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SAFETY GUIDELINES FOR THE FLEXIBLE POLYURETHANE FOAM INDUSTRY

Foreword to the first revision

These guidelines were originally published in 2016. Since then, there have been advances in the regulatory regime governing the use of substances in our industry (most notably diisocyanates) and the collective industry knowledge has grown. Hence the EUROPUR and EURO-MOULDERS Environment Health and Safety (EHS) Working Group embarked on the journey to revise these guidelines in 2021.

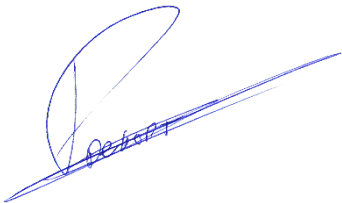
For the revision a Safety Guideline Expert Group was convened which guided the work of the secretariat in the revision, and we owe thanks to:

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Some pictures and figures included or referred to in this document are used with the kind permission of the companies Hennecke, Laader Berg and Dow Chemical.

It has been a great pleasure for the secretariat to work together with such competent experts on these guidelines that we hope will form the basis for the education of new EHS managers in our industry.

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Disclaimer

EUROPUR and EURO-MOULDERS have made every effort to present accurate and reliable information in this document in order to support the establishment of aligned safety management systems in the flexible polyurethane foam industry.

This document however merely provides advice and guidance, it does not exonerate polyurethane foam producers from implementing their own site-specific safety management systems and from monitoring regulatory or scientific developments they may need to take into account for updating their procedures. The sole responsibility for the implementation of site-specific safety management systems and compliance with all (local) legislation and requirements relies with polyurethane foam producers.

No representations or warranties are therefore made with regards to the completeness, accuracy or reliability of this document and no liability will be accepted by EUROPUR, EURO-MOULDERS nor any of their members for damages of any nature whatsoever resulting from the use or reliance on this document.



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A Introduction

These guidelines have been prepared by EUROPUR and EURO-MOULDERS and are designed for EHS managers that take up the responsibility to manage a flexible PU foam plant; to educate them on hazards and risk management measures that are specific to this industry.

The document is split into several chapters with the main chapters being on process safety and industrial hygiene. The chapter on process safety will focus on hazards that can cause major accidents (involving chemicals); their prevention and what to do if they occur. The chapter on industrial hygiene will focus on hazards and risks that one needs to control during the ordinary functioning of the flexible foam plant.

To illustrate this distinction with the hazard presented by diisocyanates. When a production run is started something can go wrong and the situation can arise that diisocyanates are released onto the conveyer belt which gives rise to massive airborne concentrations of diisocyanates exceeding limit values several times over. In the chapter on process safety advice will be given on system design to prevent this situation from occurring, which systems need to be put in place to ensure early detection of the incident (direct reading instruments linked to alarm systems), and what needs to be done after detection (shutdown and evacuation followed by specialised crew with RPE entering and remedying the situation).

When a production run is started normally, exposure should be expected to exceed limit values by a much smaller margin and only in specific areas. The guidelines provide guidance on where such exposure potential exists, how to identify these areas, and which RPE would be appropriate for these areas. Furthermore, guidance is provided in the field of continuous improvement to ensure that in these exposure critical areas are reduced in size and duration of over exposure. In addition, guidance is provided on how to measure and control diisocyanates exposure in general.

As the particular chemical hazards in our industry deserve special attention in terms of medical surveillance a separate chapter is dedicated to this which is directed towards the EHS managers in our industry. Finally a chapter with specific advice in the field of waste management is included.

However, first a chapter giving a summary process description will explain the production process for those new to the industry.

B Summary Process Description

The production of polyurethane is described in extensive detail in Ullmann's Encyclopedia of Industrial Chemistry [3]. The primary production processes to produce flexible polyurethane foam are: **Slabstock foam production** and **moulded foam production**, for both processes the handling of raw materials is nearly identical.

The finished product for both production processes (slabstock and moulded) is flexible polyurethane foam. The diisocyanates are fully consumed during the chemical reaction that creates polyurethane, due to the high reactivity of the NCO group present in the diisocyanates. They cannot be released into



the air from completely cured polyurethane foam. That is why there cannot be any exposure of consumers to diisocyanates resulting from cured PU foam [4].

B1 Raw Material

The primary raw materials for the production of flexible polyurethane foam (PUF) are diisocyanates (TDI, mMDI, p-MDI, MDI-based prepolymers or a mixture thereof) and polyol in a ratio of roughly 1:2 for TDI- and roughly 1.5:2 for MDI- based foams (though this may vary based on the NCO content of the MDI product). These are normally delivered in tank trucks and unloaded into a tank farm as shown in Figure 1.

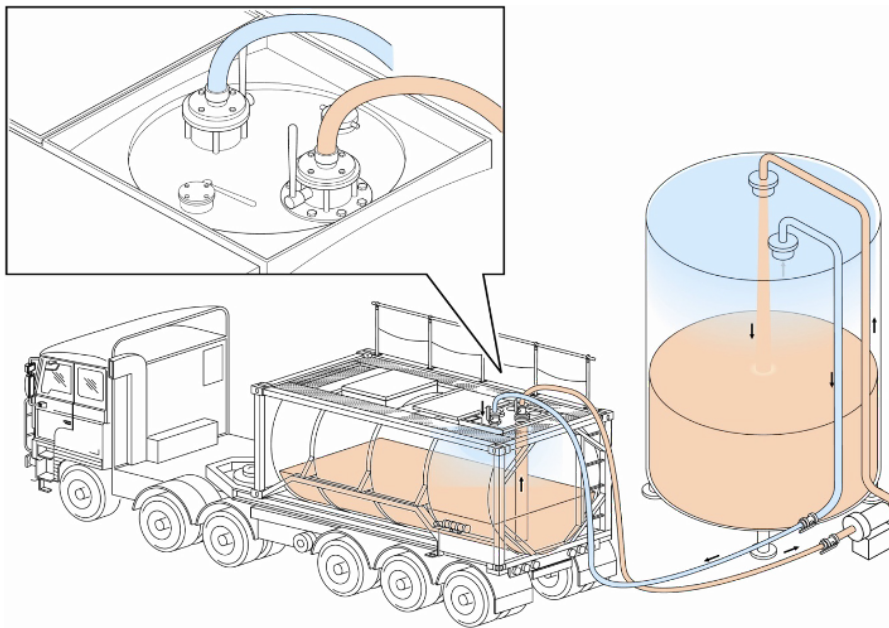


Figure 1 Tank truck unloading and storage tanks. Source: ISOPA

Catalysts and other additives are added in much smaller fractions into the formulations but are essential to the production process. They are normally liquids and delivered in IBCs or drums and may be connected to a closed piping for direct use from the container in which it came and/or the content of the container can be drained and fed into a closed tank system. The choice will be dependent on existing practice and the volume of the substance utilised. Solid additives (e.g. calcium carbonate filler) are normally delivered in either big bags or in more rare cases small bags and are normally fed into hoppers to be blended with polyol to create a suspension.

To obtain a foam structure a blowing agent is added. The primary blowing agent in the industry is water, which reacts with isocyanate groups to obtain an amine group and CO₂. For particular foam grades with typically lower densities an auxiliary blowing agent can be added. In the distant past these used to be CFCs, which are no longer used in Europe. Several foam producers utilise methylene chloride¹ as an auxiliary blowing agent, however this is progressively being phased out in favour of supercritical CO₂

¹ More formally known as dichloromethane (CAS 75-09-2)



injection, due to evolving evidence around the health, safety, environmental, and regulatory status of the substance.

Normally the formulation and blending of raw materials happens in closed systems. In some facilities, primarily in moulded foam production, polyol, additives, and catalysts are blended and subsequently stored in a day tank. This formulation is then delivered to a mixing head where it is mixed with isocyanates before being poured. In other facilities, particularly in slabstock foam production, all raw materials travel in separate lines to the mixing head where they are mixed before being poured.

B2 Flexible Slabstock Foam Production

During slabstock foam production the mixture is dispersed from the mixing head over a conveyor belt on which polymerization and foaming take place in parallel. The material is led and guided by foil² into a foaming tunnel to maintain the rectangular shape of the material. Usual dimensions of foam blocks in the industry are 2 m wide by 1 m high. The resulting densities range from 15 to 60 kg/m³ and belt speed from 2 to 10 m/minute. With higher densities the belt speed tends to be lower as dosage pumps become the limiting factor and are typically able to distribute max 500 – 600 kg/minute.

At the end of the foaming tunnel the foam liner, a paper or plastic or a combination of these, are removed. When a peelable paper is used, the plastic liner is left on the block. At the end of the production line, the foam produced is cut into blocks of up to 120m long. This **fresh foam** can be produced in a short a period as 3 minutes from the dispersion of the reaction mixture and the obtainment of the final shape.

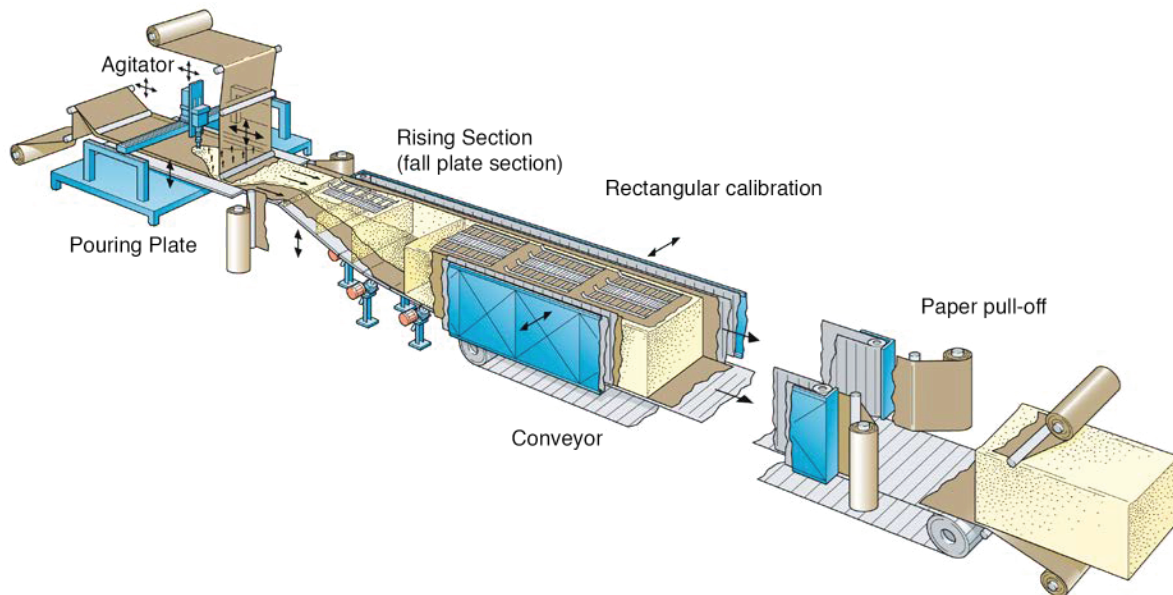


Figure 2 shows the agitator, pouring plate, rising section, conveyor and paper pull-off in a system for continuous production of rectangular flexible foam blocks. 3-D representation of a system – without metering device and cut-off saw – for continuous production of flexible rectangular foam blocks by means of the QFM process (source: Hennecke)

² The film may consist of paper, paper-PE foil, or pure PE foil.



Fresh foam is placed in dedicated curing areas for a period of 12 up to 72 hours, depending on foam type, to allow for curing of the foam, a process whereby residual substances (e.g. diisocyanates) react and the foam obtains its final physical/mechanical properties. The **cured foam** is subsequently transferred to regular storage areas. Long blocks are cut to short blocks before shipment and/or conversion on-site into (semi-)finished products. Certain foams require crushing before shipment or conversion to open the cell structure.

B3 Flexible Moulded Foam Production

In moulded foam production the reaction mixture from a mixing head is dispersed into a mould. Most moulded foam production for larger scale production series (e.g. automotive seating) is done with automatic pouring robots (see Figure 3) in a carousel system. For smaller scale production series manual pouring exists whereby an operator disperses the reaction mixture into the mould. The focus on the subsequent text will be on automatic pouring with a carousel system.

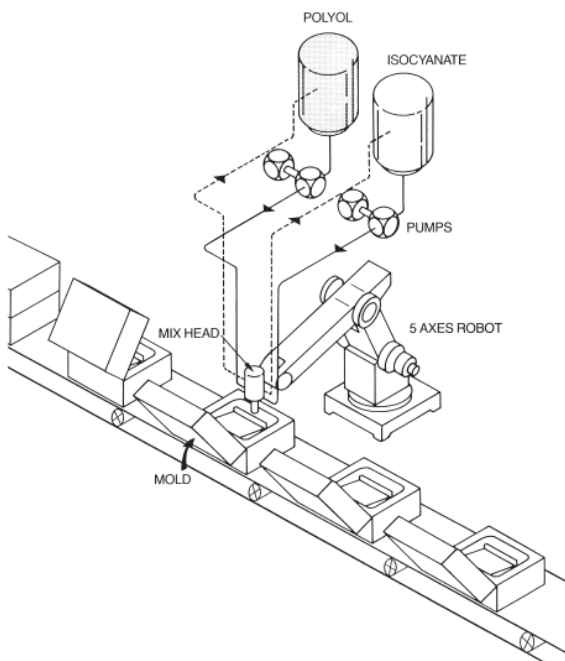


Figure 3 Schematic view of a moulded polyurethane foam production line (source: Dow Chemicals, 1997).

Within moulded foam production two variations of a similar process can be identified: hot-cure moulded foam and cold-cure moulded foam.

Hot-cure moulded foam production is schematically represented in Figure 4. Raw materials are injected into moulds automatically at the enclosed filling section of a carousel (d) thereafter the mould is automatically transferred to a closed oven (a), where temperatures of 160 – 250 °C are maintained. After foaming in the oven the mould is transferred to a working section where the mould is opened, the fresh foam piece is removed, the mould is cleaned and release agent³ is applied. After application of

³ Release agent is a wax like material that is sprayed inside the moulds to help demoulding.



release agent, the mould leaves the working section and enters the closed section where the mould is cooled (c) and the cycle repeats.

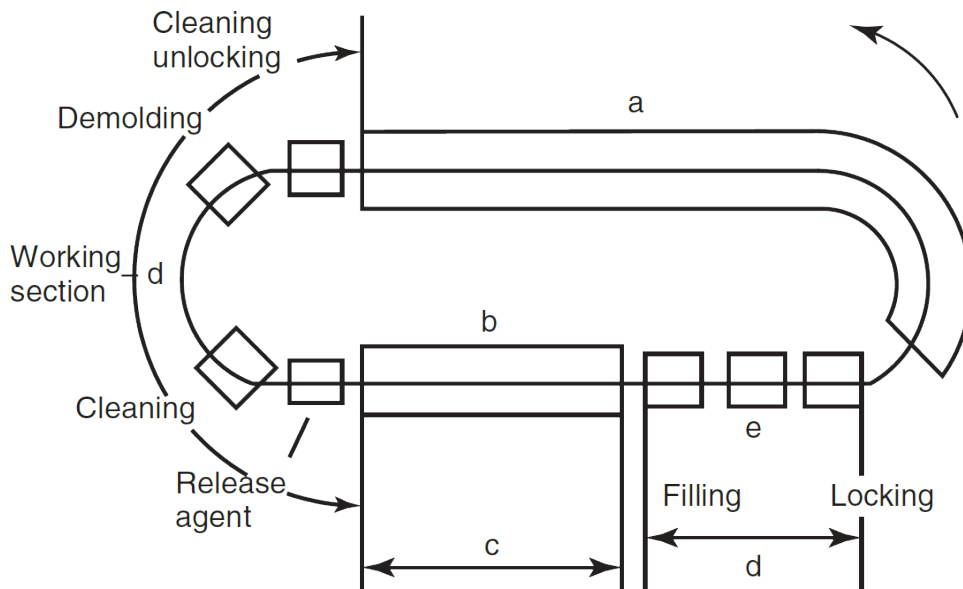


Figure 4 Plant for hot-cure mouldings: a) Oven (160–250 °C); b) Recirculating air/water bath; c) Cooling section; d) Working section; e) Inserts. Source: [3]

The cold-cure moulded foam production is performed using a similar carousel. However, instead of an oven the mould is kept at a lower temperature (e.g. 60 °C). Similarly, to the hot cure process, the pouring step till the unloading is performed in an enclosed environment.

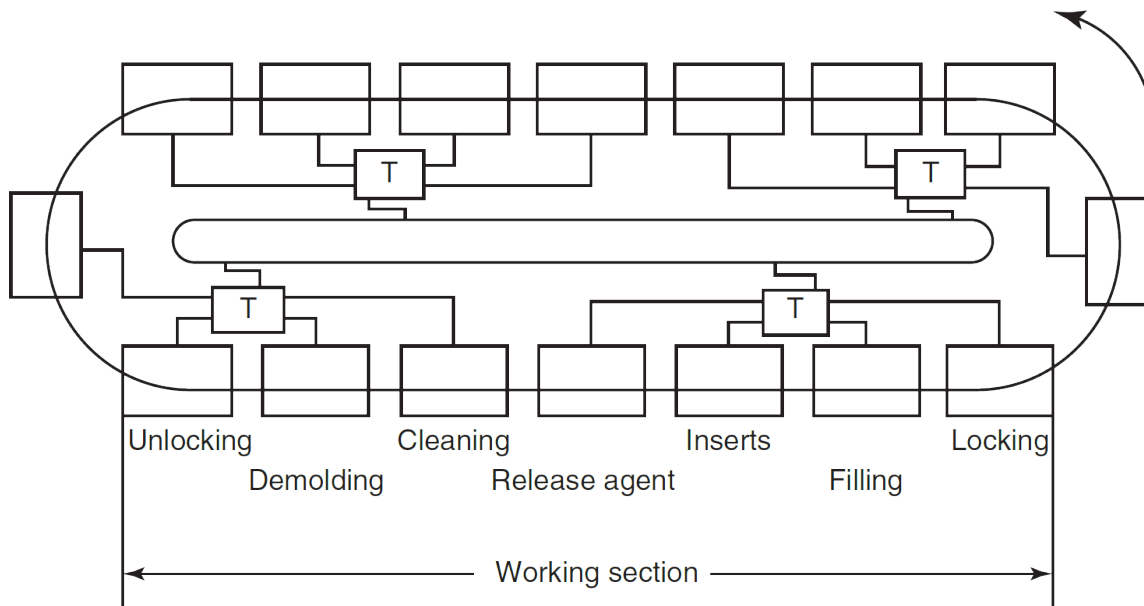


Figure 5 Plant for cold-cure moldings T=thermostatting units. Source: [3]



After demoulding foam can be crushed to break open some of the more closed cell structure formulations. This crushing prevents shrinkage and increases the air permeability of the foam. Subsequently the foam pieces typically go to a deburring and repair station where pieces are deburred and minor defects (e.g. pinholes) are corrected as needed. Subsequently the foam proceeds to either further processing/assembly (e.g. addition of a textile cover and other parts to form a car seat) or is shipped to customers.

The point at which the foam can be considered cured will depend on the temperature of the process, the size of the foam piece, and the formulation used. While it is up to each moulded foam producer to determine this point in the process, it is generally accepted that the curing time is much shorter than for slabstock foam and measured in hours.

B4 Other Foam Production

There are several other foam production processes. These guidelines might offer a source of inspiration for EHS managers in these fields, but these guidelines were not specifically designed to address the hazards and risks in these processes. Such processes include box foaming and rebond foam production.

C Process Safety

This chapter will focus on hazards that can cause major accidents (involving chemicals); their prevention and what to do if they occur. The hazards discussed here have a certain probability to occur and the harm they cause to someone or something tends to be immediate⁴ and important, i.e. they tend to be event based.

The frequency of events related to process safety should be understood as low and to be further minimised given the severity of the consequences. Such consequences can have magnitudes that exceed the boundaries of the plant. Many flexible foam production sites are therefore regulated under Directive 2012/18/EU on the control of major-accident hazards involving dangerous substances (Seveso Directive). In the chemical industry specific guidelines were developed to further elaborate on chemical process safety [5], that could offer some value to flexible foam production sites.

C1 Risk Assessment Principles and Methodology

The core of a Process Safety Management System is risk assessment. As a minimum for flexible polyurethane foam plants, risk management should ensure compliance with the Seveso Directive and local transposition provisions and that all precautions are taken to prevent incidents involving hazardous substances. Its purpose is the application of management systems and controls (programs, procedures, audits, evaluations) to manufacturing or chemical processes in such a way that process hazards are identified, understood, and controlled, so that process-related injuries and incidents are prevented.

⁴ More information on the possible immediate health consequences following process safety related events can be found in section E where the effects of diisocyanates on the human body are discussed.



Next to the requirements resulting from the Seveso directive and the hazards presented by hazardous substances, specific risk assessments can also be deployed for physical hazards (e.g. cutting risks).

There are several methods to perform risk assessments such as those listed in Table 1. These methods vary in level of complexity and specific applicability to processes in flexible foam production. It is advised to evaluate which method would be most suitable for different applications.

For example, for a newly constructed R&D lab at a facility it might be necessary to take samples of polyol from a tank farm. The activity of polyol sampling is an individual event that occurs infrequently and presents only a low hazard. Here a What ifs or Bow Ties analysis might be the most appropriate.

