L	Chemical waste- isocyanate	Chemical waste isocyanate – group Z	None, but the system can be a Water based 2 component, but that system also requires a hardener that is and an isocyanate.	"We don´t know what the total market volume is."
Protective paint for civil infrastructures	TDI (0-0.02 % (w/w)) MDI (2 - 3.5 % (w/w))	I	Outdoor	Spray / Brush	Professional	10 and 20 litre cans	Disposed as hazardous waste according to local regulations	See note below table	Not indicated	"Decreasing sales"

Product type Generic name	% MDI in product % TDI in product	Production (P) or import (I)	Application area (outdoor/ indoor, cement, wood, metal,..)	Application method (spray, brush, cartridge...)	% industrial/ % professional/ % consumer use %I / %P / %C	Typical size of packaging	WASTE		Alternatives Indicated chemistry as well as pros and cons (e.g. price, weather resistance, other quality parameters...)	*Estimated total* Danish market volume (interviewee's best guess) and market *trends* (increasing, decreasing, stable)
							Production – how disposed?	Recommendations for users		
Protective paint for on- and offshore windmills	TDI (0-0.02 % (w/w)) MDI (2 - 3.5 % (w/w))	I	Outdoor	Spray / Brush	Professional	10 and 20 litre cans	Disposed as hazardous waste according to local regulations	See note below table	Not indicated	"Decreasing sales"

Taken from SDS Section 13.1 Waste treatment methods:
The generation of waste should be avoided or minimized wherever possible.
Residues of the product is listed as hazardous waste. Dispose of according to all state and local applicable regulations.
Spillage, remains, discarded clothes and similar should be discarded in a fireproof container.
European waste catalogue no. (EWC) is given below.
European waste catalogue (EWC) : 08 01 11*

Product type Generic name	% MDI in product %TDI in product	Production (P) or import (I)	Application area (outdoor/indoor, cement, wood, metal)	Application method (spray, brush, cartridge…)	% industrial/ % professional/ % consumer use %I / %P / %C	Typical size of packaging	WASTE		Alternatives Indicate chemistry as well as pros and cons (e.g. price, weather resistance, other quality parameters…)	*Estimated total* Danish market volume (your best guess) and market *trends* (increasing, decreasing, stable)
							Production – how disposed?	Recommendations for users		
Foam sealants (general applications)	Approx. 10-25% MDI CAS-number 26447-40-5	I	In-door/outdoor	Aerosol cans	97% Professional 3% consumer	Aerosol cans, 0.5 and 0.75 l	Product imported	Hazardous waste: EAK: 16 05 04 (gases in pressure containers (including halons) containing dangerous substances) Special labelling (translated from Danish): " Spillage, waste etc. should be collected in designated containers marked "Isocyanate, risk of allergy" according to the Danish rules related to work with dangerous substances"	1. Isocyanate free foam (Silane/STP-basis) Cons: Fill effect: Foam more easily "fill" spaces. Price: Alternative about 8-9 times more expensive per volume filled with foam 2. Other insulation material e.g. rockwool Pros: Cheaper Cons: Foam more easily fill cavities	Estimated Danish market volume: 300 tonnes/year (corresponding to 30-75 tonnes MDI/year)

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2 component foam sealants (panel bonding, windmill adhesive)	Hardener: >90% MDI prepolymer	I	Outdoor	Putty knife / spraying	100% Industrial/professional	Cans, drums	NA – Product imported	Dangerous waste	Not indicated	Estimated Danish market volume: 100 tonnes/year (corresponding to approximately 90 tonnes/year prepolymer MDI)
Moisture stable wood adhesives	40-60% polymeric MDI CAS-number: 9016-87-9	I	In-door/outdoor Wood	Pouring	95% Professional 5% consumer	Plastic bottle. 0.75 l	Product imported	Hazardous waste: EAK: 08 05 01 (Isocyanate waste) Special labelling: as above.	MS/SMP adhesives Cons: Filling/foaming properties not as good 3-4 more expensive Tradition	Estimated Danish market volume: 40 tonnes/year (corresponding to approx.. 20 tonnes PMDI/year)

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							Production – how disposed?	Recommendations for users		
Joint sealants	For buildings joints: <0.1% MDI Joint seals: 0.1-0.5% 4.4-MDI CAS-number: 101-68-8	I	In-door/outdoor	Cartridge application	100 % Professional	Cartridge 0.31 l	NA (Product imported)	As above wood adhesives	MS/SMP- based joint sealants: Pros/neutral: Equal flexibility and price Cons: Lower chemical resistance (PU-based joint sealants are used when high chemical resistance is required, e.g. in stables) Tradition	Estimated Danish market volume: 140 tonnes/year (corresponding to approx. 100 to 400 kg MDI/year)
Joint sealants	0,01-0,6% MDI 0,01-0,04 % TDI, PRE	I	Outdoor, indoor, cement, wood, metal	Cartridge application, spatula	Industrial, professional and consumer	Cartridge/ bucket	NA (Product imported)	Dangerous waste	Not indicated	Estimated Danish market volume: 80 tonnes/year (corresponding to about 240 kg MDI/year and 200 kg TDI/year)
Yacht wood sealer	TDI (0,5 % (w/w))	I	Outdoor	Brush	Consumer use Professional (split is unknown)	0.75 litre cans	Disposed as hazardous waste according to local regulations	See note below table	Not indicated	Decreasing sales

Appendix 3: Cases on control of exposure to workers and the environment in Danish PUR plants

As noted in Chapter 6, it is assumed that good control is generally in place in PUR production facilities. The below cases, based on interviews, illustrate some aspects at some Danish PUR production facilities.

Information from Carpenter A/S

Carpenter A/S is the major Danish company producing flexible foams for furniture etc. The internal production site is continuously monitored for air quality to assure that legal demands for the protection of workers are fulfilled at any time.

Legal demands for reduction of escape of chemicals/volatiles are assured by monitoring the escape according to rules set up by the authorities.

The manufacturing process is continuously improved to reduce the amount of volatiles in the finished products by setting high standards to the raw material quality.

Recycling possibilities are improved by banning some hazardous substances in the raw material (e.g. some catalysts, some flame retardants).

Information from Logstor A/S

Logstor A/S is the only producer of district heating pipes and other rigid PUR insulated pipes in Demark. Logstor A/S advises that they have not had continuous control of MDI in the factory, but the company has on/off control measurements at the most critical parts of the factory for workers' exposure by an external company and in no cases have there been problems related to exposure for MDI. There are legal demands for ventilation and they are kept. There is optimisation of the processes in the factory but not with the aim of further reduction of MDI level. There is no control of the escape of isocyanate to the external environment, but risk assessments have been performed based on calculations.

Information from Gram Commercial A/S

Gram Commercial A/S is a Danish producer (Japanese owned) of refrigerators and freezers for industrial use (laboratories, hospitals etc.). Gram Commercial A/S advises that the demands from the authorities are kept regarding exposure to isocyanate in the factory, but that the demands in Japan regarding workers' protection against exposure to hazardous chemicals are more strict than in Denmark.

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