Table 1 Risk assessment methods

	Method	Applicable standard
Individual Events	What ifs	
	Bow Ties	ISO 3100 (Generic risk assessment standard)
Systemic	Fault tree analysis Event tree analysis	IEC 61025
	Failure mode and effect analysis (FMEA)	IEC 60812
	Hazard Identification study (HAZID)	
	Hazard and operability study (HAZOP)	IEC 61882
Addressing Risks identified	Layer of protection analysis	
Human Factor Technique	Safety Critical Task Analysis (SCTA)	ISBN 9781787251656 Guidance on human factors safety critical task analysis

The systemic techniques offer a formal and rigorous examination of a plant, process, or operation to identify credible risks of the complete system that can contribute to hazards or operability problems, by applying experience, judgement, and imagination, stimulated by key words, of the team. For example, the tank farm system can and should be assessed rigorously and systematically with one of the mentioned techniques.

The systemic techniques are best conducted by a cross functional team formed from Maintenance, Automation, Process, Operation, and Safety departments. The team should be led by an experienced process safety professional with knowledge of the assessment technique selected. Where knowledge or experience is not present in the organisation a competent external provider should be used.

These systemic risk techniques tend to include already some level of techniques for addressing the risks, but a more formal approach would be to perform a layers of protection analysis.



It is good practice to revisit the process risk assessments every 5 years, before any major changes are made or following an incident/near miss, by a team meeting the above requirements to ensure that the hazard analysis is consistent with the current process.

Finally, it is estimated that a large fraction of incidents and near incidents are the direct result of human failure; Safety Critical Task Analysis (SCTA) can be used to address this.

C2 Specific Risk Management Advice

C2.1 Raw Material Delivery/Storage/Blending

The most critical primary raw material to produce flexible polyurethane foam are diisocyanates. ISOPA, the European Diisocyanate & Polyol Producers Association, has developed specific guidelines on:

- Safe Loading/Unloading, Transportation, Storage of TDI and MDI in Bulk
- Safe Transportation, Unloading & Storage of Packaged TDI and MDI

These guidelines are available on the [ISOPA Website](#) in various EU languages. These guidelines are useful and to be followed. Their content will not be repeated in this document; but rather supplemented. Important elements in these guidelines include things such as:

- a good description of the hazard properties of the substances themselves,
- recommendations on the appropriate PPE,
- a detailed procedure for unloading, and
- good basics for tank farm design.

As a first point it is recommended for flexible polyurethane foam producers to only accept delivery of TDI in bulk. The volumes used are such that delivery in packaged form (i.e. drums or IBC) would result in a large number of transfer operations from such small containers to the tank farm, while bulk transport involves a single transfer with one operation minimizing the risk of an incident.

There may however be cases where a flexible foam plant only utilises relatively small quantities of a particular diisocyanate (e.g. limited volumes of MDI in a slabstock plant for occasional HR foam production). Alternatively, the plant may be operating in a country where infrastructure is lacking for effective delivery in bulk. In such cases packaged isocyanate may be received. In these cases, appropriate precautions should be taken to deal with the health and safety risks related to the used packaging on site (see chapter F).



Hazards and risks

While the ISOPA Guidelines contain good recommendations to address certain risks these are not always mentioned explicitly. Therefore, it is important to note that the following non-exhaustive list of risks exist in relation to unloading and storage of diisocyanates:

- An **adjacent fire**, during storage or unloading, this fire heating up the liquid isocyanates and inducing a tank rupture or a leak associated to a large cloud of hazardous substances.
- A **leak** followed by vapours emissions, tied to a rupture of the shell of the tanks or on the pipework, induced mainly by an external aggression, or any failure of the pipe work.
- A **tank collapse** coming from a wrong sequence of operations during unloading.
- A **runaway chemical reaction** induced by water or any incompatible chemical entering the tanks.
- An **over-pressurization** or an **overfilling** of the tanks, followed by a leak.
- An **under-pressurization** resulting in implosion and subsequent leakages.
- **Crystallization** induced by low temperature, or dimerization induced by an excessive heat strength even if both cases have only indirect consequences for safety. An implosion can occur with the offloading vehicle if the return line becomes blocked.
- An **unexpected truck motion**.
- **Risk of falling due to access at height**, for unloading.
- **Exposure to hazardous substances** (remaining liquids in hoses or due to an accidental situation or any leak) by skin contact and/ or inhalation.

Recommendations

All risks associated to a tank farm have to be assessed through HAZOP or similar method mentioned above. The foam manufacturer should develop a structure in which the risks assessments are part of a Safety Management System. Several measures that should be observed to prevent these process risks are listed below.

In addition to what is written in the ISOPA guidelines, the following principles for tank farm design should be observed:

- Tank farm design should take into account a risk assessment which includes the risk of earthquakes, heavy snow fall, flooding, and lightning; where applicable. In earthquake risks zones, the hanging of the pipework shall take this risk into account, to keep some flexibility of the pipework. In flooding risk areas, the submersion of the bund and the flotation of partially empty tanks shall be considered, by increasing the height of the bunds.



- There are three hazards that need to be addressed around **unloading of diisocyanates**: falling from height hazard, leakages, and adjacent fire:
 - With regards to falling from height, the best solution would be a safety platform with a safety cage enclosing the area and preventing falling from the tank. The next level would be a safe access through a gantry or stairs combined with a harness fall arrest system with guide rails. The next would be safe access through the tank container ladder, while wearing / using a “harness fall arrest” system. Any safe working system utilising a harness fall arrest must also ensure people are trained to use it; have supervision while using it; and have a rescue plan for the suspended person in case of a fall, unless the fall arrest block is a self-lowering block. All technical protection and harnesses should have in place an inspection and maintenance regime in accordance with the manufacturers guidelines.
 - With regards to the leakage hazard it should be noted that particularly with TDI, any leakage will result in concentrations of diisocyanates exceeding occupational exposure limits and workers with insufficient respiratory protective equipment (RPE) can suffer immediate health consequences⁴.
 - In the event of a large leakage a pool of diisocyanates may form around which any individual without RPE may suffer immediate health consequences⁴. Hence the unloading area must be bunded to prevent the spread of this pool.
 - A pool of diisocyanates would volatilise sufficient diisocyanates to cause exceedance of OELs in different parts of the plant or even beyond the plant. In the case of TDI the exceedance may be so great that there can be immediate health consequences⁴ in such an event. Therefore, it is recommended to have either or a combination of 1) a drainage system of the bunded area leading to an underground tank and/or 2) a closed unloading bay.
 - In the event a drainage system to an underground tank is installed, care should be taken to avoid the ingress of water into this underground tank. Drainage of diisocyanates into an underground tank containing water would cause a CO₂ generating exothermic reaction to start in the underground tank. This may cause an explosion or a large volume of CO₂ to exit the drainage system displacing air around the inlets of the drainage system that may result in incapacitation of workers around this area. Ingress of water may be prevented by the creation of cover over the unloading area from rainwater and/or by the use of a valve system that allows the drainage system to be directed towards rainwater collection or the underground tank. In case the latter option is used, during unloading the valve to the underground tank would be open and the one to the rainwater collection would be closed and when not unloading the reverse would be true.
 - A closed unloading bay would prevent ingress of water into such an underground spillage containment system. In addition, it would prevent access by unauthorised personnel if designed with access restriction. At the same time, any incident would result in even greater airborne concentrations within the unloading bay and the evacuation of workers engaged in



the unloading operation can be made more difficult by the creation of the closed unloading bay. Care should be taken to ensure that RPE is worn, and evacuation is not hindered. For example, designing access restriction in such a way to restrict access into the bay, but not requiring a badge to exit the bay and ensuring emergency exits on all sides of the unloading bay.

- Regardless of the design of the unloading area/bay wheel chocks should be placed before unloading commences to prevent unexpected truck movement that may cause leakages.
- With regards to an adjacent fire, it would be good if trucks are parked in such a way that would facilitate their departure in the event of an adjacent fire. For example, in the case of a simple unloading bay with one entrance, the truck should enter rear first. Should a fire be detected on the site a decision should then be made to determine if it is safe to remove the truck to prevent the content of the truck from catching fire.
- Such a decision is not to be taken lightly, as it may present a hazard for the person removing the tank truck. It should be clear within the plant at all times who has the authority and the responsibility to take this decision. Furthermore, all those with the authority and responsibility to take the decision should be involved in a what-if analysis of when to do what. There will be cases that are clear: if the fire is detected at the other end of the plant and the tank truck is not connected yet, the truck should be removed. As well as less clear cases, the fire is detected in the middle of the plant and disconnecting the truck would take minutes. Lastly, with fire it will be impossible to foresee each and every single scenario. The persons with authority and responsibility should be instructed to err on the side of caution, particularly in unforeseen situation, and not remove the truck when in doubt. Care should be taken to explicitly instruct these people to disregard the value of the content of the truck.
- Small **leakages** or containment breaches in containment of gases will result in concentrations of diisocyanates in the tank farm that can result in immediate health consequences⁴. Therefore, access to the diisocyanates tank farm should be restricted (by badges or keys) to authorised personnel. When unloading or maintenance operations take place authorised personnel should be equipped with suitable respiratory protective equipment and chemical suits. In addition, direct reading instruments for diisocyanate concentrations should be installed in the tank farm (see section D2.2 for more details on DRI), that is connected to a traffic light signalling system at the entrance to the tank farm. Lastly, cameras may be installed to enable operators to remotely monitor the status of the tank farm more accurately and appraise the situation safely in the event direct reading instruments shows elevated concentrations.
- The tanks need to be **equipped** with a safety system preventing the risk of overfilling and over pressurization. This system must be compliant with the IEC 61511 standard and should achieve a Safety Integrity Level (SIL) of 1 or 2 depending on a LOPA study. Care should be taken to ensure that the safety instrumented system operates to the specified level, by the correct selection of appropriate SIL rated sensors, safety logic control and final element such as a valve. The



installation of a SIL rated high level sensor alone will not meet this requirement. The design of these systems is normally performed by a function safety engineer.

- **Underpressure** can develop in the tank farm because of unloading blockages, the use of material from the tank farm, and/or a temperature drop (especially when tanks are very full). Such underpressure can cause tank implosion resulting in leakages and potential major damage. Underpressure should be (automatically) corrected through the ingress of gas. Nitrogen, dry air, or ambient air can be used. In the latter case the air needs to be dried for which a silica gel system is normally used. When using silica gel, it is best to utilise indicating silica gel in transparent columns, which discolours upon saturation with water enabling rapid detection of when such filters need to be replaced. Regardless of the method chosen the humidity of the gas in the tank farm should have a dew point of -20 °C or lower⁵ and the gas feed system should be able to ensure this. Ideally the tank pressure should be continuously monitored, and dew point should be measured at the gas inlet into the tank farm system.
- **Overpressure** can develop as well within tank systems as a result of the ingress of water, pumping into a closed system (especially with a high-pressure feeding pump), and/or an increase in temperature (especially when the tanks are very full). This can cause a tank rupture and subsequent leakages. To prevent overpressure a Safety Relief Valve (SRV) can be used to vent gas in the event of overpressure, as a second line of defence a separate bursting disk can be used that ruptures at a higher pressure than an SRV⁶. These safety systems should be SIL capable and equipped with sensors to warn operators. It should be noted that, if overpressure is corrected in this way, gases from diisocyanates containing tank farm systems will contain diisocyanates. Particularly when the system contains TDI these gases can cause immediate health effects⁴, and these should be vent through a suitable scrubber device such as activated carbon drum to an unoccupied area or at high level, according to local permitting conditions.
- Whenever designing new or retrofitting existing installations it is important to note that glass sight level monitoring tubes are not best in class, and should over time be replaced by alternatives (e.g. magnetic level indicators or ultrasound sensors) which are better suited to resist overpressure and are more resistant to physical damage.
- **Pipework** should be made from stainless steel (304L); especially when there is risk of condensation under the insulation of pipework. For diisocyanates carrying pipework regular steel is also acceptable, if there is proper treatment against corrosion and a maintenance/inspection regime to maintain this protection. The thickness should be selected so that it can resist the maximum pressure of the transfer pump and the expansion of organic liquids staying in a pipe if a difference of temperature appears along the pipework. Connections of pipework should be done by welding,

⁵ Some members aim for a dew point of -40 °C.

⁶ The difference between an SRV and a bursting disk is that an SRV opens when a set internal pressure is reached and closes the moment pressure drops below this point. A bursting disk will break would need to be repaired to be closed.



as threaded connections represent a risk of leak, and the use of flanges shall be limited to a minimum.

- **Flexible hoses** and tubing are used extensively in moulded and slabstock foam production, typically nearer to the point of dispersion than in the tank farm. They are, for example, connected to the release agent and connected to the mixing head of reaction mixture dispersion robots. Frequently these hoses carry material under high pressure (e.g. up to 150 bar) and represent a large risk for loss of containment. Regarding such flexible tubing the following recommendations apply:
 - Hose material and construction should be selected considering impulse, working pressure load, bend radius, and weight of the hoses. Furthermore, the chemicals that are being carried in the line can make the material harden. These elements must be discussed with the supplier of equipment to select appropriate materials of construction and set up a maintenance and replacement frequency.
 - Furthermore, a breach of containment of a hose or tube can result in ejection of material at high velocity causing spread of the content over a larger area. This can be prevented by applying an outer sleeve (e.g. a simple fabric layer). An added benefit of such outer sleeve is that it prevents, to an extent, chafing.
- Each **gasket**, valve seal and seat must be suitable for a contact with diisocyanates. This is of high importance as only some specific gaskets are resistant to diisocyanates.
- In terms of **pumps**, the best-in-class solution consists in magnetic coupling pumps where the risk of leakage is reduced for both unloading and transfer pumps. To avoid an overpressure induced by a sudden closure of a valve, associated to a concomitant failure of the internal safety relief valve of the pump, external safety relief valves or bursting disks are added as by-pass or to the pump. This solution has been made necessary by several incidents linked to crystallization of the internal safety relief valves. The pumps are normally the part of a tank farm more susceptible to leaks and should therefore be in a closed room or integrated into the tank farm with access restriction.
- Too low temperatures can cause **crystallisation** of diisocyanates which is primarily important for TDI, while too high temperature can cause dimerization of MDI. Both crystallisation and dimerization can cause the formation of solid material in the tank farm systems causing blockages. Therefore, temperature management is crucial in a tank farm system for which the following considerations apply:
 - It is important to take note of the temperatures of raw materials received. Particularly with diisocyanates too low or too high temperatures can cause issues. Furthermore, if the tank container cools too much during transport, the haulier may have heated the truck. This may have been done by circulating warm water around the tank ensuring gradual heating of the tank content. There are cases where steam is applied to this circuit since it is faster – but may also risk overheating.



In the case of low container temperature, there is a possibility that TDI in the tank consist of both liquid and solid TDI. Typically, this will only become known during unloading and safety systems should be in place to deal with this eventuality.

- Internal heating inside the tanks is not acceptable due to the risks it creates.
- Oil based heat management systems, while beneficial from a safety point of view, due to the lack of reaction potential with diisocyanates, are quite inefficient heat transfer media and therefore not frequently used. When designing water-based heat management systems the potential runaway chemical reaction between diisocyanates and water should be considered. The use of water-based heat management systems for polyol and most other substances used in flexible foam production do not present this concern.
- (Plate) Heat exchangers are a typical component of heat management systems in tank farms (see Figure 6). A raw material circuit exchanges its heat with another liquid circuit (normally water). When using this technology with water and diisocyanates it is strongly recommended to use double wall plate heat exchangers with leak detection. A breach of the water circuit (e.g. due to corrosion caused by poor quality water) would then not automatically result in contact with the diisocyanates circuit and vice versa.

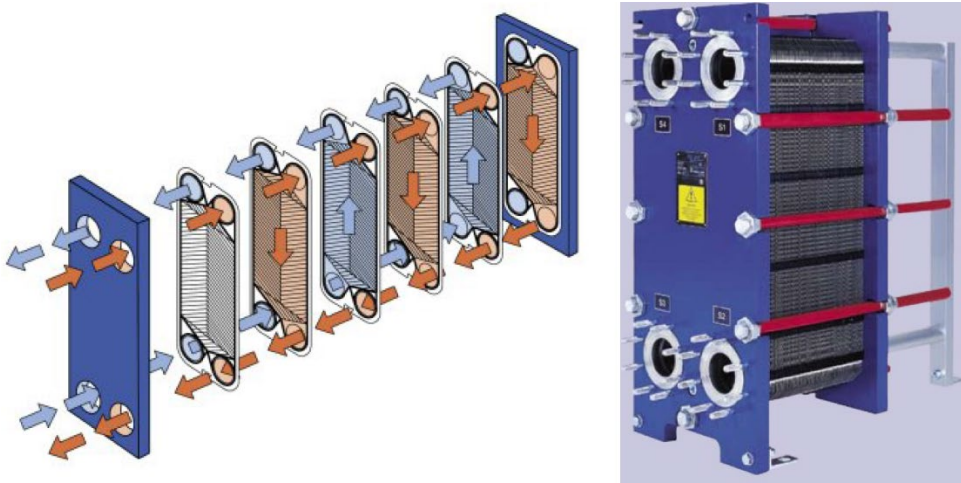


Figure 6 Example of a plate heat exchanger

- For non-double wall plate heat exchangers, the following pressure considerations should be made:
 - If water is used in a heat exchanger in contact with diisocyanates it is advisable to ensure that the pressure of the line carrying diisocyanates is slightly higher than that of the water line. In this way should a breach occur, the diisocyanates will flow out and react with excess water, which would generate CO₂ and heat and may damage the heat exchanger. However, the alternative is that water would ingress into the closed tank system generate CO₂ and heat, with more severe consequences.



- For most other combinations (e.g. oil and diisocyanates or water and polyol) the same pressure differential should be applied to prevent ingress of the heat exchange liquid into the tank farm system.
- Lastly, extreme care should be taken when installing or maintaining these heat exchangers to ensure that there is no mismatch in the connections, since this could result in the heat carrying liquid to move into the tank farm system and vice versa. In case of diisocyanates this could result in a runaway reaction with large consequences. A best practice would be to apply a colour system to lines carrying water, diisocyanates, and polyol and a similar marking on the heat exchanger.
- The storage building shall be protected from adjacent external and internal fires. The best-in-class standard integrates two separate rooms, one for diisocyanates and one for polyols, with separate bunds, and both integrated into a fire-proof compartment. The tank farm should be equipped with a fire detection and a fire suppression system. A sprinkler protection is compatible with isocyanates storage. Suitable extinguishing agents include dry powder, carbon dioxide, protein-based foam, and water⁷. No combustible storage nor flammable storage can be allowed in the tank farm.
- Similar arrangements should be made for diisocyanate and polyol storage close to the point of use. It is normal to store polyol blends and diisocyanates separate from each other in the same room as the risk from cross contamination is reduced by configuration of the equipment and presence of smaller quantities. It is normal in these areas for pumps to increase the pressure to a high level before dispersal from the mixing head. This presents an increase in risk from spraying of liquid due to small leaks and increased temperatures of the chemicals requiring the use of heat-exchangers. Equipment should be designed with internal safety relief systems, magnetic couplings. Where water is used as a cooling medium it should be pumped at a lower pressure than the diisocyanate to avoid contamination of the day tank . A small local closed loop cooling circuit connected to the wider plant via a conditioning unit should be used.
- Release agents used in moulded foam production can be made from combustible or flammable solvents. It is recommended that a Hazard Area classification (EU ATEX Directive) assessment is made for this location and appropriate zoning requirements respected. This may include a dedicated fire-resistant and bunded room, used for storage and/or pumping. The entire pipework used for the release agent should be grounded and clearly labelled to reduce the risk from electrostatic discharges. Wherever possible, flanges and gaskets should be fitted with guards to control releases. Exhaust systems should be put in place at the location of use.
- Catalysts and additives are transported in drums or IBC. Such substances can present specific hazards (e.g. certain catalyst are corrosive, respiratory irritants/sensitisers, toxic for skin contact or may cause serious eye damage). Therefore, during pumping and manipulation, air emissions should be reduced to a minimum by the usage of closed batches, efficient local exhaust ventilation

⁷ If water is used, it must be in very large quantities. Care must be taken as the reaction between water and hot TDI / MDI may be vigorous.



and air balance, and seals placed on top of the drums during pumping. If the additives or catalysts are pumped out of a drum placed vertically, the exhaust tube shall be cleaned after use and stored in a well-ventilated area. In case there is a dedicated blending room it must be installed in a bund. The precautions usually applied for chemical usage are applicable here as well.

The above are design-related recommendations. The following more organisational measures should be considered as well:

- To prevent the risk of a runaway chemical reaction occurring due to a reaction between diisocyanates and polyols, strict checks should be put in place of incoming materials to ensure that the right material is unloaded into the right tanks. Wherever possible, off-loading connections should be of different design and not placed next to each other. ISOPA guidelines recommend that diisocyanates are offloaded from the top of a tanker and polyols from the bottom.
- The ISOPA guidelines describe a procedure for dealing with spillages of diisocyanates, specifying amongst other things a decontaminant solution that contains 5 – 10% sodium carbonate, 0.2 – 2% detergent, and adding water to make up 100%. Some SDS for diisocyanates specify the following decontamination solution as an option: 3 – 8% concentrated ammonia solution, 0.2 – 2% liquid detergent, rest water. Such a solution would have the beneficial effect of the noticeable odour, alerting any worker with an incorrectly fitted mask. Care should however be taken in the preparation and handling of the solution as a concentrated ammonia solutions present their own hazard.
- Regardless of the decontaminant solution used, there should be sufficient of it and also a solid sorbent material (e.g. sand) available and ready to go in case of spillages. The procedure for dealing with spillages should be to first apply solid sorbent to the spillage and only afterwards to apply liquid decontaminant solution. Only for very small spillages liquid decontaminant solution can be applied directly. More information on the reaction between diisocyanates and water can be found in appendix 1 of the [ISOPA Guidelines](#).

C2.2 Slabstock Foam Production

Some of the recommendations given in section C2.1 apply here up until the slabstock foam line. For example, the use of stainless-steel piping and the recommended avoidance of threaded connections apply also for the mixing head where the diisocyanates, polyol, catalysts and additives are dispersed. These will not be repeated in this section. Instead, specific risks will be mentioned as well as means to prevent and control such risks.

Diisocyanate overexposure incidents

Certain events can cause a spike in diisocyanate concentrations on the mixing platform and potentially the entire foam hall or other areas. These include:

1. A wet laydown: a situation in which only diisocyanates or a mixture of diisocyanates and water or additives without polyol is dispersed from the mixing head.



2. A situation whereby the foam block is prevented from progressing down the line (e.g. a saw not moving up at the end of the line) resulting in reaction mixture spilling onto and over the mixing head.
3. A piece of tubing from the mixing head into the trough disconnecting while foaming.
4. Failure of containment of diisocyanate containing piping or pumps.
5. Absence or lack of ventilation due to, for example, extraction ventilation failure (e.g. not switching on or saturation or blockage of carbon filters).

Such events typically result in concentrations of diisocyanates well above occupational exposure limits⁸ and can cause immediate adverse health effects (more details in section E on medical surveillance). Such events should be prevented as much as possible by technical and organisational control mechanisms such as:

1. The start-up program for the line should specify that the polyol should always be dosed into the mixing-head before the diisocyanates and the diisocyanates may not start flowing until pressure is detected in the mixing head.
2. Emergency stop buttons should be located along the line particularly at the sawing station at the end of the line.
3. Procedures to check the tightness of the connection of tubing from mixing head to the trough by two operators.
4. Periodic checks and maintenance to ensure tightness of the piping system and pumps.
5. Setting up a system that prevents the start-up of the line in the event of extraction ventilation failure.

In addition, while such events should be prevented, direct reading instruments should be located on the mixing platform that gives a first alarm when a first lower threshold is exceeded informing workers to wear respiratory protective equipment. A second alarm should be set at a higher threshold triggering a manual or automatic (emergency) stop procedure and subsequent evacuation of the production hall (see D2.2 for more details on DRI). Afterwards a specialised team may go in with suitable respiratory protective equipment to remedy the situation.

Most of such overexposure incidents occur during the start-up of production. Therefore, operators must use respiratory protective equipment during the start-up phase, as these are vital in preventing immediate adverse health⁴ effects following overexposure incidents.

Hot formulations and start/stop/changeover pieces

The reaction that produces flexible polyurethane foam is exothermic meaning that heat is formed over the course of the reaction. A foam block peak temperature may be reached between 4 – 6 hours after foaming due to curing reactions. At this time the foam is present in the curing area. Formulations that

⁸ For example, verbal reports provided to the secretariat revealed that during incidents direct reading instruments indicated levels around 100 ppb and in rare cases 200 ppb (the maximum level the equipment can detect). At the moment of writing, the short-term exposure limit (STEL) varies between countries, but is generally <20 ppb.



result in a peak foam core temperature of more than 175 °C, present a high risk of self-ignition, while formulations, that result in a peak foam core temperature of less than 165 °C, are generally considered to have no fire risk. For foams with a peak foam core temperature between these temperatures there is a chance that the foam will self-ignite as well, this thus needs to be avoided as well. The foam core temperature should be checked especially after start-up and during recipe changes.

A formula was developed for that can be used to estimate the peak core foam temperature⁹ [6]:

$$T_p = 69 + T_{RM} + 1.394 \times C_{TDI} - 1.17 \times C_{MC}$$

Where

T_p	Peak foam core temperature (°C)
T_{RM}	Temperature of the raw material used at the mixing head (°C)
C_{TDI}	Concentration of TDI in the formulation (pphp ¹⁰)
C_{MC}	Concentration of Methylene Chloride (pphp ¹⁰)

It should be noted that while this formula has a good predictive value overall, it does not factor in density of the foam, ambient temperature/humidity, size of the cross section of the foam block, and other factors that can play a role in the temperature development in the core of the foam block. The formula result should be used as indication which requires experimental verification especially in the critical area $T_p \geq 160$ °C.

Another factor to consider is the importance of antioxidants in the prevention of combustion and/or scorching events. Polyols that are designed for slabstock foam production contain a stronger antioxidant package than polyols used for other polyurethane applications (e.g. CASE polyols). Normally suppliers of polyols for flexible foam will take this into consideration, however one needs to be aware of this factor when blending different polyols for flexible foam production or when approving new polyol grades.

For the reason above it is important to measure the foam block core temperature, particularly when producing new formulations and riskier formulations. Riskier formulations are formulations where the formula above indicates temperatures around 165°C, lower densities, and/or foams that have shown to approach a value of 165 °C in previous measurements. It is advisable to maintain a database of time/temperature graphs linked to formulations to develop competence in prediction peak foam core temperatures.

To perform such measurements, it is recommended to install temperature monitoring systems in the curing area. The best practice is to use an electronic thermocouple type thermometer which consist of

⁹ The formula assumes the use of polyol with antioxidant packages designed for flexible foam production. If polyols with insufficient antioxidants are used (e.g. CASE Polyols) the formula does not apply. Polyol suppliers could be contacted to learn how to correct the antioxidant deficiency of such polyols.

¹⁰ pphp stands for parts per hundred parts polyol, a common unit in the creation of flexible foam formulations.



a direct reading temperature metre and probe. The probe may be detachable so that one direct reading meter can be used to service as many probes as required for insertion in polyurethane foam blocks to measure their temperature profile as a function of time. The operating temperature should be 0 – 200 °C, with a resolution of at least 0.1 °C and an accuracy of ± 0.5 °C.

The thermocouple of the probe must have provision for cold junction compensation effective over the operating temperature range of the instrument. The hot junction of the thermocouple shall be situated in the extreme end of the probe tip and shall also be insulated from the rest of the probe to eliminate any cooling effect on the tip of the probe by conduction of heat along the probe length.

The probe shall consist of a 2 – 5 mm diameter metal shaft of robust construction, resistant to kinking and normal handling hazards experienced during the process of inserting the probe into the block of foam under test. The length of the probe should be chosen to allow the tip of the probe to reach the centre of the foam being tested.

The thermocouple shall be calibrated according to manufacturer's specification and consider the range of typical polyurethane foam block peak exotherm temperatures.

When producing short blocks, the first and last **production** blocks of a single formulation should be measured. When producing long blocks both ends of the long blocks should be measured at no less than 1 meter from the block ends. Deviations from this procedure should be justified and deliver the same results.

The start, stop and changeover blocks should not be measured but simply moved to a dedicated area (more details on what those are and what needs to be done with them can be found below).

It is important to note the time of production of the sections of foam being measured and the probe should be inserted as soon as possible to be able to make a time-temperature curve where the pouring of the reaction mixture is set at time zero. The probe may be inserted at any face and should be inserted to such a depth to reach the centre of the block considering the dimensions of the block. To overcome the effect of polyurethane foam densification in front of the probe tip during and at the end of its insertion the probe shall be withdrawn about 1 – 2 cm. The temperature should be logged every 10 minutes until the temperature has fallen at least 40 °C below the peak foam core temperature after which the measurement may be discontinued, and the probe removed.

Blocks indicating a core temperature above 165 °C should be removed from the curing area. In addition, the temperature profiles of measured formulations should be stored and periodically reviewed by the ones who decide as to whether to keep the new or riskier formulations in the curing area. This enables to build up competence in prediction the time/temperature graphs. Should it be clear to this person that a foam block will exceed a temperature of 165 °C, this person should be authorised to remove the foam from the curing area.

When removing this foam, it should be placed in a dedicated area, best outside, away from any combustible material. Ideally the blocks should be cut to short blocks in the removal process. When temperatures develop in such a way that it is clear they are going to reach 170 °C in the core of the



block or if the foam has reached 170 °C in the core of the block; preparation should be made for the possibility that the blocks will combust, meaning sufficient firefighting capacity should be readied to extinguish the blocks.

Since combustion in these blocks starts at the core and moves towards the skin and as foam is an insulator, applying water to the outside of the block will only have limited effect. It is therefore strongly recommended to use water lances (see Figure 7). These tools were originally developed for management of container fires. Water lances can be connected to firefighting hoses and used to make small holes in the foam to deliver water under pressure into the core of the block. When using these devices, it is important to make sure that you have long small sharp pins to assist in making holes, enough connection with the water supply, and enough pressure to feed all the lances needed for multiple blocks at the same time.



Figure 7 Water mist lance. Source: [Viking](#)

The procedure above is for controlling the fire hazard of foam with known composition within certain parameters. However, during start-up, stop- and changeover-¹¹operations the mixing ratio of the different components of a formulation fluctuate and are thus not according to specifications. This results in start, stop and changeover (SSC) sections that can behave unpredictably in terms of temperature development. Such SSC sections must be removed from the line and dealt with as a fire hazard.

Foam producers have various ways to deal with these SSC pieces. Some simply remove these and place them outside in a dedicated area. Others move them to specifically designed bunkers where they can be monitored, and a fire suppression system might be in place. Both options are acceptable, but the dedicated bunker system is preferred. In a dedicated bunker system environmental emission of substances from foam by rainwater are prevented. As most pieces do not combust, the foam itself may be used as a B-grade foam, flocked for cushion filling or used for rebonding.

Regardless of the site of disposal these SSC blocks themselves form a fire hazard from the moment of their creation till their cooling sets in 4 – 6 hours later. The degree of their hazard can however be

¹¹ A changeover operation is an operation whereby the formulation is changed to produce another grade of foam without stopping the production.



minimised by better production planning and proper sequencing of the dosing of formulation components and the following rules should be taken into account:

- When planning a foam production run, in which several grades of foam will be produced with changeovers in between, it is advisable to start with the lowest density foam and move to increasingly dense formulations, whenever possible. Furthermore, during changeovers, the greater the change in formulation (resulting in density variation), the riskier the changeover piece becomes. This holds true especially for formulations with a density below 30 kg/m³.
- With regards to dosing of formulation components, there are currently systems on the market whereby start-up, changeover, and stop procedures are digital and timing of opening and closing of valves and such is done automatically. In such equipment suppliers will be able to assist in the programming to ensure safe and controlled dosing of formulation components. There are also, however, (older) analogue systems, that require manual interventions on a control panel. For such systems it is important to note that:
 - In the start-up procedure it is important to ensure material streams are opened in the following order: polyol then diisocyanate then water.
 - When increasing foam density, water dosage should be lowered before the dosage of diisocyanates is lowered and finally adjustments in other components can be made.
 - When decreasing foam density, diisocyanates dosage should be increased first followed by the increase in water loading.
 - During a shutdown sequence first stop water, then diisocyanates, then lastly stop polyol.

The aim here is to ensure that no sections of foam are created that cause a fire hazard through inappropriate more risky mixing ratios (e.g. too high water or diisocyanates). Such sections could be non-uniformly distributed throughout the block, meaning thermocouples would not necessarily measure these sections.

Compression of fresh foam can also occur by (malfunction of) conveyer belt systems, for example if a first conveyer runs at a faster speed than a second conveyer. Incidental generation of such foam should be avoided and fresh foam that has been compressed should be carefully monitored with temperature measurement as described above.

Curing areas and regular storage

Fresh foam blocks should be stored in dedicated curing areas, as such fresh foam will emit residual diisocyanates¹² during their curing time. Furthermore, even if there are no hot formulations, there is still a residual fire hazard.

¹² The levels of diisocyanates that can be found around fresh foam should not be confused with the levels around overexposure events. These levels are much lower and should not result in immediate health consequences, they are further addressed in the section on industrial hygiene.



Such curing areas typically are in the form of a rack system but may also be simple halls in which the foam is placed on the floor. Regardless of the system employed, at least 5 cm of space should be kept between adjacent blocks to allow the internally generated heat to dissipate.

The minimum time that a block needs to remain in the curing area will need to be determined by each company based on the temperature developments recorded for each foam grade. A few rules of thumb can be mentioned however:

- Lower densities reach higher temperatures but also cool down faster
- VE grades tend to require longer time for curing than conventional ether foams

A best practice would be to locate the curing area away from any other building and/or to install a deluge sprinkler protection with dispersion points above each foam block to control the fire risk. The curing area should also be access-restricted as much as possible to limit diisocyanate exposure.

After curing the foam can be moved to regular storage. It is a best practice to maintain a fire suppression system here as well. The amount of foam stored, and the storage height should be according to the design of the warehouse fire suppression system and the tipping risk¹³.

C2.3 Moulded Foam Production

Some of the recommendations given in section C2.1 apply here up until the dispersion of reaction mixture (i.e. polyol, diisocyanates, catalysts and additives). For example, the use of stainless-steel piping and the recommended avoidance of threaded connections apply up until the mixing head where the diisocyanates, polyol, catalysts and additives are dispersed. These will not be repeated in this section. Instead, specific risks will be mentioned as well as means to prevent and control such risks.

Diisocyanate overexposure incidents

Certain events can cause a spike in diisocyanate concentrations around the pour point and potentially spread to other areas. These include:

1. Miss-pour: a situation whereby only diisocyanates are poured into the heated mould.
2. Failure of containment of mixing-head via flexible hoses or pipe junctions.
3. Absence or lack of ventilation due to, for example, the extraction ventilation not switching on or the saturation/blockage of carbon filters.

Such events typically result in concentrations of diisocyanates well above occupational exposure limits and can cause (immediate) adverse health effects (more details in section E on medical surveillance). Such events should be prevented as much as possible by technical and organisational control mechanisms such as:

1. The use of pressure sensors to detect lack of polyol pressure and/or a camera system that monitors the pours into the mould. Emergency stop buttons to enable operators to stop the machine in the

¹³ While foam is a low-density material, a block falling from a certain height can harm workers.



event this happens. Direct reading instruments connected to a safety system stopping the line in such an event.

2. The selection of a suitable hose material and construction should be made including impulse and working pressure loads. An outer sleeve to avoid chafing, and regular maintenance checks and replacement, bend radius and supporting of the hose weight also merits consideration.
3. Setting up a system that prevents pouring of reaction mixture if ventilation is not working properly.

In addition, while such events should be prevented, direct reading instruments should be located near the mixing-head, that give an evacuation alarm should a certain threshold be reached. This alarm should trigger a production stop and evacuation of the foam production hall (see D2.2 for more details on DRI). Afterwards a specialised team can go in with suitable respiratory protective equipment to remedy the situation.

Release agent flammability

Release agent (RA) is a material normally sprayed on a mould prior to the pouring¹⁴ to ensure that the foam does not adhere too strongly to the mould preventing removal from the mould. RAs are normally a wax like material that are dispersed in a carrier fluid. Depending on the carrier fluid the following classifications can be made:

- Water-based; this is wax that is kept in solution/suspension in water
- Solvent-based; this is wax dissolved in an organic solvent
- Hybrid; this is wax in a combination of water and solvent
- Solvent-less; direct spraying of wax

The selection of RA depends on the finetuning of the moulds and the desired skin effect in the moulded foam pieces. From a safety perspective application of solvent-based RA presents the greatest fire hazard, followed by solvent-less dispersion, and hybrid RAs. Water-based RA is the safest option practically devoid of fire hazard.

Unfortunately, there are downsides to water-based RA in terms of efficiency. The carrier fluid needs to be largely evaporated before the reaction mixture is poured. For cold-cure lines operating at lower temperatures (e.g. 50 °C) the use of water-based RA will not result in dry moulds before pouring. However, for lines operating at lower speeds or at higher temperatures, switching to water-based RA can improve safety. Furthermore, due to the wax being in suspension rather than in solution in water, the total volume of wax that needs to be applied to ensure complete coverage of the mould is greater, thus increasing the frequency at which moulds need to be cleaned.

In some cases, electrostatic spray guns are used, which are devices used to spray the RA onto the mould while using charged molecules and electric fields. The RA is given a negative charge by the electrostatic spray gun while the mould being coated is given a positive charge. This creates an attraction between the RA and the mould, thus increasing efficiency. This technology however increases

¹⁴ Automation is being investigated and has been deployed successfully for moulds with less complex geometries.



the probability of two hazards by being able to cause a spark (e.g. by contact with a metal part or an insert and an insufficient current decrease of the high voltage generator).

1. When solvent-based RA is used a spark can result in jet fire, i.e. the sprayed material combusting to form a jet of fire. Should the trigger be locked, and the operator lose control of the gun (letting go could be an instinctive reaction) the gun would start moving with its movement being restricted by the hose connecting the gun to the piping system.
2. Should there be insufficient ventilation, the concentration of flammable VOC concentration around the release agent spraying station can reach explosive concentrations in the air, which can be ignited by a spark.

The combination of electro spray and solvent-based RA thus presents a unique hazard that needs to be managed accordingly. A combination of electro spray technology with water-based solvent systems does not present this hazard.

To control the fire risks the following guidance is offered:

- A release agent with a flash point as high as possible or an inflammable release agent should be selected. The presence of heavy metal salts in the wax should be carefully evaluated, and tin-based substances should be substituted to less hazardous substances whenever possible.
- Electrostatic spray guns should be replaced by pneumatic or other types of spray guns.
- The spray gun should be designed in such a way that release of release agent requires active pressing on a trigger. There should be no possibility to lock the trigger in place so that if an operator drops it the flow of material is stopped.
- Ideally the production line is fully enclosed (i.e. boxed) to allow a good capture of the emissions.
- Exhaust walls must be placed behind the demoulding stations, release agent spray booths, inserting and pouring booths. Compensation by an equivalent air volume is required compared to the volume extracted, with possibly heating or partial air cooling or air/air heat exchangers. Extraction should be positioned to pull vapours away from operators, and extractions should not be placed behind the operator or above their heads as this will increase their exposure. There is a risk that if extraction is not properly placed an opening mould may negatively affect the extractions performance. Especially when the production line is fully enclosed/boxed, care should be taken to ensure sufficient air is replenished so that exhaust ventilation operates optimally.
- The exhaust air volume inside the spray booth must be calculated to keep the concentration of flammable vapour well below 25 % of the lower explosive limit (LEL) of the solvents (This dilution has no effect on the risk of jet-fire).

Even if water-based RA is used, wax and dust will be extracted through the air extraction system. This could result in a build-up of combustible material on the walls of the ducting system of the air extraction system. To prevent this, filter systems should be installed at the intake point of this extraction system.



These filters need to be regularly maintained (i.e. primarily cleaned, sometimes replaced). The frequency of maintenance can be determined in cooperation with the manufacturer and/or be informed by a system to measure the pressure differential of air before and after the filter.

Depending on local circumstances it may be needed to install a system to capture solvent and residual release agent prior to emission through the exhaust system.

C2.4 Conversion

In both moulded foam production and slabstock foam production there are conversion activities, but these differ significantly in nature. In moulded foam production this involves mainly deburring and repair activities to correct small defects (e.g. fixing pinholes). The conversion processes with slabstock foam are more extensive in nature and may occur on site or at other facilities.

The hazards associated with conversion activities are mainly mechanical in nature. Most of these hazards are addressed in EN 14886 and will not be discussed here. It is highly recommended to adopt the practices mentioned in EN 14886.

With regards to use of gloves the standard does mention that: "The manufacturer shall indicate that for freehand cutting suitable hand protection should be used and that appropriate cut-resistant gloves should be worn; however gloves should not be worn when working with toothed bandknives.". Here it should be noted that use of gloves with toothed saws or blades carries the risk of the gloves getting stuck and pulling on the operator's extremities. The risk is particularly pronounced should chainmail cut-resistant gloves be used. Such gloves are typically the superior gloves when dealing with cutting risks, except if toothed blades are used and thus should be avoided in (maintenance) operations with toothed blades.

The standard also indicates that "harmful" dust emissions must be controlled. To clarify, dust from fresh, uncured foamblocks can indeed be considered harmful, as there are residual unreacted diisocyanates in such foam and should thus be controlled. Dust from fully cured foam should not be considered particularly harmful, and its management is something to be controlled by standard industrial hygiene practices.

Polyurethane foam dust is a combustible material. However, due to the flexible nature of the material, the volume created is small and particle size is large, meaning there is little to no explosion risk. There is however a particular point where it may accumulate, especially in dust pots of cutting equipment. These dust pots are designed to contain water to eliminate the risk. However, there should be a control procedure around these dust pots that there is sufficient water in them (e.g. at least visual inspection before the machine is turned on) and regular cleaning and replenishment of the water level.

C3 Emergency Response

A person within the company should be dedicated as responsible for the development of the emergency response plan. The emergency response plan is a document in which all scenarios are evaluated, described and the corresponding actions defined.



All possible types of emergencies with corresponding scenarios (e.g. fire, leak of chemicals, gas leak, flood) should be identified. A plan for what to do in each scenario should be drafted. These plans should identify clear responsibilities for those involved and employees should receive a document clearly summarising what needs to be done. In addition, regular training should be established.

For scenarios that require the assistance from emergency services (e.g. fire brigades) these should be consulted. These emergency services should be contacted and asked to participate in exercises simulating accidents involving these scenarios (e.g. issues with the unloading of diisocyanates). In these exercises it is important to record the response time and what kind of services/equipment can be provided. It may be appropriate to involve neighbourhood bodies when the scenarios indicate a risk (e.g. if a foam plant is located next to a school or supermarket).

Each emergency response exercise or real application is evaluated in order to learn from the possible deviations seen and to update the emergency response plan accordingly. In addition, the emergency response plan must be updated after each significant change in the installation and should be reviewed once a periodically.

C4 Audits

For multi-site companies a good practice is to organise safety audits whereby relevant personnel review each other's practices and procedures. This enables to exchange best practices.

ISOPA has developed an assessment tool for tank farms which can be used for self-assessment or assessment by ISOPA member companies. The supplier of diisocyanates can be contacted to provide such a tank farm assessment.

EUROPUR and EURO-MOULDERS strongly recommend to their members to have their tank farm assessed (internally or by a third party)

D Industrial Hygiene

This chapter will focus on the hazards (of chemicals) to workers that need to be controlled under normal operating conditions. In the context of this chapter the hazards tend to be ever present (e.g. airborne vapours of certain substances), where dose makes the poison and whether there is a risk for adverse health effects depending on whether the hazard is controlled to a level below thresholds.

For example, it is impossible to completely avoid diisocyanate exposure during normal running of a polyurethane foam plant, but the level of exposure needs to be controlled to comply with occupational exposure limits and/or to reach As Low As Reasonably Practicable (ALARP).



D1 Chemical Agents

In the production process of flexible foam production, the primary raw materials are diisocyanates and polyols. Furthermore, many other substances are used in the formulation such as amine catalyst, metal catalysts, and silicone surfactants. Depending on the desired foam properties, other classes of substances may be used as well, such as flame retardants, fillers, colour pastes, and auxiliary blowing agents. Next to foam ingredients, other substances or mixtures may be used, such as solvents for cleaning/flushing of equipment, cleaning agents, paints for direction markings, glues (e.g. for converting).

The highest exposure risk during the foaming operation is probably due to the diisocyanates. As such this will be discussed in the subchapter below, followed by best practice advice for other intentionally used substances, and finally to conclude with a note on non-intentionally used substances. A workplace assessment is required and will show whether the measures applied to control the risk of diisocyanate exposure will also cover the risk from other chemicals used.

D1.1 Diisocyanates

There are two main diisocyanates used in the production of flexible foam: TDI and MDI. MDI used in flexible foam production is a mixture of polymeric MDI (pMDI) and monomeric or “pure MDI” or an MDI-based prepolymer¹⁵. TDI and MDI have nearly identical hazard classification and the most critical endpoint is respiratory sensitisation, which can result in occupational asthma. More details on sensitisation and occupational asthma can be found under section E.

Table 2 Harmonised Hazard Classification of TDI and MDI

	TDI	MDI
Name	m-tolylidene diisocyanate; toluene-diisocyanate	methylenediphenyl diisocyanate
Cas	26471-62-5	26447-40-5
EC	247-722-4	247-714-0
CLP Index	615-006-00-4	615-005-00-9
Harmonised Classification	Acute Tox. 1 * Resp. Sens. 1 Skin Sens. 1 Carc. 2 Eye Irrit. 2 Skin Irrit. 2 STOT SE 3 Aquatic Chronic 3	Acute Tox. 4 * Resp. Sens. 1 Skin Sens. 1 Carc. 2 Eye Irrit. 2 Skin Irrit. 2 STOT SE 3 STOT RE 2 *
Vapour pressure (25°C)	1.5 Pa	0.0014 Pa

¹⁵ Sometimes “MDI Prepolymer” is used, which is in essence a product of the same MDI mixture and polyol.



At the moment of writing, most EU Member States have set Occupational Exposure Limits for diisocyanates at a level of 5 ppb for the 8-hour time weighted average (TWA) and 10 or 20 ppb for 15 minutes short term exposure limit value (STEL). This means that average exposure over a shift should not exceed 5 ppb and that there should not be any period of 15 minutes during the shift with an average exposure exceeding 10 or 20 ppb in most EU countries. There are notable exceptions such as Sweden with a TWA of 2 ppb and a STEL of 5 ppb, Poland for TDI with 1 ppb TWA and 3 ppb STEL, and Italy for TDI with 1 ppb TWA and 5 ppb STEL. Some countries can have peculiarities in their system, such as Germany which maintains a ceiling value for TDI, a limit which may not be exceeded even for a moment.

For an overview of EU National limits applicable in 2021, the European Chemicals Agency has drafted a [report](#) containing these in tables 5 – 7 [7]. Alternatively, the [GESTIS International Limit Value Database](#) contains a broader view of limit values adopted across the globe. Furthermore, the OELs of substances or substances in mixtures must be placed on the respective National safety data sheets of the raw materials supplied. These limits are going to change in the years to come (see section D4 for more information).

Every plant must know the actual limits applicable to it which is normally enshrined in national law and note must be taken of any national particularities (e.g. the German ceiling value). All sources discussed above might be helpful, especially in the absence of national limits, but they may simply be incorrect. The quality of safety data sheets varies, the GESTIS database is only periodically updated and does not cover each and every country. Therefore, for nationally applicable limits, it is imperative that the plant identifies the means of the state by which limit values are communicated, such as the relevant law or regulation or other distribution means.

Some countries have no national OELs applied for all or some diisocyanates. In these cases, the Derived No Effect Level (DNEL) values given in the safety data sheet should be respected.

It is important to understand that the vapour pressure curves of TDI and MDI, respectively, are radically different. As with most substances their vapour pressure increases dependent on the temperature, however TDI is far more volatile than MDI (see Figure 8); at room temperature about 400 times more volatile. Since the vapour pressure of TDI is much higher than that of MDI, it has a greater tendency to volatilise. Consequently, TDI presents a greater inherent risk than MDI. To exemplify this, for TDI a single droplet on a table in a medium size meeting room would result in an immediate airborne concentration of more than 5 ppb¹⁶ **at room temperature**; MDI should result in an airborne concentration well below 5 ppb at room temperature and typical air exchange rates in buildings.

¹⁶ A droplet with less than 2 mm diameter and 10 mg TDI would result in an air concentration of 0.37 mg/m³ (10 times above TWA of 5 ppb or 0.035 mg/m³ in a 3 x 3 x 3 m room w/o assuming air exchange rates. Note: The saturation concentration of TDI at 25°C is in the range of 100 mg/m³.



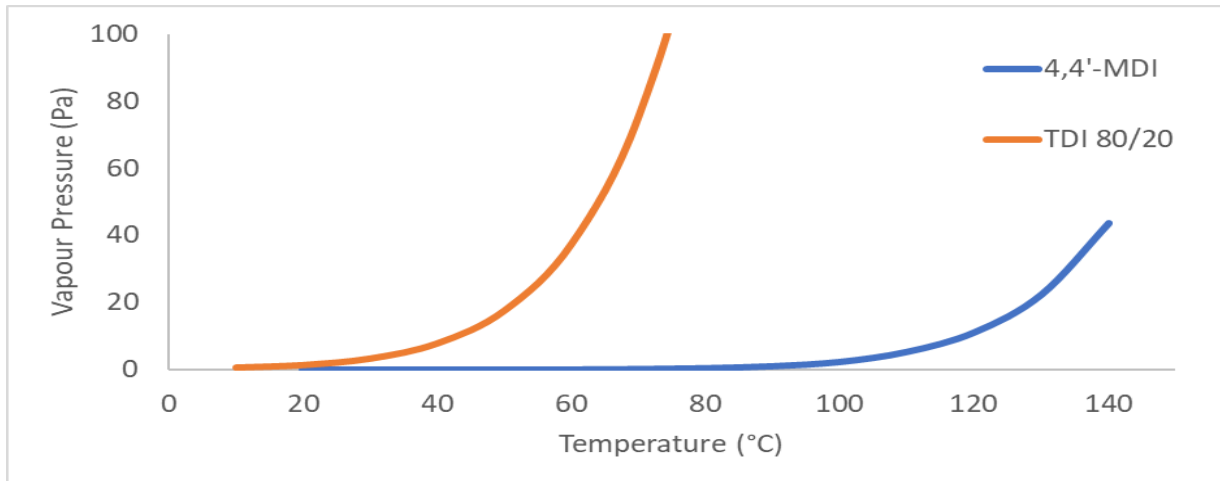


Figure 8 Vapour pressure of TDI 80/20 and 4,4'-MDI. Source: Covestro

The majority of slabstock foam is produced using TDI, however MDI is used for certain grades as well (e.g. HR foams). Moulded foams are produced using both, MDI and TDI (e.g. for lower density, light weight car seats). In slabstock foam production it would not be unusual to pour 500 kg/minute: assuming 1/3 TDI content and that a droplet is 1 ml, that means that about 140 000 droplets are poured per minute. For moulded foam production the quantities are somewhat less extreme.

There are two reasons why these thousands of droplets do not result in airborne concentrations exceeding the OEL several times over. Firstly, the risk management measures in place, which include enclosures and specifically designed extraction ventilation, reduce airborne concentrations around the workers. Secondly, the diisocyanates, when poured, are in a mixture with other components engaged in a polymerisation reaction. Particularly during the first moments of this reaction the reaction rate is high already eliminating a large fraction of diisocyanates. Furthermore, the liquid matrix of polyol reduces volatilisation. Hence the “wet-laydown”, in which no polyol is poured together with diisocyanates, is one of the causes of overexposure incidents described in the section on process safety (section C2.2). Nevertheless, the increasing temperature in the foaming mixture is raising the volatility of residual TDI or MDI, hence the whole foaming process has to be recognized potentially as a significant exposure source.

Typical exposure in Slabstock foam production

Responsible persons at plants should have good insights into the (potential) exposure to hazardous chemicals used in foaming. EUROPUR has performed an extensive TDI measurement campaign in 4 Slabstock Foam Plants in the Netherlands [8]. In three of the plants data, representative of normal operating conditions, was collected and in one plant an incident occurred during the measurement, resulting in data representative for the incident situation. This report is available for EUROPUR Members on the dedicated extranet and for other foam producers on request. Summary statistics (Table 3) and some key observations on discrepancies within a slabstock foaming hall operating under normal conditions are shared below.



Table 3 Summary statistics of TDI exposure for various activities within flexible slabstock foam plants as measured in 2020 - 2021. The $\mu\text{g NCO}/\text{m}^3$ values can be converted to $\mu\text{g TDI}/\text{m}^3$ by multiplying them by 2.07. Source: [8]

Activity/location	Static / Personal	Average ($\mu\text{g NCO}/\text{m}^3$ ppb)	90th percentile ($\mu\text{g NCO}/\text{m}^3$ ppb)	Maximum ($\mu\text{g NCO}/\text{m}^3$ ppb)
Unloading and TDI Storage	Static	0.14 0.04	0.22 0.07	0.25 0.07
Slabstock Foaming	Personal	8.9 2.6	21.3 6.2	33.3 9.7
Handling uncured foam	Mix	4.0 1.2	9.5 2.8	20.4 5.9
Handling cured foam	Mix	0.022 0.006	0.031 0.050	0.170 0.050
Cleaning	Personal	3.0 0.9	7.4 2.1	8.9 2.6
Laboratory Operations	Personal	1.6 0.5	2.9 0.8	3.2 0.9

At the point of dispersion on the mixing platforms the diisocyanate concentration in the liquid being poured is the highest, yet, at this station, the measured airborne concentrations were low. Static measurements revealed concentrations of 0.004, 0.268, and 0.663 ppb TDI. This appears counterintuitive if compared to the high concentration of diisocyanates in the reaction liquid. There are two factors that can explain this. First and foremost, the engineered extraction ventilation draws air from the tunnel, which in turn draws air from the area around the mixing platform. Secondly, the volatility of diisocyanates is governed by the temperature, which is typically ambient when mixed and not yet significantly elevated when dispersed.

Towards the end of the foam line the situation is reversed. The concentration of diisocyanates in the foam has greatly reduced, however the core temperature has increased to levels seriously driving volatility upwards. In plant A the end of the foam line was enclosed in a large boxed area in which individuals could move with appropriate RPE. In this area a personal measurement revealed airborne concentrations of 7.5 ppb, while a static measurement revealed 3.1 ppb. Plant B had enclosure systems tightly around the line, meaning that there were no measurements taken of activities or areas within the enclosure. However, a measurement at a paper windup station – where paper is torn from the foam allowing openings to emerge from which diisocyanates can escape – had some less-than-optimal enclosure, as was demonstrated by a static measurement of 6.3 ppb. Plant D had an extremely long tunnel where halfway through a paper windup station was located where a static measurement revealed a concentration of 5 ppb. However, at the very end of the tunnel a measurement of the sawing area revealed a relatively low concentration of 0.7 ppb.

Covestro, an isocyanate producer, developed a model based on lab experiments with reported key data like NCO-decline, foam rise and temperature considering the temperature to estimate a vapour pressure of TDI at the surface and core of a piece of fresh hot foam (presented in Figure 9). While the exact details of this model were not shared, it is clear that the model takes the residual diisocyanate concentration in some way into account, as the “vapour pressure” on the secondary X axis seems to be not exclusively related to the surface and core temperature.



The model indicates that the TDI vapour pressure at the surface increases over time, as temperature increases. Afterwards, TDI vapour pressure decreases and takes quite a while before reaching a similar level as seen at the point of dispersion. Furthermore, the model indicates, that core temperatures remain higher and thus the vapour pressure in the core of the foam remains higher than at the surface. Thus, any activity that reveals more of the core material, results in a greater exposure potential, such as, for example, the paper windup, whereby some skin material is torn from the block, or the moment of cutting the block into either long or short blocks.

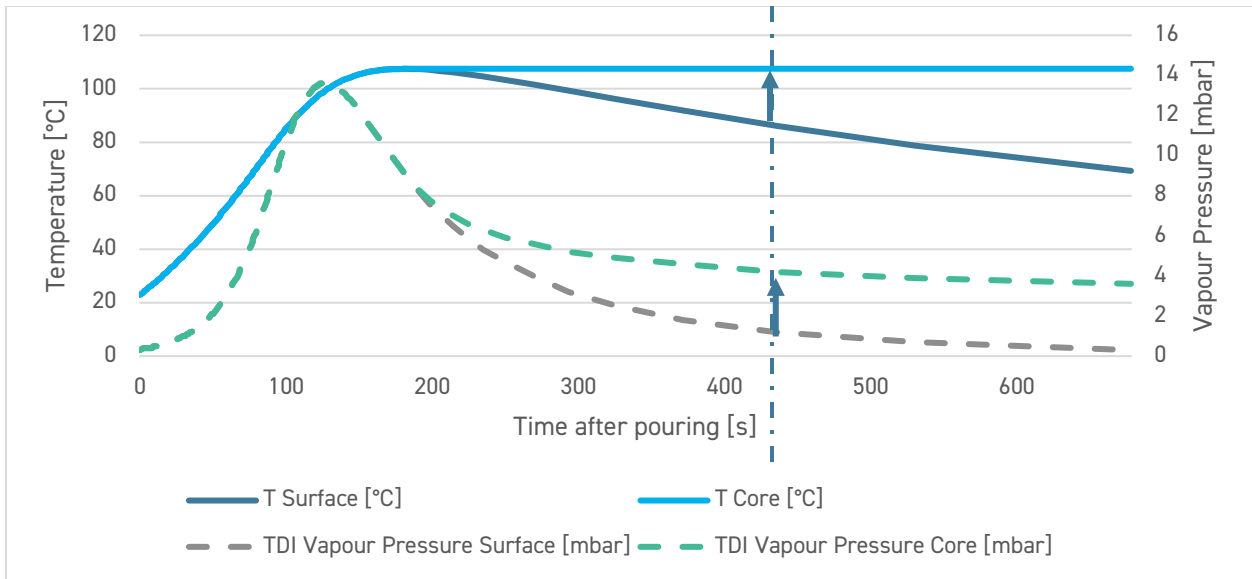


Figure 9 Measured surface and core temperatures and their theoretical effect on TDI Vapour Pressure. The vapour pressure model assumes that all residual TDI in foam could evaporate w/o foam interaction and is therefore overestimating the effective TDI evaporation to some extent. Dashed line represents the cutting into a block. Source: Covestro

The model has some explanatory value but should not be taken to be the absolute truth. Different formulations will give rise to different temperature and reaction profiles. Furthermore, ambient pressure, temperature, and humidity may influence the foaming process to a degree, that sometimes require minor, on the spot adjustments to standard formulations, and hence will impact the exposure potential as well. It does explain why, although a large fraction of diisocyanates should have reacted already, foam still presents a hazard within the slabstock tunnel and at the end of the line.

Lastly the model only addresses the inherent properties of the reaction and not the risk management measures aspect of occupational exposure. To return to the example of the low exposures at the mixing platform, it should not be assumed that there is no risk whatsoever, because the model shows that the vapour pressure is lower at the point of dispersion. As already explained, the air extraction system also



draws air from this area. If windows along the foam line are left open¹⁷ this draft of air at the mixing platform will surely become less potent.

As already mentioned in section B, once foam is fully cured, all diisocyanates have reacted and the foam is devoid of any hazard related to diisocyanates. The measurements confirm this, since many investigating cured foam were below the limit of detection. Those that were slightly above the limit of detection, showed values, that should not be considered of any relevance for human health, but rather a testament to the extraordinarily sensitive measurement method. Such findings might also be the result of some limited low-level spread from the foaming hall to other locations.

Typical exposure potential in Moulded foam production

EURO-MOULDERS performed a measurement campaign in 2017 in 4 moulded foam plants in Germany, Poland, and Slovakia using a similar methodology [9]. The data was reassessed in 2021 and a report is available to all EURO-MOULDERS members on the extranet and for non-members it is available on request [10]. Summary statistics are presented below as well as some pertinent observations.

*Table 4 Summary statistics of measured airborne concentration of TDI in moulded foam plants. *Pouring was done automatically in boxed pouring booths, meaning no operators are present and this is not a workplace. Manual pouring does exist, but these measurements are not representative of that activity. The $\mu\text{g NCO}/\text{m}^3$ values can be converted to $\mu\text{g TDI}/\text{m}^3$ by multiplying them by 2.07. Source: [10]*

Activity/location	Static / Personal	Average ($\mu\text{g NCO}/\text{m}^3$ ppb)	90th percentile ($\mu\text{g NCO}/\text{m}^3$ ppb)	Maximum ($\mu\text{g NCO}/\text{m}^3$ ppb)
Pouring*	Static within pouring booth	11.3 3.30	21.9 6.38	46.3 13.5
Demoulding	Personal	0.63 0.18	1.40 0.41	2.08 0.61
Post-Treatment	Static	0.27 0.08	0.45 0.13	0.73 0.21

It should be noted that all these plants were suppliers to the automotive industry and thus running large production volumes, where automatic pouring was the norm. Such pouring happens in closed boxed areas ('pouring booth') without the presence of operators. Measurements within this booth are included here as an explanation of the TDI release pattern. In moulded foam plants for furniture, public transport, and/or other smaller scale operations, manual pouring happens too. The results of measurements in the pouring booth displayed above are by no means representative for manual pouring operations as one would expect MDI to be used there and/or a much more specifically designed air extraction system to be present.

In plants with automatic pouring the first point where diisocyanates exposure can occur is the demoulding station where the foam pieces are demoulded. Here the surface temperature of the foam

¹⁷ Foam line operators tend to need to perform some operations through these windows such as correction of side paper drift. It is imperative that these windows are closed afterwards, but compliance to this practice tends to less than optimal.



is normally “warm” (e.g. between 40 – 75 °C)¹⁸. However, the core of the foam block can have somewhat higher temperatures. The foam pieces are however much smaller, so the temperature decreases far more rapidly and more evenly throughout the foam than in slabstock foam. This difference also explains **partly** why airborne concentrations in moulded foam production are generally lower than in slabstock foam production. The other part of this equation is the extraction ventilation that is in place at the demoulding station to prevent exposure.

One additional process step worth mentioning is crushing which occurs relatively rapidly after demoulding. During this activity the foam is crushed to force open cells in the internal foam structure. Closed cells are thus opened, and gas is forced out of the foam. These stations must be as closed as possible (also from a perspective of physical safety) and a best practice is to have air extraction on the crushing station or vacuum assisted crushing.

D1.2 Other intentionally used substances

Each foam plant should have an inventory of all relevant (hazardous) products (substances or mixtures) present in the foam plant and keep this up to date at every point in time. Such inventories might already exist since they can be a permit requirement. In this overview the following should be included:

- The Safety Data Sheet of the substance or mixture
- Hazard classification of the substance, mixture, and mixture component substances
- The purpose of the product such as:
 - Formulation component
 - Polyol Raw Material
 - Diisocyanate Raw Material
 - Amine catalysts
 - Flame retardant
 - Cleaning Agents
 - Other (e.g. paint for floor markings)
 - Fuel (e.g. for forklifts)
- Quantity stored (ideally tracked or otherwise an average or range)
- Storage location in the plant
- Type of packaging (e.g. Tank, IBC, drum, big bag, small bags)
- Department of use.
- Occupational Exposure Limit Values or equivalent values (e.g. DNEL)

Care should be taken when storing these chemical products and zoning should be applied. For example, oxidising substances should not be stored in the vicinity of flammable liquids (e.g. certain release agents). Furthermore, containers should not be reused, but rather disposed in appropriate manner in line with national legislation (see chapter F).

¹⁸ In the hot-cure moulding process the mould temperature can be greater than 100 °C. This was not done at the investigated sites.



For all activities involving chemical agents that might generate a risk to health and safety, especially substances that have a hazard classification for human health effects, a risk assessment needs to be performed.

A good guidance for such assessments has been developed by the UK called: [A step by step guide to COSHH assessment](#). Principally it explains that most of the assessments can be done by combining the properties of the substances or mixture available in the Safety Data Sheet with expert judgement by a competent person. Most workplace risk assessments can and should be done in this way.

There may however be more complex situations or use of substances that have a more critical toxicological profile for which a more detailed quantitative assessment may be required.

A cost effective approach to obtain an estimate of exposure is to use exposure modelling tools such as [ECETOC TRA](#), [Stoffenmanager](#), and [Advanced REACH Tool \(ART\)](#). These tools give a worst-case conservative exposure estimate based on scenario- and substance-specific parameters. Such an exposure estimate can be compared to the toxicological benchmark in the generated overview of used substances (e.g. OELs, DNELs). For example, if a non-volatile powder raw material with a class 2 carcinogen classification is fed into a hopper, ART can be provided with information on the coarseness of the powder, the drop height, and other risk management measures to lead to an estimate of exposure. If the exposure estimate is below the benchmark the use can be considered safe.

These models are, however, very conservative in the sense that they tend to overestimate exposure significantly. Another approach is to perform workplace exposure measurements to generate data to inform risk assessment. Several methods for this are explained in section D2. Such methods tend to give the most reliable estimate of exposure as they take all parameters of the existing workplaces into account, but also tend to be resource-intensive and should be reserved for the most critical substances (e.g. diisocyanates) and processes.

D1.3 Non-intentionally used substances

The production of flexible polyurethane foam is a complex chemical process whereby many raw materials interact with one another and the environment. It deserves careful attention that in such processes it is possible for certain new substances, that were not in the ingredients of the formulation, to be formed.

Aromatic amines

In the production process water is added to the formulation so that water can react with isocyanate groups to produce an amine group and CO₂. This CO₂ is the primary blowing agent and causes the foam structure. The amine groups tend to subsequently react with isocyanate groups to form a urea bond. The affinity of isocyanate groups to amine groups is magnitudes higher than that of isocyanates to hydroxyl groups on the polyol. Hence, concentration of, residual amine groups will be low. However, fully hydrolysed diisocyanates, aromatic diamines, may persist to some extent in the flexible foam; particularly in the skin of moulded foam this can reach ppm levels in the material in freshly produced foams. These concentrations decay over time, at first quite rapidly, but decay to non-detectable concentrations can take weeks.



Toluene diisocyanate (TDI) based foams will contain toluene diamine (TDA) and methylene diphenyl diisocyanate (MDI) based foam will contain methylene diphenyl diamine (MDA). The 2,4-TDA isomer is a known carcinogen (2,6-TDA is not). For MDA chronic carcinogenicity studies have been performed for 4,4'-MDA showing that it is a carcinogen (see Table 5), for the other isomers no such study has been performed, but *in vitro* test indicate, that these may be less hazardous. Also, these amines are known skin sensitizing substances. Regarding this property, aromatic isocyanates and aromatic amines have similar handling requirements.

Table 5 Hazard classification of TDA isomers and 4,4'-MDA

	2,4-TDA	2,6-TDA	4,4'-MDA
Name	4-methyl-m-phenylenediamine	2-methyl-m-phenylenediamine	4,4'-methylenedianiline
Cas	95-80-7	823-40-5	101-77-9
EC	202-453-1	212-513-9	202-974-4
CLP Index	612-099-00-3	612-111-00-7	612-051-00-1
Harmonised Classification	Carc. 1B Muta. 2 Repr. 2 Acute Tox. 3 Acute Tox. 4 STOT RE 2 Skin Sens. 1 Aquatic Chronic 2	Muta. 2 Acute Tox. 4 * Acute Tox. 4 * Skin Sens. 1 Aquatic Chronic 2	Carc. 1B Acute Tox. 3 Muta. 2 Skin Sens. 1 STOT SE 1 STOT RE 2 Aquatic Acute 1 Aquatic Chronic 2
Vapour pressure at ambient temperature	0.017 Pa	0.029 Pa	0.00025 Pa

The vapor pressure of these amines is typically more than a factor of 10 lower than the respective diisocyanates. In both measurement campaigns for slabstock foam and the measurement campaign for moulded foam TDA and MDA were included in the analysis of the samples. In the slabstock production process no airborne concentrations of TDA or MDA were detected. In moulded foam production only 2,6-TDA was detected in a single air measurement of a demoulding operation in one of the plants at a concentration of 1.63 µg/m³. In general, inhalation exposure to aromatic diamines is of lower concern in flexible slabstock and moulded foam production.

Of concern, particularly with moulded foam production, is dermal exposure since the initial concentration of aromatic amines is greater in the skin of moulded foam. Specific advice for dermal protection when handling moulded flexible polyurethane foam can be found in section D3.2.

Formaldehyde

A substance that can be emitted from flexible PU foam but that is not deliberately used is formaldehyde. The substance is thought to be present in certain raw materials as an impurity (e.g. certain amine catalysts) or generated through photodegradation or partial oxidation of the polymer backbone. One



known reaction to generate formaldehyde is that of degradation of amine catalyst (not to be confused with aromatic amines) containing methylamino groups and the photodegradation of polyols (and basically all organic matter).

Formaldehyde tends to be reported for VOC tests of certification schemes for flexible foam such as CertiPUR, at levels not giving rise to concern for consumer exposure. However, during flexible foam production, higher temperatures are the norm and the reservoir of formaldehyde that may degrade from the foam is greater since it is freshly produced. On the other hand, there should be risk management measures in place such as engineered extraction ventilation. At present, the state of knowledge of this kind of exposure is not as elaborate as with diisocyanates and aromatic diamine exposure. Should the workplace assessment give rise to concern over formaldehyde exposure, a limited series of measurements could be performed during foam production and/or storage.

D2 Exposure Monitoring

Exposure monitoring is a key aspect of industrial hygiene especially for those hazardous substances for which safe use cannot be demonstrated via standard risk assessment or through exposure modelling (see section D1.2); it should be reserved for critical substances in critical processes. The most notable ones for the flexible foam industry are diisocyanates, as these substances have the lowest Occupational Exposure Limits (OELs). The most common method for occupational exposure measurement is a sampling campaign. For certain substances – notably diisocyanates – direct reading instruments have been developed, allowing (near) real time determination of airborne concentrations. These two methods are explained below and best practices on how to use them are explained. Biomonitoring and dosimeters also exist as methods to evaluate diisocyanate exposure.

D2.1 Air Sampling Campaigns

In air sampling campaigns, air is pumped over a cartridge that is designed to trap a certain substance or material. By measuring the quantity of the substance on the cartridge and knowing the volume of air passed over a defined period, it is possible to calculate the airborne concentration over the sampling period. Due to the required effort, these measurements are typically done relatively infrequently (e.g. once a year or once every two years).

Local legal context

It will depend very strongly on the national circumstances who does these measurements. In certain countries the government will visit the site and perform the measurements to determine if there is compliance to national limit values (e.g. Poland). In other countries there are independent organisations/institutes (e.g. the German Berufsgenossenschaften) that can be contacted for the performance of such measurements. In other countries the company is simply obliged to have evidence that the occupational exposure risk is controlled, which can be proven best by performing measurements (e.g. the Netherlands and Italy).

Similarly, the interpretation of the results of such air sampling campaigns can be strongly dependent on national practices. In certain countries it is possible that once measurements show airborne concentrations below the OEL, no further action is needed.



However, an air sampling campaign is a single measurement that does not capture the variability in the occupational exposure over the year. In some countries therefore it is customary to grade the measured level relative to the OEL value along the lines of: <10% of OEL green, <50% of the OEL yellow, <100% of the OEL orange, and >100% of the OEL red¹⁹. The category determines whether (immediate) corrective action is needed in the form of increased risk management measures and/or when the next sampling campaign should be held.

A widely applied and certainly by this guidance recommended standard is EN 482²⁰ in which basic performance requirements of measurement methods are specified. Particularly, EN 482 states that a method should be selected with a limit of quantification (LoQ) that is at least 10 times below the long-term OEL and at least 2 times below the short-term exposure limit (STEL).

In a limited number of countries (e.g. Netherlands and Belgium), a more scientific methodology is demanded in the form of the compliance evaluation defined in EN 689²¹. This involves grouping workers in similar exposure groups for which the measured airborne concentrations must be normally distributed, and a detailed statistical analysis must be performed. Subsequently a test is done to see if the measured exposure is between 10 – 20% of the OEL depending on the number of measurements. If this fails, a statistical test is done to determine, if compliance with the OEL can be established with a certain degree of certainty. While such an evaluation scheme can be considered as “more scientific”, it will not work in cases where it would be impossible to group workers in similar exposure groups **with normally distributed exposures**. This is of relevance for slabstock foam production. A more detailed insight into this aspect can be found in the EUROPUR report on measurements in 4 Dutch Slabstock foam plants [8]. For moulded foam production measurement, campaigns in compliance to EN 689 would likely be more feasible, however they do require more measurements to be performed and therefore cost significantly more. Regardless of whether measurement campaigns are done in full compliance with EN 689, the standard does offer a good insight into the theory behind air sampling campaigns and should be known by EHS managers.

How to perform air sampling campaigns

To perform an air sampling campaign an industrial hygiene consultant with the required experience and capabilities should be contacted and will, generally for a fee, come to the plant. In consultation with local management, the consultant will develop a sampling strategy, perform the air sampling onto cassettes/tubes, and sent such cassettes/tubes for analysis. The industrial hygienist will draft up a report, explaining whether exposure is adequately controlled and may formulate recommendations if needed.

¹⁹ Exact thresholds may be different and the way of categorization may be different (e.g. A, B, C, F instead of green, yellow, orange, red).

²⁰ EN 482:2021 Workplace exposure - Procedures for the determination of the concentration of chemical agents - Basic performance requirements

²¹ EN 689:2018 Workplace exposure - Measurement of exposure by inhalation to chemical agents - Strategy for testing compliance with occupational exposure limit values



Depending on the local legal context and sometimes even the relationship with the local labour inspector, measurements performed by the plant staff itself without involvement of an external party may be accepted to demonstrate compliance. However, a report from an external party tends to be preferred by authorities and worker representatives.

Short term measurements

For certain substances peak exposure is also of concern. This is particularly true for diisocyanates, and it is the reason why normally short-term exposure limits (STEL) are set. The activities/phases of the process with the highest exposure potential should be identified together with the industrial hygienist for inclusion in the sampling plan. However, verifying compliance to such STEL values using air sampling techniques is analytically and practically challenging.

From the practical perspective, it is simply a lot more difficult to ensure that the peak exposure moment is captured. To minimise these practical difficulties, it is useful to try to select an industrial hygienist that has some experience with the specific flexible foam processes and either look at the processes together or have good pre-discussions before the day of the measurement campaign.

From the analytical perspective, the laboratory performing the analysis will normally have a LoQ per sample. The LoQ in air is calculated by dividing by the total volume of air that passed through the sampling tube/cassette. With the flow rate being normally fixed to the method, a shorter sampling time means a severely reduced LoQ. This is partially compensated by a lower LoQ requirement of just 2 times below the STEL compared to 10 times below the 8-hour TWA as specified in EN 482 (factor 5). The compensation is only partial since the volume of air that can be passed over the sampling device during typical long-term measurements (e.g. 4 – 8 hours) is still a factor 16 - 24 times greater than what can be sampled over a short term period of 15 minutes.

Such measurements thus demand a lot more sensitive analysis method than longer term measurements. Such methods may not be available everywhere and/or be (prohibitively) more expensive.

The following normal operating activities may cause short term peaks in exposure and would ideally be measured when possible:

- In Slabstock Foam Production:
 - Operations involving the mixing head such as the operation of capturing the first fraction of material in a plastic bag that is required on some slabstock foam lines or the mixing head cleaning that is normally done at the end of the day.
 - Opening of windows to perform manual manipulations in the tunnel.
 - Operations around the paper windup areas (e.g. roll replacement).
 - Operations inside of enclosures.
 - Operations in the curing area including the cutting area.
- In Moulded Foam Production:
 - Bucket/bag shots (e.g. to perform rise tests)
 - TDI Calibration shots



Given these practical and analytical difficulties it is worthwhile to consider the use of direct reading instruments (DRI) to support STEL compliance verification (see D2.2). While these instruments tend to have a lower accuracy than sampling campaigns, they do excel in their temporal resolution and marginal cost per measurement (i.e. they give a reading every few seconds and at almost no additional cost). While, particularly for diisocyanates, an air sampling campaign should include at least some STEL measurements for higher exposure operations, a company that regularly performs well thought out measurements with DRI and maintains good logs should be able to use this to demonstrate compliance to STEL values.

D2.2 Direct reading instruments

Direct reading instruments (DRI) measure airborne concentrations of substances in near real-time and provide a direct readout. This technology does not exist for a wide range of substances as sampling campaign methods; however, it has been developed for TDI and MDI and the use of this technology is highly encouraged.

The most common technology uses a cassette or paper roll that contains a ribbon that changes colour upon contact with airborne diisocyanates. By pumping a constant air flow over the paper and controlling the movement of the paper, the concentration of airborne diisocyanates is determined spectrophotometrically. Other technology based on infrared or ion mobility are being developed that may be able to detect multiple substances at the same time and may be able to measure a wider palette of substances.

There is a role for these devices for leak detection, mainly for the tank farm where they should be connected to a signalling system at the entrance(s) to the tank farm and to a warning system. Furthermore, these devices can be used at or around the mixing head to detect things like mis pours, i.e. incidents where an incomplete mixture (e.g. without polyol) is dispersed giving rise to huge airborne concentrations that may result in immediate health consequences⁴.

However, these devices can also offer immense value in the field of industrial hygiene as they can provide a temporal special view of exposure that would be difficult to achieve with sampling campaigns, for both longer and shorter exposure times. Worker can react quickly when unusual peak appear and have direct feedback if when the issue is resolved. Below some best practices and examples are highlighted for slabstock and moulded foam industries.

The limit of detection of these devices varies between 0.5 and 1 ppb for diisocyanates. However, care should be taken when interpreting these results since so close to the LoD, the accuracy falls off and can be influenced by things such as NO_x, humidity, and dust become more pronounced. Maintenance according to manufacturer's instruction should be performed.

Slabstock Foam Production

At the minimum a mobile DRI should be used to spatially map exposure during normal production runs. This should result in a clear understanding of airborne concentrations in different areas of the production hall.



A best practice would be to place static DRI at a few strategic locations throughout the production hall where exposure can be expected. For example: one near the mixing head, one near the control panel at breathing height, one near paper wind up and the cut off saw (if not well encapsulated), and one in the curing area. Ideally such positioning should be between the normal operating position of operators and the production process. Such static DRI should be tied into a data logging system to obtain a temporal insight into the production process.

An example of such a readout can be found in Figure 10. In this case the plant learned that after stopping production the airborne concentration of diisocyanates does not reach “0” until well after production was stopped in a large boxed/encapsulated area where the saw and paper windup was located. This insight was translated in a rule that RPE must always be worn when entering the boxed area, even if there is no foam present in the boxed area. Furthermore, the measurement outside of the enclosure will inform if there is leakage from the boxed area, which happened for a brief period during the production run when a door was left open.

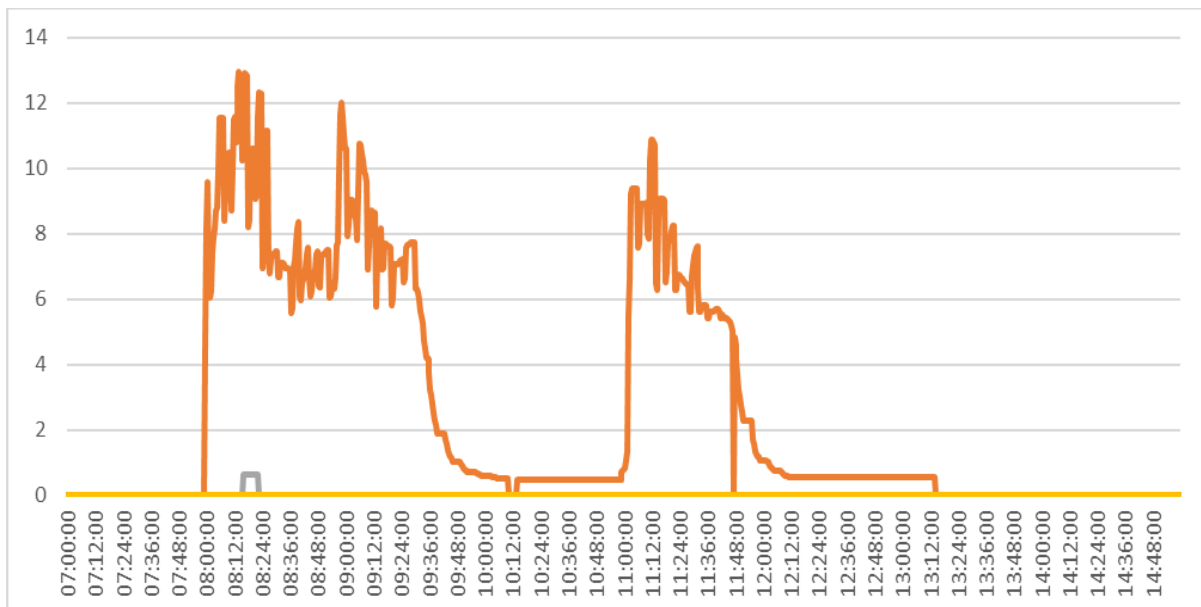


Figure 10 TDI concentration in ppb as detected by a static DRI in a slabstock production process for two production runs. Yellow line represents the mixing platform. The orange line is the concentration inside of a large boxed area containing the cut off saw and the paper wind up activity. The grey line is a measurement point outside of the large boxed area near a door leading to the boxed area.

Another insight obtained by another slabstock foam producer was that not all foams are equal in terms of exposure potential. Lower density standard ether foam based on TDI has a higher exposure potential than high density HR foam based on MDI. This slabstock foam producer manufactured short blocks on the foam line and transported these over a long conveyer system to a tilting station where the blocks were placed upright and subsequently moved by forklifts to a curing hall. The tilting station was manned by two operators that were in close proximity to the foam. The use of DRI allowed the company to determine for which foam grades RPE would have to be worn.



In the foam production hall, the need to wear RPE due to unexpected rise of concentrations should also be reinforced with a visual and/or auditory warning system. For example, if a certain threshold is passed on a static DRI that is located at the control panel of a foam line, a yellow light could indicate the need for RPE to be worn. Such a threshold may be set at the locally applicable OEL value. For the selection of **threshold values** inspiration can be taken from locally applicable occupational exposure limits and/or historical data of normal operations. For an example of such a system see Table 6.

Table 6 Example of a reaction table with threshold values to be used for alarms systems in combination with DRI technology in slabstock foam production.

Level	Colour	Sound	Possible Trigger	Possible Consequence
1	Green	-	Concentration below the 8-hour time weighted average (TWA) for TDI or MDI (or another chosen concentration based on historical data of normal operations).	
2	Orange	Small auditory signal that can be turned off after equipping RPE.	Concentration between the TWA, and the 15-minutes short-term exposure level (STEL) or the ceiling value (or another chosen concentration based on historical data).	Everybody in the area to wear respiratory protection.
3	Red	Louder auditory signal	Concentration above the 15-minutes short-term exposure level (STEL) or the ceiling value (or another chosen concentration based on historical data).	Stop foaming immediately (i.e. within 5 minutes) and evacuate the foaming hall.

It should be noted that at very low levels approaching the detection limit of DRI the accuracy of the device decreases. The use of DRI alone is insufficient for OEL compliance verification when OEL value are close to the DRI limit of detection. Rising values of the DRI in this range can however be used to determine if an unusual event is occurring.

Another best practice is to utilise the DRI for the generation of data for training purposes. To give a practical example, there was a plant where a paper wind up station was enclosed and during a production run a worker would have to equip RPE and change the paper wind up role once or twice. An operation lasting about 5 minutes. Upon completion the workers were not always diligent in closing the enclosure system. The EHS manager placed a mobile DRI in front of this station with the enclosure closed took a picture showing a concentration of "0" ppb and a picture with the enclosure partially open showing a concentration of 4 ppb. This was shared in a short training with the operators, and they then understood why it makes sense to diligently close the enclosures.

A more serious example can be found in the practice of the old hands in the industry that open windows on the tunnel, take a deep breath and do some manual operations with their head in the tunnel, and remove their head from the tunnel to resume breathing. A slabstock foam producer once held a mobile



DRI in the tunnel and found that the device indicated a concentration of “200” ppb²². Showing such data to the operator might make the operator think twice about performing such a risky activity.

Moulded foam production

The use of static DRI emplacement should be based on a risk evaluation of the expected concentrations under normal operating conditions and the probability of process safety events. Both are impacted by the vapour pressure of the diisocyanate, meaning that priority should be given to moulded foam lines using TDI where static DRI technology is a must have.

Static DRI may be placed in between the pour point and the nearest operator (insofar as possible) and/or at the point where the mould is opened. The former will detect issues with loss of containment of the pouring booth, while the latter may ensure early detection of mis-pours²³. Also, the crusher area might be a potential area for such a device.

A best practice would be to have this DRI operating continuously or at least have it automatically switched on when the line becomes operational and able to record the concentrations over a period of time. The monitors should be placed between 1,2 to 1,5 m high. This static DRI must be connected to an alarm system with visual and/or audible alarm signals that trigger organisational measures. An example of such a system can be seen in Table 7.

Table 7 Example of a reaction table with threshold values to be used for alarms systems in combination with DRI technology in moulded foam production.

Level	Colour	Sound	Possible Trigger	Possible Consequence
1	Green	-	Concentration below the 8-hour time weighted average (TWA) for TDI (or another chosen concentration based on historical data of normal operations).	
2	Orange	Small auditory signal that can be turned off after equipping RPE.	Concentration between the TWA, and the 15-minutes short-term exposure level (STEL) or the ceiling value (or another chosen concentration based on historical data).	RPE should be used to review and resolve the situation
3	Red	Louder auditory signal	Concentration above the 15-minutes short-term exposure level (STEL) or the ceiling value (or another chosen concentration based on historical data).	Stop pouring reaction mixture immediately (i.e. within 5 minutes) and evacuate the relevant production area.

²² In this case 200 ppb was the maximum value the device can display, meaning the concentration was likely >200 ppb.

²³ A process safety related event in which inappropriately mixed reaction mixture is poured into the mould. In the worst case pure diisocyanates are poured into the warm mould.



Mobile DRI has less of a utility in moulded foam production, but one could use it to periodically check the containment of boxed areas such as the pouring booth, the crusher and carousel ventilation effectiveness; especially when using TDI.

D2.3 Biomonitoring

Urinary biomonitoring has been developed to monitor diisocyanate exposure. These methods measure the chemical hydrolysis products of diisocyanate-metabolites in urine, quantified as various MDA and TDA isomers. When detecting one of these isomers in urine (e.g. 2,4-TDA and 2,6-TDA) it will not be possible to say whether these substances are there because of exposure to 2,4-TDI and 2,6-TDI or exposure to 2,4-TDA and 2,6-TDA or a combination of diisocyanates and diamine exposure. It is also not possible to differentiate whether the exposure is based on inhaled or skin adsorbed route. For example, this is relevant for employees that have a potential for skin contact in moulded foam operations, where airborne diisocyanates levels may be low, but diamine concentration in the skin of handled foam that is being manipulated may be relatively high.

While this should be kept in mind when evaluating results, urinary biomonitoring can be a complementary non-invasive method to monitor exposure. It can be used to ascertain individual good or bad behaviour. For example, if a group of people are working in a similar job, but only one has an increased urinary TDA value; further investigation can reveal that the person has been too infrequently changing his gloves since he believed it to be a waste or that the person put the gloves in his pockets for reuse later resulting in direct skin contact with the outside of the gloves.

The amine content in urine after hydrolysis can be quantified as $\mu\text{g/L}$ urine or as $\mu\text{mol/mol}$ creatinine²⁴. While this method can be replicated by other laboratories, the HSE Science and Research Centre, a semi-government body of the UK offers the testing service. This service can be extended beyond the borders of the UK. Other public and commercial services may offer this service too.

The UK maintains a Biological Monitoring Guidance Value (BMGV) of 1 μmol isocyanate-derived diamine/mol creatinine. UK Guidance on biological monitoring [11] indicates that these BMGV is not legally binding, exceedance does not necessarily mean that airborne concentrations have been exceeded, or that ill health will occur. Similarly, compliance to this value does not mean that no further reduction in airborne exposure is needed, since it does not replace air monitoring values.

Other limit guidance values include:

- Biological Exposure Index (BEI) established by the American Conference of Governmental Industrial Hygienists (ACGIH) for TDI of 5 μg TDA / g creatinine (\approx 5 $\mu\text{mol/mol}$ creatinine). According to ACGIH this is based on a correlation between airborne TDI exposure and urinary TDA levels and the value of 5 μmol TDA / mol creatinine should correspond to an airborne TDI level of 1 ppb.

²⁴ Creatinine is a breakdown product of muscle and there is a relatively stable flow of this from the human body into urine. The flow is more stable than the flow of water and is therefore frequently used as denominator in urinary measurements.



- Germany established a BAT value ("Biologischer Arbeitsstoff-Toleranz-Wert": biological tolerance value for occupational exposures) for MDI of $10 \mu\text{g}$ 4,4'-MDA/L urine, based on an airborne limit of $50 \mu\text{g}/\text{m}^3$ (≈ 4.9 ppb).

At the moment of writing, to the best of our knowledge, not a single biological limit value is legally binding. However, plants that perform biological monitoring will have a greater insight into exposure patterns of individual workers²⁵ than plants that do not perform this monitoring. Performing biomonitoring and maintaining detailed records of this could be beneficial in discussions with regulatory authorities.

Before engaging in biomonitoring, it is relevant to check local legislation regarding biomonitoring, privacy, and personal data. In some countries, one may need permission from workers councils before engaging in urinary biomonitoring. In other countries, such as the UK, such bodies do not exist, but regulations specify that under no circumstances are workers to be obliged to contribute urine to these campaigns; participation must be voluntary. In most countries, workers need to be informed about exactly what will happen with the provided urine and what will be tested for and may decline participation. The information generated could be considered personal and there may be rules on whether the individual worker must or may be told of their result.

When performing the biomonitoring campaign, it is important that urine is collected towards the end of the work week (or equivalent period of several consecutive days at work) at the end of the shift. This ensures that the results would be worst case should accumulation of metabolites occur during the work week.

Lastly, it is possible to use urinary biomonitoring after a process safety related event to ascertain the degree of overexposure that was incurred, by collecting a urine sample a number of hours after the event.

D2.4 Dosimeters

Dosimeters are badges that can be worn by workers on their clothing that discolour when exposed to vapours of a particular substance. Based on the level of discolouration an exposure metric in the form of airborne concentration x time (e.g. ppm*hours) can be obtained. By dividing this value by the time of contact one can obtain a rough estimate of the average airborne concentration the worker was operating in. It does not allow for the evaluation of peak exposure and tends to only provide a relatively rough estimate. Specific badges for diisocyanates have been developed. At present it is unclear how well and reliably these badges work.

²⁵ Biomonitoring data may be confidential information between the medical service and the individual worker and can only be handled by the foam plant on an anonymous basis, please check local legislation.



D3 Personal Protective Equipment

D3.1 Respiratory Protective Equipment

There is excellent general guidance available in English from [UK HSE](#) and an even more elaborate guidance in German [DGUV Regel 112-190 Benutzung von Atemschutzgeräten](#) [12, 13]. Below specificities of RPE used in flexible PU foam production is discussed.

Mask types

There are various types of masks that have different benefits and drawbacks in terms of level of protection awarded, the degree of wearing comfort, and finally cost. The main types of masks will be discussed below.

Non-powered respirators rely on wearer's breathing to draw air through a filter. These exist in two variants, half face masks such as shown in Figure 11 and full-face masks such as shown in Figure 12. When used correctly half face masks offer a degree of protection that might be suitable for certain situation. However, these masks do not need to fit all facial morphologies (e.g. under EN 140 the mask only has to fit 8 out of 10 test subjects) and thus it is imperative to perform fit tests according to the manufacturer's instructions. Full face masks tend to offer a greater degree of tightness, thus have lower leakage levels, and are less prone to incorrect fit.

Both types of non-powered respirators filter air to the wearer with an additional breathing resistance. This may be acceptable for short term operations with lower work rates but becomes disproportionately uncomfortable with longer wearing times and heavier work rates. Wearers may remove these masks due to discomfort.



Figure 11 Reusable Half Mask Respirators. On the left one with particle filters and on the right one with gas filters. Source: UK HSE [12]





Figure 12 Full face masks. On the left one with particle filters and on the right one with gas filters. Source: UK HSE [12]

Powered respirators use a motor to pass air through a filter before supplying this to either a mask or hood (with or without helmet). Examples can be seen in Figure 13. These devices are more expensive than unpowered respirators. However, do not require the wearer to pull air through the filters and are thus vastly less burdensome to wear. The powered respirators with hoods (with or without helmet) have the greatest comfort properties as there is no tight-fitting mask pressing against the face and fresh clean air is blown over the face²⁶. These properties make it so that longer periods of wear can be tolerated when using these devices.



Figure 13 Powered Respirators. On the left one with a full-face mask on the right one with a hood/helmet. Source: HSE [12]

²⁶ In fact, some it has been reported by some flexible slabstock foam producers that workers keep these on even in areas or during activities not requiring their use. When asked why they indicated that the air just smells fresher, and they like the airstream over their face.



Also, there are **air fed breathing apparatus** that require plant infrastructure to feed air from uncontaminated zones to the masks. Examples of these can be seen in Figure 14. Similarly, to powered respirators wearers do not have to pull air through filters vastly decreasing the burden of wear. Comfort of hood systems is likewise even greater than the half mask or full-face mask equivalents. Compared to powered respirators they tend to be lighter to wear since no motor with filter cartridges needs to be carried around. On the other hand, movement is somewhat restricted since the air tubing is connected to plant infrastructure.

When using air fed breathing apparatus it is imperative that the supplied air is treated with filters and that the air quality is tested frequently to ensure that oil, moisture, dust, and other contaminants are not present, and the air is safe to breath.



Figure 14 Constant flow airline breathing apparatus. On the left with half mask (light duty), in the middle with full face mask, on the right with hoods/helmet. Source: HSE [10]

With regards to the powered respirators or fresh air supply breathing apparatus particularly those with hood, in case of insufficient air supply, the wearer will draw unfiltered air from the surrounding. The required air supply rate is at least 3 times the average respiration rate²⁷, which is dependent on the work intensity. Respiration rates and minimum required air supply rates per activity levels can be found in Table 8.

²⁷ This is because humans inhale 1/3 of the time and exhale for 2/3 of the time, meaning that the inspiration rate is 3 times the average respiration rate.



Table 8 Respiration Rate, required air supply rate, and wearing time adjustment factor for various activity levels. Based on: UK and German Guidance [12, 13]

Activity Level	Description	Respiration Rate (l/min)	Required air supply rate (l/min)	Wearing time adjustment factor
Light	Sedentary work: assembly or sorting of light materials, arm and leg work, drilling.	20	60	1.5
Medium	Sustained hand and arm work: sawing, planing or chiselling wood, plastering, filing, work with pneumatic breaker, intermittent handling or carrying moderately heavy material, shovelling, sledgehammer work, concrete block laying, pushing or pulling heavily laden hand-cart.	20 – 40	120	1
Heavy	Heavy manual work: shovelling or digging, climbing, ramps or ladders.	40 – 60	180	0.7

Finally, there is self-contained breathing apparatus where air is supplied by a bottle of compressed air. An example of such a system is shown in Figure 15. These systems are superior in terms of the level of protection that is provided but are expensive, heavy, cumbersome in use, and requiring training. Frequently, depending on the local legislation, a medical check needs to be performed to determine if a person is fit to use this type of equipment. They are normally reserved for emergency situations such as spillage management.



Figure 15 Self-contained breathing apparatus. Source: UK HSE [12]



The level of protection that these different mask types provide can be expressed as a protection factor. This factor can be used in quantitative risk assessments to predict the exposure level in the breathed air based on the airborne concentration outside of the mask. There are nominal protection factors (NPF), which are based on the standards for RPE systems²⁸. However, there are also assigned protection factors (APF) that various bodies have determined considering various factors such as heavy or inappropriate use of the RPE systems.

These APFs tend to differ from country to country in height, but also in status. In some countries these factors have been derived and included in official agency documentation (e.g. UK), in others they are simple guidance documents made by the local industrial hygienist association (e.g. NL), and in yet others they are made by bodies that fit between these two extremes. An overview of these factors for most of the types of masks discussed above can be found in Table 9. In most countries however no assigned protection factors have been derived. In those countries one may use the German factors since the guidance explains in setting these up the maximum permissible leakage and other influencing factors such as breathing resistance with high respiratory volumes or the remaining protection in the event of a device malfunction were considered.

Table 9 Nominal and assigned protection factors of masks that can be used in the flexible foam production. Based on [14-16]. NPF means Nominal Protection Factor. * SCBA efficacy dependent on certain conditions see [16]

Standard	Description	Class	NPF	FI	DE	IT	SE	GB	NL	FR	
EN 149	Disposable half mask respirator	FFP1	4	4	4	4	4	4	4	10	
		FFP2	12	10	10	10	10	10	10		
		FFP3	50	20	30	30	20	20	20		
EN 140	Reusable half mask respirators	P1	4	4	4	4	4	4	4	10	
		P2	12	10	10	10	10	10	10		
		P3	48		30	30		20	20		20
		Gas	50	20	30	30	30	10	10		10
EN 136	Full face mask respirators	P1	5	4	4	4	4	4	4	30	
		P2	16	15	15	15	15	10	10		
		P3	1000	500	400	400	500	40	40		40
		Gas	2000	500	400	400	500	20	20		20
EN 12941	Powered respirators with hoods/helmets	TH1	10	5	5	5	5	10	10	40	
		TH2	50	20	20	20	20	20	20		
		TH3	500	200	100	200	200	40	40		40
EN 12942	Powered respirators with masks	TM1	20	10	10	10	10	10	10	60 100	
		TM2	200	100	100	100	100	20	20		
		TM3	2000	1000	500	400	1000	40	40		
		TM3 P (120 l/min)									
		TM3 P (160 l/min)									
EN 137	Self-Contained Breathing Apparatus (SCBA)	Demand	2000	500	>1000	1000		2000	2000*		

²⁸ For example, in EN 12941 it is stated that the maximum permissible leakage is 10, 2, and 0.2% for TH1, TH2, and TH3 masks resulting in NPF of 10, 50, and 500, based on the assumption that filters work perfectly.



Generally, use of RPE for non-standard operations (e.g. maintenance) or to protect against process safety events (e.g. leaks during unloading) is considered acceptable. However, long-term use of RPE during normal daily tasks is not in line with the hierarchy of control and should be minimised as much as possible. This general principle remains correct however more concrete maximum permissible wearing times have been established in Germany that may be used as guidance in the flexible polyurethane foam industry.

In Table 10 maximum continuous wear times (CWT), recovery times, and total wear times (TWT) for various types and classes of masks have been described. CWT is the time a mask may be worn in one go and the recovery time is the period that the worker should be allowed to recover away from the exposure situation where the RPE is mandatory. The TWT is the total amount of time a particular piece of RPE is allowed to be worn during a full shift.

For the CWT in Table 10 a medium workload is assumed. Should the workload be light or heavy then these CWT values should be multiplied by the wearing time adjustment factor specified in Table 8. Furthermore, when working in hot, cold, humid, or otherwise uncomfortable situations the CWT should be reduced by a, to be determined factor, depending on the severity of the conditions.

*Table 10 Wearing times for different types of masks. * if the total wear time per shift is used, the device should not be worn for more than 2 working days in a row and not more than four days per week. * Combination of gas and particle filters ** SCBA wearing times of devices weighting less than 5 kg is dependent on how long the air in the device lasts. Based on: UK and German Guidance [12, 13]*

Standard	Description	Class	Continuous Wear Time; CWT (minutes)	Recovery Time (minutes)	Total Wear Time; TWT (minutes)
EN 149	Disposable half mask respirator	FFP1 or FFP2	75	30	360*
		FFP3	150	30	420
EN 140	Reusable half mask respirators	P1 or P2	150	30	420
		P3 or Gas	135	30	420
		Combination ⁺	120	30	360
EN 136	Full face mask respirators	P1 or P2	135	30	420
		P3 or Gas	120	30	360
		Combination ⁺	105	30	300
EN 12941	Powered respirators with hoods/helmets	<3 kg	No Limit		
		>3 kg	180	30	450
EN 12942	Powered respirators with masks	<3 kg	150	30	420
		>3 kg	120	30	420
EN 137	Self-Contained Breathing Apparatus (SCBA)	<5 kg	Device Dependent ^{**}		
		>5 kg	60	30	240*



The following advice on the type of mask to use during which activities in flexible foam production is general and may be deviated from based on local plant conditions and locally applicable legislation/regulation:

- During unloading of TDI a respirator (normally full-face mask according to EN 136) should be worn to offer a first protection for if an incident occurs²⁹. However, if a (larger) incident occurs (e.g. a leak resulting in a large spill) the workers should evacuate the area and a specialized crew fitted with SCBA should resolve the incident situation.
- During any activity where powder is handled and dust or aerosol is formed (e.g. feeding big or small bags into a hopper) respirators with dust filters should be worn, unless measurements or modelling shows that this is not needed.
- During activities involving diisocyanates a respirator should be worn with a level that is dependent on the activity performed. For example, dismantling and cleaning of a flushed mixing head that may contain traces of residual diisocyanates can be done using a half mask respirator. However, if a TDI filter in the tank farm needs to be replaced a full-face mask should be considered the minimum.
- In the slabstock foam production hall, respirators are used:
 - during start-up for process safety reasons,
 - while performing activities with known higher exposure potential (e.g. changing side paper rolls, entering the encapsulation, working around the cut off saw at the end of the foam line)
 - if direct reading instruments shows unusually elevated concentrations.

Here a choice can be made, and a risk assessment is needed to substantiate the choice between half mask respirators, full face mask respirators, powered respirators, and fresh air supply breathing apparatus.

- In moulded foam production, depending on a risk assessment, activity near high pressure lines/system may require wearing RPE. In many of these areas a leak will result in a sizable discharge due to the high-pressure systems of mixing heads or head pressure of in bulk tanks.
- In both slabstock and moulded foam production halls incidents can occur requiring an evacuation (e.g. a miss pour in moulded production or a wrong mixing ratio of the liquid laydown in slabstock production) in these cases workers with SCBA should resolve the incident situation, unless the scale of the incident allows for lower levels of respiratory protection.
- RPE should be worn in the curing area of a slabstock foam plant unless measurements demonstrate that the presence of fresh foam in the area does not cause concern for human health.

²⁹ While the ISOPA guidelines do not recommend this for MDI it may be useful to require the use of RPE when unloading MDI as well, based on a local risk assessment. Particularly if the to be unloaded MDI temperature is elevated.



Filter Selection and replacement rates

A crucial part of (powered) respirators is the filter since this determines which substances are removed from the surrounding air before the air is inhaled. An overview of the core filter types can be found in Table 11.

Table 11 Overview of filter types and the model gases used for testing.

Type	Use	Model Gas used for testing (EN 14387)
A	For use against certain organic gases and vapours with a boiling point > 65 °C	Cyclohexane
B	For use against certain inorganic gases and vapours	Chlorine Hydrogen sulphide Hydrogen cyanide
E	For use against sulphur dioxide and other acidic gases and vapours	Sulphur dioxide
K	For use against ammonia and organic ammonia derivatives	Ammonia
P	For use against particles	

Combination of these filter types can also be found. Common examples are AP and ABEK filters, that filter a combination of volatile organics and particles or a combination of gasses. The type indication letters can also be followed by a number 1, 2, or 3, indicating that the filter has a low, medium, or high capacity (e.g. A2P2 filters have medium capacity for vapours and particles). In the absence of a number after the type indicator a level of 1 should be assumed (e.g. a A2P filter has a medium capacity for organic vapours and a low capacity for particles).

Filters can become saturated resulting in a loss of efficacy. The rate at which this happens is influenced by the concentration of substances that are filtered from the air, humidity, temperature, duration of use and the breathing rate of the wearer. RPE manufacturer's instructions frequently state that filters need immediate replacement when the odour of the contaminant is detected. While technical true, it is highly inappropriate to rely on odour detection alone since many substances, including diisocyanates, cause adverse effects at far lower levels than the odour threshold.

A more appropriate understanding of when filters should be changed can be obtained by understanding how these filters are tested. EN 14387 describes that air containing a certain model gas (see Table 11) in a defined concentration should be passed through the filter for a defined time and that the filter effluent concentration may then not exceed a certain threshold. By multiplying the minimum breakthrough time with the test gas concentration, a measure of the filter capacity is calculated that can be expressed in ppm*minutes.

Since most substances in the workplace air of flexible foam plants can be considered (semi-)volatile organic compounds ((S)VOC) the most relevant of the filter types is the A type filter. Table 12 provides the minimum breakthrough time and test gas concentration for the different levels of A-type filters. The capacity of the A2 is 2.5 times greater than A1 and A3 is having an almost 3 times greater capacity than



A2. From a theoretical perspective **if one assumes** that all (S)VOCs behave as cyclohexane and the (S)VOC concentration in the workplace air is known then a maximum wear time can be calculated. For example, if the (S)VOCs level would be 3 ppm then the maximum time an A1 filter would be effective would be 388 hours, assuming the mask would be used for 2 hours per day, the filter would need to be replaced every half a year. Of course, this is only theoretical since not all (S)VOCs will behave as cyclohexane, the total (S)VOC level in workplaces is often not known, the tests are done under ideal laboratory conditions, and other previously mentioned factors such as humidity are not taken into consideration. Also, all kind of substances in the air of a workplace count for such an evaluation including catalysts, surfactants, mould release agents, diisocyanates and polyols.

Table 12 Calculated service life based on EN 14387 of A type filters

Type	Minimum breakthrough time (min)	Test gas concentration (ppm)	Capacity (ppm*min)
A1	70	1000	70 000
A2	35	5000	175 000
A3	65	8000	520 000

With regards to the type of filter to be used the following recommendations apply:

- When working with pure diisocyanates (e.g. tank farm filter replacements) or to protect against potential pure diisocyanates exposure (e.g. unloading of tank trucks), AP type filters are required. It is recommended to use at least A2P level filters.
- When used in slabstock foam production AP type filters are required to protect against diisocyanates exposure and will cover most other substances used as well. It should however be considered as to whether other filter types are needed based on the formulations used and expected airborne substances.
- When performing certain conversion activities involving controlled limited combustion of foam (e.g. flame lamination and/or reticulation) volatile organics, hazardous particulate matter, and hydrogen cyanide can be formed requiring APB type filters.
- It should be noted that methylene chloride (MC) is likely to pass most normal filter types. Users of MC should contact their filter supplier to determine if they have specialised AX filters that protect against MC or switch to non-filter dependent solutions such as air fed breathing apparatus or SCBA when using MC.

Filter suppliers should be consulted to determine the adequate replacement frequency. In the absence of more specific advice from suppliers the following rules of thumb apply, which may be deviated from based on risk assessments:

- When working with pure diisocyanates and diisocyanates in a non-reacting mixture, filters should be replaced every 15 days or after significant exposure events.



- Filters used in regular slabstock foam production should be replaced every 15 days, but also following significant exposure events.

Use and training advice

When it comes to the use of RPE it is imperative to follow manufacturer's instructions. In addition, the following practices should be observed:

- All RPE should be made personal and every employee that has to use RPE should receive a dedicated RPE system that is to be stored in a dedicated sealed personal container.
- Before using the RPE system a face fit test should be conducted dependent upon the type of mask. This will vary from a spray where a substance with a particular taste/odour is used to verify that the mask fits well and there is no breakthrough, this is referred to as Qualitative. For full face and SCBA masks quantitative analysis is performed using calibrated and certified equipment. All face fit testing should be carried out by trained professionals.
- Facial hair can impact the functioning of RPE by interfering with the seal. See Figure 16 for a description of facial hair styles that disrupt the seal of half mask respirators. Workers that must use such RPE should ideally be clean shaven or at the very least restrict their facial hair style to one that does not impede the functioning of the RPE that they have to use and have the remainder of the skin freshly shaven. A study by UK HSE showed that even a light stubble appearing within 24 hours after shaving may adversely impact the awarded protection [17].
Alternatively, for employees that have facial hair as a protected characteristic (e.g. for religious reasons), RPE that is compatible with facial hair may be considered (e.g. powered respirators with hood).



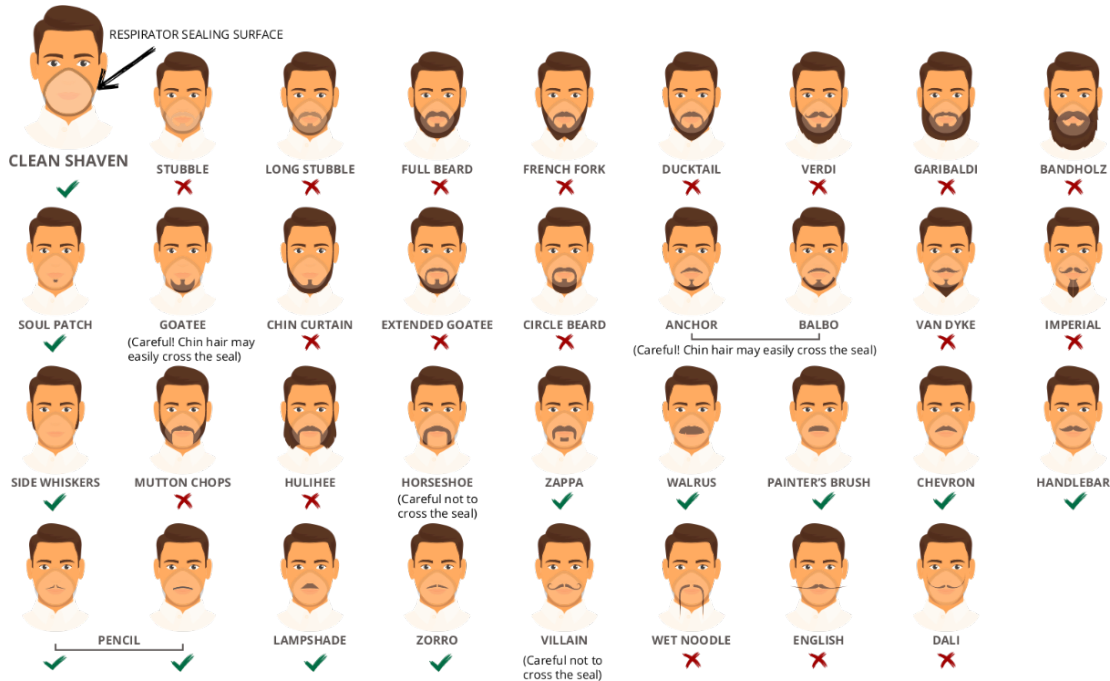


Figure 16 Facial Hairstyles and filtering facepiece respirators: for workers who wear tight-fitting respirators. Source: [US CDC](#)

D3.2 Dermal Protection

For certain substances, such as diisocyanates, dermal contact should be avoided.

Gloves

EN 374 Chemically Resistant Gloves should be worn by those working with pure substances or such substances in a mixture that have a dermal contact hazard. In the Safety Data Sheet of the substance or mixture it will be explained which glove material needs to be used to ensure sufficient breakthrough time when handling the pure substance.

For operation with potential contact with liquid reaction mixture (i.e. the material coming out of the mixing head in flexible foam plants) thick nitrile gloves according to EN 374 should be used.

For operations with the potential for contact with (semi-)solid (e.g. towards the end of a slabstock foam line) reaction mixture EN 374 thick nitrile gloves may be used. However, for operations with very short duration (seconds to a minute) dermal contact such as the taking of a sample of foam for quality control purposes where visual and **tactilely** the foam is inspected³⁰, a thinner glove that is immediately disposed of after the performance of the operation can be preferred. If possible, the glove material should still be nitrile.

For operations with uncured foam particularly moulded foam it should be noted that there is a potential for aromatic amine exposure explained in D1.3. For this reason, chemically resistant gloves should be

³⁰ This is a relatively common practice and allows for slight corrections to be made in the formulation, thus improving quality and preventing the formation of poor-quality foam or even foam waste.



worn during demoulding of moulded foam pieces. If required thermally and/or mechanically resistant gloves can be worn over the chemically resistant gloves.

Two studies by the International Isocyanates Institute (III) have shown that it is possible for certain types of non-chemically resistant gloves to result in a degree of protection as well. These studies - III Report 11667³¹ focusing on MDI/MDA and III Report 11787³² on TDI/TDA - can be obtained from any diisocyanates supplier that is a member of III. Following careful study of these reports and after performing a risk assessment, it may be possible to deviate from the requirement to wear chemically resistant gloves when handling uncured foam pieces in favour of assessed non-chemically resistant gloves with adequate changeout schedule. Especially, this may be the case for refining moulded foam cushions or moving curing slabstock blocks.

If the requirement to wear chemically resistant gloves is deviated from, it may be prudent to generate data using similar methodology to evaluate whether this can be done safely particularly for glove (types) that have not been assessed previously. Alternatively, biomonitoring could be performed before and after the switching to non-chemically resistant gloves to ascertain their function.

Other work clothing

With regards to other protective clothing ISO 13688 and EN 340 describe the general requirements and ISO 13688 contains a table with icons explaining which hazards clothing can protect against. Of relevance would be protection against liquid chemicals and dependent on the site specificities further hazards need to be protected against (e.g. in sites with ATEX zones, work clothing protecting against electrostatic discharge tested under EN 1149 might be required).

For all operations involving liquid mixture containing a substance with dermal hazard (e.g. every slabstock foam line operator) work clothing that meet the requirements of EN 13034 should be worn.

When performing higher risk activities with pure diisocyanates or other substances that have a dermal hazard (e.g. unloading of tank trucks), full body clothing (type 3 or 4) according to EN 14605 should be considered a best practice. Alternatively, clothing meeting EN 13034 (type 6) may be considered sufficient based on risk assessment.

D4 Continuous Improvement

At the moment of writing the Advisory Committee on Health and Safety at Work (ACSH) a body at EU level with representation of unions, employers, and governments has adopted the [opinion](#) that EU wide occupational exposure levels (OELs) should be set for all diisocyanates expressed in $\mu\text{g NCO}/\text{m}^3$. This opinion will form the basis for a regulatory procedure that will establish EU-wide binding OELs.

The proposed values tend to be lower than the limits currently in place in different EU Member States of 8-hour time weighted average (TWA) and 10 or 20 ppb for 15-minute short term exposure limit value

³¹ Vangronsveld and Ahrika (2015) - Evaluation of glove effectiveness with MDI and MDA during flexible foam moulding. III Report 11667

³² Lesage, Daoud, Cloutier (2022) - TDI/TDA: assessing glove effectiveness during handling of fresh flexible PU foam



(STEL) (see Table 13). Furthermore, when considering the hazard properties of TDI and MDI, it should be noted that they qualify for the ALARA/ALARP principle, and the exposure should be reduced to **as low as reasonably achievable / practicable**.

*Table 13 **Gzrgevgt** future limit values for diisocyanates following the completion of the regulatory procedure. While very unlikely the final values that come out of the regulatory process could be different and naturally take precedent over what is written here. The $\mu\text{g NCO}/\text{m}^3$ values can be converted to $\mu\text{g TDI}/\text{m}^3$ or to $\mu\text{g MDI}/\text{m}^3$ by multiplying them by 2.07 or 2.98, respectively.*

Period	TWA ($\mu\text{g NCO}/\text{m}^3$ ppb)	STEL ($\mu\text{g NCO}/\text{m}^3$ ppb)
After adoption of legislation until 31 December 2028	10 2.9	20 5.8
From 1 January 2029	6 1.7	12 3.5

Given current exposure levels, particularly in slabstock foam production, it is expected that exposure reduction measures should be taken to reduce exposure. In reducing exposure the hierarchy of controls should be followed.

In terms of **substitution** very little can be achieved in most cases for the production of flexible polyurethane foam, diisocyanates are a core ingredient. So called non-isocyanate polyurethane (NIPU) is currently confined to the world of academia and has little to no industrial applications.

Technical control such as enclosures, specifically engineered extraction ventilation and general ventilation are measures that are already extensively deployed in the flexible polyurethane foam production. However, these can be further improved. Specific consultancies or even local labour inspectorates might be able to assist with analysis of the current situation and recommendations for improvements. Alternatively, some competence can be present or developed within the plant itself. For example, HSE managers can cooperate with technical service departments and use smoke tests to map airflow in the production hall or investigate the overall situation with mobile DRI.

The REACH Restriction should ensure a strong improvement by deploying uniform high level training which is an **organisational** control measure. The training should however not be the sole source of improvements. Further plant specific improvements might be possible. For example, using camera's visual observation needed in flexible foam production can be performed at a greater distance from the production process, thus reducing exposure. Workers would need to be trained to use such plant specific systems.

Finally, while **personal** protective equipment is a less preferred measure in the hierarchy of control, this does not mean that improvements should not be made. Particularly a move away from non-powered respirators to powered respirators or air fed breathing apparatus could improve the exposure situation, reduce the strain on workers and improve wearing time during production runs.

To illustrate the above with a practical example, most slabstock foam lines have a tunnel encapsulation with windows that can be opened to observe the foam and make corrections where needed (e.g. to correct side paper drift). When windows are closed air is drawn by extraction points in the tunnel from



the ends of the tunnel ensuring that workers at the mixing head are protected. However, when windows are opened air will be drawn through this opening reducing the extraction from the ends of the tunnel as shown in Figure 17, thus potentially increasing the airborne diisocyanate concentrations on the mixing platform. Hence the vital importance of closing windows on the foam line whenever they do not need to be open. An already deployed organisational measure are workplace instructions that specify that workers should close these windows when they do not need to be open. However, this can be reinforced by behaviour-based training explaining them that if left open, their colleagues at other points of the line will be less protected. A technical control measure could also be introduced in the form of automatically closing windows. However, this presents a physical hazard of a window closing crushing/cutting workers. A technical-organisational measure would be to alert workers at the beginning or ending of the line with a light signal that a colleague has opened a window enabling them to take precautions in the form of wearing RPE and address their colleague if the window remains open.

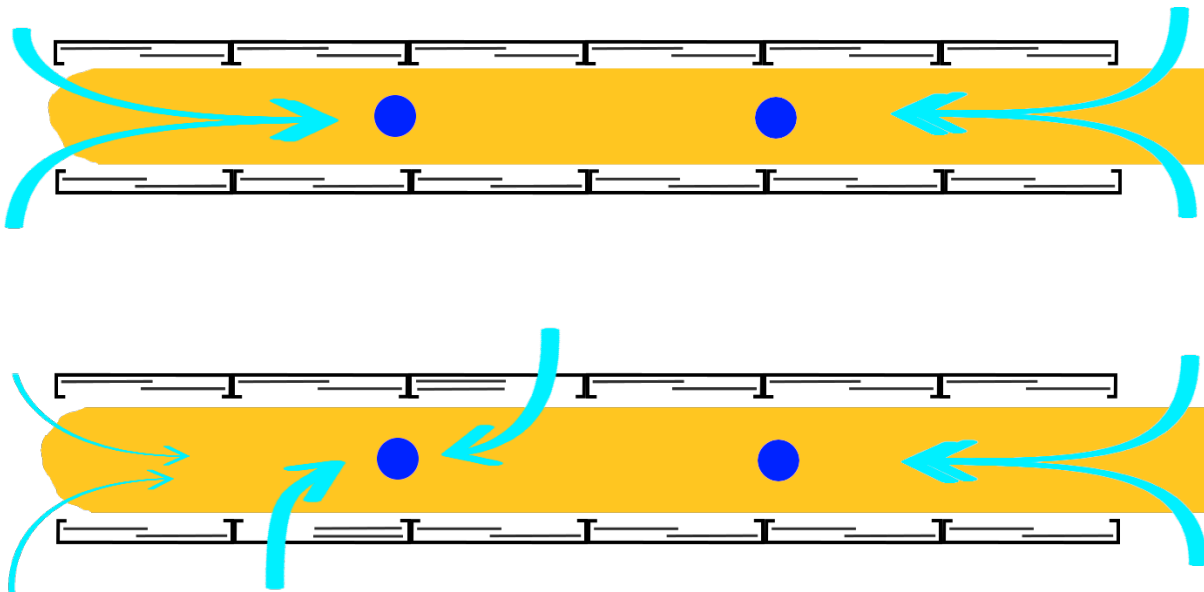


Figure 17 Graphical illustration of relative air flow. Top picture: all windows are closed, air flows into the tunnel from the ends of the tunnel. Bottom picture: two windows are opened, airflow at the start of the tunnel is reduced.

The outcome of modifications to such systems is always to a degree unpredictable and form an iterative process. Only after the modifications have been put in place and measurements have been performed, one can assess the efficacy of their implementation. As such, it is recommended to set up a continuous improvement plan where engineering improvements are added in between the normal measurement campaigns with an aim of reducing exposure.



E Health surveillance

This chapter will focus exclusively on the health hazards of diisocyanates. There might be other substances deserving special attention in health surveillance or other aspects that should be included in health surveillance of workers. This chapter will explain in brief layman's terms the mechanism of action on human health of diisocyanates, the tools that can be used in medical surveillance, and describe what kind of medical surveillance should be performed.

E1 Mechanism of Action of Diisocyanates

When it comes to diisocyanates and the effects on the human body it is important to understand that in the context of process safety there can be events with such overexposure that there are immediate health consequences. However, there is also the aspect of sensitisation, which can have relevance at more subtle levels of overexposure that are in the realm of normal operating conditions and industrial hygiene. Finally, there is a relevance of process safety related overexposure events for subsequent sensitisation. All of this will be tackled below.

When process safety incidents happen airborne diisocyanates concentrations can rapidly exceed all OELs by orders of magnitude, which have been set to control exposure during normal operations considering the sensitization effect. In Table 14 the acute effect of such higher concentrations of TDI on human volunteers in the 1960s is reported.

Table 14 Observed acute effects in 6 human volunteers of various concentrations of TDI. Six healthy male volunteers were exposed to one concentration per day in random order. For reference, the current median 8 hour TWA OEL in the EU is 5 ppb (0.035 mg/m³). Source: data from Henschler et al. 1962. reproduced in [18]

Concentration		Acute Effects during or after TDI Exposure
ppb	mg/m ³	
10 or 20	0.07 or 0.14	2,4/2,6; 2,4; 2,6: no odor perception, no acute effects
50	0.36	2,4/2,6: odor noted immediately upon entering the room; after about 5 min of exposure, 3/6 volunteers experienced a slight "tingling" sensation of the eyes described as lacrimation urge without tears
		2,4: weak odor perception, no eye irritation
		2,6: odor was stronger as compared with the 2,4-isomer
75	0.53	2,6/2,4: odor became stronger; slight burning of the eyes occurred after 1–6 min, but there was no lacrimation; with deeper breaths, volunteers experienced tickling or a slight stabbing pain in the nose
80	0.57	2,4: slight conjunctival irritation and tickling of nose
		2,6: eye and nose irritation more severe as compared with same concentration of the 2,4-isomer; effects on throat were perceived as dryness, not scratching sensation
100	0.71	2,4/2,6: eye and nose irritation became more severe described as resembling a cold (catarrh)
		2,4: more pronounced conjunctival irritation and tickling of nose



Concentration		Acute Effects during or after TDI Exposure
ppb	mg/m ³	
		2,6: eye and nose irritation more severe as compared with same concentration of the 2,4-isomer; effects on throat were perceived as dryness, not scratching sensation
200	1.4	2,4: eye irritation was perceived by 2/5 as stinging and uncomfortable
		2,6: eye and nose irritation more severe as compared with same concentration of the 2,4-isomer; effects on throat were perceived as dryness, not scratching sensation
500	3.6	2,4/2,6: lacrimation, but eye irritation was still tolerable; one had copious nasal secretion that was associated with "stinging" nasal pain; all had scratchy and burning sensations in the throat, without cough
		2,4: eye irritation was perceived by all as stinging and uncomfortable with lacrimation
		2,6: effects similar to the 2,4-isomer
1300	9.2	2,4/2,6: two individuals were able to remain in the room for 10 min; irritation was intolerable; several hours later, cold-like symptoms with cough persisted

When it comes to these acute effects it should be noted that it has been observed that there may be a so-called "delayed onset", meaning that symptoms can develop minutes or even hours after the acute exposure event. It is therefore imperative to keep workers that were involved in a process safety event under observation for a period after the event has occurred.

Based on the table above and other data Acute Exposure Guideline Levels (AEGs) have been developed by the US EPA. AEGs are used by emergency planners and responders worldwide as guidance in dealing with rare, usually accidental, releases of chemicals into the air. AEGs are expressed as specific concentrations of airborne chemicals at which health effects may occur. They hold no formal legal status in EU legislation, but can be relevant for the establishment of major-accident prevention policy required under the Seveso Directive (2012/18/EU).

Table 15 Acute Exposure Guideline Levels for TDI in ppb. Based on [18]

Classification	10 min	30 min	1 h	4 h	8 h	End Point
AEGL-1 (Nondisabling)	20	20	20	10	10	Chest tightness, eye and throat irritation
AEGL-2 (Disabling)	240	170	83	21	21	Severe eye and throat irritation, lacrimation
AEGL-3 (Lethal)	650	650	510	320	160	4-h LC50 in the mouse



Next to these acute effects in the case of significant overexposure, there is also the chronic effect of sensitisation that can happen at much lower levels of (peak) overexposure. The following text is a layman's explanation of the phenomenon of respiratory sensitisation.

When inhaled, diisocyanates react with molecules in the respiratory tract. One molecule in the respiratory tract in particular is the partner of choice for diisocyanates: glutathione. The reaction with glutathione allows for diisocyanates to be bound and transferred to the protein albumin. Both glutathione and albumin can carry the diisocyanate away from the lungs through the blood to be excreted in a relatively benign bound state. However, the supply of glutathione in the respiratory tract lining, while constantly being produced by respiratory tract lining, is not infinite. Particularly peak overexposure can overwhelm this normal clearance mechanism resulting in reactions with water which results in the formation of solid particles of polyurea and reactions resulting in the direct binding of diisocyanates to albumin and other proteins.

Under normal circumstances proteins in general are constantly broken down and reconstructed, the diisocyanate-protein conjugates (such as albumin-diisocyanate conjugates) are no different and would normally be cleared over time. However if triggered, the immune system may develop a specific immunity to these diisocyanate-protein conjugates. Once this immunological memory is established the person is sensitised.

Upon even very low level of subsequent exposure (e.g. below normally applicable OELs) the sensitised individual may demonstrate a specific immunological reaction, the symptoms of which may include: redness of the eyes, runny nose, sneezing, chest tightness, coughing, wheezing, and shortness of breath³³. Initially the more benign symptoms may present (e.g. runny nose), but the longer the sensitised individual keeps working in the exposure situation, the more severe the symptoms become. Because of this, a worker who notices these symptoms recurring should consult an occupational physician to diagnose the cause. Should the sensitised individual with symptoms keep working in the exposure situation for too long the symptoms can become permanent and thus permanently disrupt the functioning of the respiratory system.

³³ Also, these types of reactions can have a delayed onset and may emerge after the shift has ended. This should be kept in mind since workers may develop symptoms after work at home and not immediately associate them with work. When presenting these symptoms to a general practitioner, the GP may not be aware of the occupational exposure and start symptom management for rhinitis, asthma, and/or hay fever that enables the worker to keep working in the exposure situation for a time.



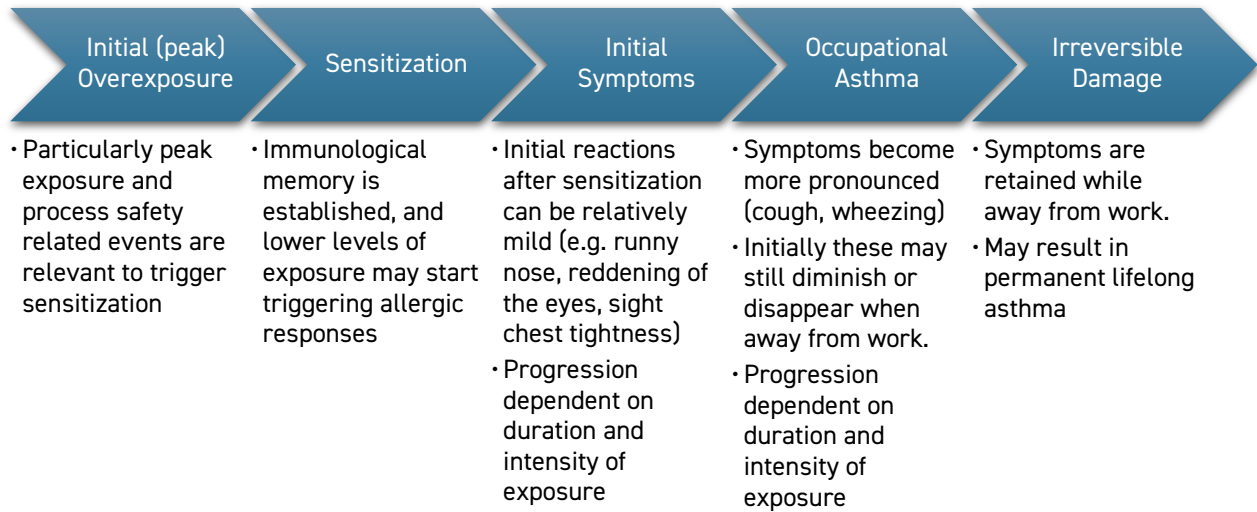


Figure 18 schematic representation of disease progression for respiratory sensitizers in general

The initial symptoms are very similar to those of people suffering from hay fever, which makes perfect sense since this is also the result of a specific immunity to certain pollens. Whereas it is very much unclear what triggers the immune system to develop specific immunity to pollens, it is clear that one of the potential triggers for the immune system to develop specific immunity to protein-diisocyanate conjugates are diisocyanates themselves.

Here the science becomes a bit hazy, but potential triggers are too high levels of protein-diisocyanates conjugates, a degree of local irritation, polyurea particulates, or a combination of these factors. Regardless of the mechanism, the level of exposure required to trigger the specific immune response to develop sensitisation does not need to be at the level that would trigger the acute symptoms of process safety related events. Thus, low levels over overexposure (e.g. somewhat above OELs), could trigger sensitisation in the absence of overt irritation symptoms as described in **Table 14**.

Finally, while process safety related acute overexposure is not needed to cause sensitisation, it certainly is a very strong risk factor for the development of sensitisation. It may be beneficial to allow a period of rest before restarting work with diisocyanates and to monitor the health of workers that were involved in such incidents that are returning to work attentively.

E2 Tools used in Medical Surveillance

Below is a short description of the diagnostic tools that can be employed by occupational physicians:

- **Work history interview** can be a useful tool to obtain information on where the worker was employed before and is relevant in the sense that sensitisation by diisocyanates does not disappear and may be carrying immunological memory to diisocyanate-protein conjugates from previous exposures. Such a work history interview should include questions on whether allergic skin or lung reactions ever occurred.



- A **questionnaire** can be used to ask specific question on whether the person experiences symptoms that may be related to diisocyanates and whether these symptoms disappear while away from work. Such a questionnaire should also include questions about allergic skin reactions. The tool has a good specificity and good sensitivity.
- Specific immune responses can be mediated by antibodies, also known as immunoglobulins. Immunoglobulin E (IgE) is normally associated with allergic type reactions. A **general IgE blood test** can be performed. A high result can be caused by diisocyanates induced allergic responses or allergic responses to other allergens (e.g. pollen). Also, a sensitised symptomatic individual can still have a low result if the immune response is not IgE mediated. Therefore, the method has a low sensitivity and a low specificity. The test is however widely available and cheap and may contribute a small piece to a larger puzzle for a physician.
- There are also **specific IgE blood tests** determining whether there are IgEs in the blood that react to TDI-HSA or MDI-HSA conjugates³⁴. If positive the person is nearly certainly sensitised to the specific diisocyanate. The test has an extraordinary specificity for sensitisation. However, the person may have developed other specific IgEs that react to other proteins to which diisocyanates can bind or have developed a non-antibody mediated immune response. A negative test does not exclude the possibility that the person is sensitised and thus the test has a low sensitivity. Furthermore, the test is typically not widely available and may require cooperation with laboratories outside of the Member State the plant is located in.
- **Spirometry**, also known as lung function test, can be done to determine the lung function and compare this with statistical values for the persons sex, age, height, and race. Lung function can also be negatively affected by other influences (e.g. smoking) and by itself is not very useful. However, when performed before and after provision of a salbutamol, a bronchodilating substance (i.e. a substance that opens the airways further), it can be used to determine if the person has asthma. This will not tell the physician if the asthma is work induced or not but contributes to the diagnostic puzzle.
Furthermore, the value of spirometry measurements increases if they are performed periodically; greater than normal decline is an indicator as well. Regular spirometry is widely available.
- A **Methacholine Challenge Test** is a variation on regular spirometry where lung function is measured before and after inhaling increasing doses of methacholine. Methacholine can cause a non-specific hyperresponsiveness meaning that at a certain level it may include sharp decline in lung function or not. It is normally used to determine "hyperactive airways" or non-specific bronchial hyperresponsiveness; which can be a symptom of occupational asthma related to diisocyanates. The test is normally widely available and can contribute to the diagnostic process.

³⁴ HSA stands for Human Serum Albumin, a protein that is relatively abundant in blood and can be artificially manufactured. By reacting HSA and a diisocyanate a diisocyanate-protein conjugate is formed.



- In a **Specific Challenge Test (SIC)** the individual is exposed to an artificially generated known concentration of the allergen (e.g. TDI) and lung function is monitored periodically for several hours. It is the gold standard for the diagnosis of occupational asthma. However, it is very resource intensive (1 day at a clinic) and thus expensive. Furthermore, the technique is not available in every country (see Figure 19). Lastly, deliberately exposing an individual to a sensitising substance should of course be avoided. It is for these reasons that SIC, when used is reserved for final stages in diagnostics.



Figure 19 European centres where specific inhalation challenges are used in the diagnosis of occupational asthma. The size of each circle is proportional to the number of patients challenged each year. The biggest circle (Helsinki) represents 136 patients per year and the smallest circle (Aarhus) represents one patient per year. Information was derived from an online survey of members of the European Respiratory Society Occupational and Environmental group in 2012. The following centres are shown: Finnish Institute of Occupational Health, Helsinki, Finland; Nofer Institute of Occupational Medicine, Łódz, Poland; Hospital Vall d'Hebron, Barcelona, Spain; Fundacion Jimenez Diaz, Madrid, Spain; Strasbourg University Hospital, Strasbourg, France; Centre Hospitalier Universitaire de Mont-Godinne, Yvoir, Belgium; General University Hospital, Prague, Czech Republic; Birmingham Heartlands Hospital, Birmingham, UK; The Institute for Prevention and Occupational Medicine of the German Social Accident Insurance, Bochum, Germany; Seinäjoki Central Hospital, Seinäjoki, Finland; Oulu University Hospital, Oulu, Finland; Royal Brompton Hospital, London, UK; Helsinki University Central Hospital, Helsinki, Finland; Universitair Ziekenhuis, Brussels, Belgium; University of Padova, Padova, Italy; Institute for Occupational and Maritime Medicine, Hamburg, Germany; University of Pisa, Pisa, Italy; Fondazione Salvatore Maugeri, Pavia, Italy; University of Munich, Munich, Germany; North Manchester General Hospital, Manchester, UK; University Hospitals Leuven, Leuven, Belgium; Republican Klaipeda Hospital, Klaipeda, Lithuania; Haukeland University Hospital, Bergen, Norway; Aarhus University, Aarhus, Denmark. Taken from [19].



- An alternative to SIC would be to perform **Serial Peak Expiratory Flow (PEF)** measurements to confirm the diagnosis. Here the worker is trained to use a PEF measuring device and is asked to keep a log of measurements, ideally every 3 – 4 hours while awake for a period of weeks. In the log the worker keeps track of which days they are at work and what kind of activities are performed, as well as whether they have any symptoms or use any medication for these symptoms. The results are then either visually or statistically analysed to determine if PEF values drop while at work compared to periods away from work.

E3 Medical Surveillance

Medical surveillance should be performed for all workers that are at risk of developing sensitisation at work and occupational asthma. It may be mandatory in some countries. In determining which workers meet this criterion it should be determined whether there is a chance of involvement in process safety related events and general workplace airborne concentrations. This should be done for one very simple reason:

The earlier a sensitised person is removed from the exposure situation, the better the chances of making a full recovery.

The inverse is also true, the longer a sensitised person works in the exposure situation the greater the chance of permanent and severe damage (see Box 1 for a description of a study supporting this).

Removal from the exposure situation can sometimes be achieved by moving the person to another department. For example, moving a demoulding operator to packaging in moulded foam production or restricting the work of a sensitised laboratory operator to physical/mechanical properties testing of cured foam.

In this subsection we will discuss what should be done during pre-employment examinations (E3.1) and regular medical surveillance (E3.2) and finally how to confirm a case of sensitisation and/or occupational asthma (E3.3).

Box 1 Summary report of study demonstrating importance of early cessation of exposure following sensitisation.

Pistati et al. have demonstrated that the duration of symptomatic exposure at work is the most important prognostic variable in determining if clinical symptoms continue after cessation of exposure [2]. They found 25 workers that were willing to undergo a specific inhalation challenge (SIC) years after they were diagnosed with occupational asthma and recorded whether they had symptoms in daily life with a questionnaire. In a SIC the person is exposed to the allergen and the decline in lung function is measured. Those that responded to the SIC and had symptoms affecting them in daily life had worked on average 4 years with symptoms in the exposure situation, those that did not respond to the SIC but had symptoms in daily life 2.1 years, and finally those that did not respond to the SIC and no longer had any symptoms had worked on average for a period of 0.6 years in the exposure situation.



E3.1 Pre-employment examinations

Pre-employment examinations are medical checks performed before engagement of an employment contract to determine if the person is fit to work in a specific job. Most countries maintain specific legislation in relation to pre-employment examinations which normally involve a need to establish a protocol and justify any performed examinations. When possible, it is highly recommended to perform pre-employment examinations for all prospective employees that are to be working with diisocyanates. These examinations should include:

- Work history and questionnaire methods to establish whether the person may already be sensitised to diisocyanates or has other pre-existing respiratory and/or allergic ailments. Already sensitised individuals should be excluded from employments since subsequent exposure would result in development of symptoms and eventually irreversible damage. Pre-existing respiratory and/or allergic ailments could be indicative of atopy and a value judgement must be made by the physician on whether the person is fit for employment (see Box 2).
- Spirometry to establish baseline lung function. Should the results indicate a reduced lung function compared to the expected values the test may be repeated after inhalation of salbutamol to establish whether or not the person has general asthma, which is a contra-indication for working with diisocyanates subject to the medical evaluation. The baseline lung function should be stored with the records of the person hired for reference in subsequent regular medical surveillance.

Box 2 Explanation of Atopy

Atopy is the tendency to produce an exaggerated IgE immune response to otherwise harmless substances in the environment [1]. There is no real perfect test for such a status and the diagnosis of this is a bit subjectively based on things like whether the individual has many other allergies (e.g. hay fever), spirometry, general IgE blood tests and simply asking questions about previous respiratory system ailments. Since the atopy status is subjective there can also be degrees in this. An individual allergic to pollen, nuts, and dust mite; in combination with a statement from the individual that he has been in and out of treatment facilities for related respiratory issues his entire life, might not be suitable for working with diisocyanates. A person that has well controlled hay fever for a few weeks per year, might still be able to work in a flexible polyurethane foam production plant. Here the case should be left to the discretion of the occupational physician evaluating the candidate's status.



E3.2 Regular Medical Surveillance

Normal regular medical surveillance should be performed at least biennially, with annual frequency considered a best practice. During this regular medical surveillance, the following screening methods should be applied:

- A questionnaire asking whether the worker has experienced any respiratory symptoms or allergic skin reactions and whether these go away/diminish when away from work.
- Spirometry comparing lung function with average values, but more importantly with previous years to determine if there is a more than normal decline in lung function.

If these methods give an indication that the person may be sensitised to diisocyanates, more specific methods must be used to determine if this is indeed the case.

E3.3 Diagnostic Guideline

David I Bernstein MD has developed a guide for primary care physicians in evaluating diisocyanate exposed workers presenting lower respiratory symptoms for the International Isocyanates Institute (III). This guidance is available [online](#)³⁵ or may be obtained from the EUROPUR/EUROMOULDERS secretariat or from any diisocyanates supplying member company of III. An [online training](#) for this guide has been developed as well. This resource should be provided to the physician performing medical surveillance of the diisocyanates exposed workforce.

This guide uses a combination of work history interview, questionnaire, spirometry, serial PEF, and methacholine challenge testing. All methods are widely available.

³⁵ <https://www.americanchemistry.com/industry-groups/diisocyanates-dii/environmental-health-and-safety/worker-industry-health-and-safety-guidance/diisocyanate-related-asthma/a-guide-for-the-primary-care-physician-in-evaluating-diisocyanate-exposed-workers-for-occupational-asthma>



F Waste Management

F1 Chemical Waste

Chemical waste will be generated in all flexible polyurethane foam plants. The main process safety hazard of chemical waste handling is the potentially violent reaction between diisocyanates and other substances including (rain) water and polyol. When developing and/or reviewing chemical waste management programs it is important to keep diisocyanates containing waste segregated from non-diisocyanates containing wastes.

While diisocyanates are particularly reactive, other combinations of chemicals might result in hazards as well. Information on incompatibilities should be in the SDS section 7, however information in this section should not be assumed to be exhaustive. A tool that can be used to assess the possibility of reactivity between different chemicals is the chemical reactivity worksheet³⁶. Please note that it is not possible to select “polyol” in this tool. It can potentially be modelled by selecting a molecule like glycerine.

In a chemical waste management program, it is important to establish what kind of chemical waste is generated and how to treat it. An **example** waste management matrix is shown in Table 16. The matrix will be different for each plant and depends on the equipment and substances being used.

Table 16 *Gzco ring* Waste Management Matrix for Chemical Waste

Waste	Source	Collection and Sorting	Disposal
Material containing diisocyanates	Filter change spillage	Should be collected in a closable bucket and transported (closed) to dedicated waste collection area where it is drained into the IBC labeled “ISO-Waste”. In case TDI containing waste is stored inside, local exhaust ventilation should be applied closed to the storage and preferably stored in a drum vs. IBC.	To be provided to hazardous waste disposal company.
MDI + Solvent	After foaming with MDI the foaming head is flushed with solvent	To be collected in bucket with lid. After collection, lid is to be placed on bucket, the bucket transported to the waste collection area and the bucket drained into the IBC labeled “ISO-Waste”.	ISO-Waste IBCs when 75% full are transported to dedicated area X and hazardous waste disposal company is contacted to organize collection.

³⁶ <https://www.aiche.org/ccps/resources/crw-overview>



Waste	Source	Collection and Sorting	Disposal
Amine Catalysts	Before to start foaming, the amine circuits are primed with the amines. This liquid is collected as amine waste.	To be collected in bucket and transported to waste collection area and drained into IBC labeled "Polyol+Additives".	Waste IBCs when 90% full are transported to dedicated area X and specialized waste disposal company is contacted to organize collection.
Polyol Waste	Before to start foaming, the polyol circuits are primed with the polyol. This liquid is collected as polyol waste.	To be collected in bucket and transported to waste collection area and drained into IBC labeled "Polyol+Additives".	Waste IBCs when 90% full are transported to dedicated area X and specialized waste disposal company is contacted to organize collection.
Polyol solvent +	After the final production run, the polyol circuits are filled with solvent-polyol blend. This material is flushed from the system each morning.	To be collected in bucket and transported to waste collection area and drained into IBC labeled "Polyol+solvent".	Waste IBCs when 90% full are transported to dedicated area X and specialized waste disposal company is contacted to organize collection.
Other Chemical waste or residues		Chemical residues or waste are collected as far as possible in the original packaging. If other packaging is used, it must be labeled.	To be brought to storage area X for evaluation by waste management responsible.

For chemical waste that is generated regularly in sufficient quantities, dedicated collection infrastructure can be established near to the point of waste generation. An example of this can be found in Figure 20. Based on risk assessment a maximum quantity should be established, which, once reached, triggers the draining of this local infrastructure to storage containers located in a dedicated area.

Finally, if waste storage is located indoors, local exhaust ventilation has to be implemented in case of collecting waste of volatile hazardous substances like TDI residues.





Figure 20 Dedicated waste collection infrastructure. In this facility, certain liquid waste streams are collected in fixed containers and once at a certain level will be pumped into dedicated IBCs that are moved to a dedicated waste storage location.

F2 Chemical Packaging Waste

Waste chemical packaging is subject to the Packaging and Packaging Waste Directive (PPWD; 94/62/EC) and its (sometimes more stringent) implementation in EU Member States. The PPWD does not specify how waste chemicals packaging should be handled since it is a more generalist directive for all packaging. In national implementation and national waste plans there tends to be regulation stimulating that packaging is directed towards specialised decontamination facilities³⁷ to prepare for recycling whenever possible. The following is written as guidance, but certain aspects may be mandatory in certain countries/regions.

F2.1 Liquid chemical containers

Depending on the residual amount of material in the chemical container it may be appropriate to drain the residual amount into a container for chemical waste. ISOPA Safe Transportation, Unloading & Storage of Packaged TDI and MDI guideline³⁸ describes a procedure for the emptying of IBCs and drums containing diisocyanates, which can be followed for other liquid chemicals. When doing so care should be taken to avoid contact between diisocyanates and other substances as explained in F1, however blends of non-diisocyanates substances can be created for disposal as chemical waste (e.g. blends of polyol, polyol with amine catalyst, polyol with solvents).

It is normally not possible to completely empty liquid chemical containers on site. The empty chemical containers should be directed to waste management companies that specialise in the treatment of

³⁷ For example, the Netherlands has taken the principles of various EU waste directives to adopt legislation which is then further worked out in a regulatory instrument called the National Waste Plan (Landelijk Afval Plan; LAP). The [sector plan 43](#) covers “packaging of other hazardous substances”, but when such packaging is properly decontaminated (*schud-, schrap- en schraapleeg*) [sector plan 41](#) on “general packaging” becomes applicable.

³⁸ Available at: <https://www.isopa.org/documentation/> (Direct links: [\[EN\]](#) [\[DE\]](#) [\[ES\]](#) [\[IT\]](#) [\[FR\]](#) [\[NL\]](#))



empty chemical containers. For these specialised waste management companies, it is imperative that the original labels remain affixed to the packaging, and these may thus not be removed.

For empty drums that originally contained diisocyanates a procedure is described in the ISOPA Safe Transportation, Unloading & Storage of Packaged TDI and MDI guideline³⁸ for “decontamination” (i.e. neutralisation). Essentially a process to let the residual diisocyanates react in a controlled manner to polyurea/polyurethane compounds and CO₂. It should be discussed with the specialised waste management company whether it would prefer to perform this procedure itself or have the procedure performed at the foam production facility.

If the plant is in an area with a lower waste management infrastructure and such specialised waste management companies are not available, the packaging should be directed towards incineration. In any case, the decontamination/neutralisation procedure for empty diisocyanate drums must be followed when these are not provided to specialised waste management companies.

F2.2 Solid chemical containers

The use of solid raw materials is limited in flexible polyurethane foam production. Solid raw materials can be delivered in tank truck, big bags, and/or small bags, the latter two generate packaging waste with residual content. Here a differentiation should be made based on the original content. Packaging that originally contained non-hazardous material (e.g. the filler calcium carbonate) should be segregated from packaging that contained hazardous material; particularly material with an environmental concern.

Empty containers containing non-hazardous material, particularly calcium carbonate, can be discarded according to local legislation for normal packaging waste. A best practice would be to try to ensure reuse or at least recycling of such bags.

For empty big bags and small bags which originally contained hazardous material or material with particular environmental concerns the suppliers should be contacted to learn if there are any special programs/recommendations for this waste (e.g. take back programs). In the absence of this, such bags should be carefully folded and sealed in a secondary plastic bag. The sealed secondary packaging should be directed towards incineration.

F3 Other Wastes

Various other types of waste are generated. An example waste management matrix can be seen in Table 17. Care should be taken to identify specific hazards related to the different types of other wastes. For example, paper windup rolls with uncured foam present a diisocyanates emission source.



Table 17 *Gzco ring* Waste Management Matrix for Other Waste

Waste	Source	Collection and Sorting	Disposal
Clothing, textiles, and PPE contaminated with ISO	After cleaning of a mixing head rags may contain residual diisocyanates.	Each contaminated item should be placed in a plastic bucket with a lid and marked with the content. The buckets should be placed in a drum at dedicated area A with extraction turned on. The lid should be placed on the bucket but not tightly sealed.	Depending on degree of contamination to discarded as hazardous or non-hazardous waste.
Side, top, bottom paper contaminated with uncured foam.	During production paper is removed from line A which is contaminated with uncured foam.	Paper roll with uncured foam is an emission source of diisocyanates and thus placed in a dedicated outdoor area away from the production hall.	Once the foam has cured, it is disposed of as industrial non-hazardous waste.
Side, top, bottom paper without foam	During production paper is removed from line B but the inner plastic layer is left on the foam ensuring that no foam is on the removed paper.	Waste paper roll is left next to line until after production run is completed.	Separately collected and sent to paper recycling company.
First fraction of production run	The first fraction of material exiting the mixing head of the slabstock line is captured in a plastic bag.	Plastic bag is placed outside and allowed to react and cure for a day.	Once the material has cured, it is disposed of as industrial non-hazardous waste.
PU Foam Waste	Damaged blocks, collapsing pieces, changeover segments.	Material presenting fire hazard is stored in dedicated locations until cured. Other material is simply allowed to cure.	After curing disposed of as industrial non-hazardous waste. Unless material has sufficient foam structure to be sold as trim foam by-product.

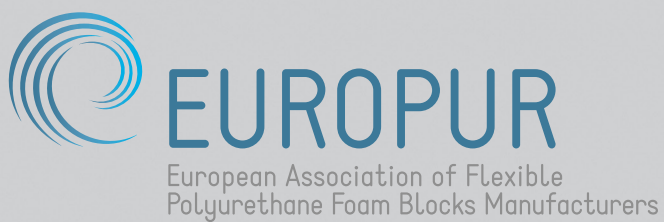
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