

# POLITECNICO DI TORINO

Collegio di Ingegneria Chimica e dei Materiali

**Corso di Laurea Magistrale  
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Tesi di Laurea Magistrale

## **Dealing with MDI in an automotive interiors industry**



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# TABLE OF CONTENTS

<b>Riassunto .....</b>	<b>III</b>
<b>1. Introduction .....</b>	<b>1</b>
<b>2. MDI's properties .....</b>	<b>3</b>
2.1 Vapor pressure .....	4
2.2 Reactions .....	6
2.3 Presence in PUR hot melt .....	7
<b>3. Effects on health .....</b>	<b>9</b>
3.1 European regulations.....	9
3.2 MDI's H-phrases, P-phrases and pictograms.....	10
3.3 Occupational exposure limits.....	11
3.4 Main consequences .....	13
3.4.1 Respiratory hazards.....	13
3.4.2 Skin hazards .....	14
3.4.3 Cause of cancer .....	15
<b>4. Situation in Adient Interiors .....</b>	<b>17</b>
4.1 The process involving MDI .....	19
4.1.1 Adhesion zone .....	22
4.1.2 Pre-fixing zone .....	23
4.1.3 Pre-centerfield zone .....	23
4.1.4 Centerfield zone .....	24

4.1.5	Folding zone.....	25
4.2	Existing preventive measures.....	26
4.2.1	Protective gloves .....	26
4.2.2	Local exhaust ventilation system.....	27
4.2.3	Medical checks.....	27
4.3	Healthy workplaces.....	28
<b>5.</b>	<b>Approach and suggested solutions.....</b>	<b>31</b>
5.1	Chemical risk assessment.....	31
5.2	Air measurements.....	39
5.2.1	Gas chromatography .....	41
5.2.2	Results .....	42
5.3	Suggested solutions.....	45
5.3.1	New LEV and other minor solutions .....	45
5.3.2	Chemical risk assessment after the implementations .....	49
5.4	Possible future implementations .....	51
<b>6.</b>	<b>Conclusions .....</b>	<b>53</b>
<b>7.</b>	<b>Appendix A .....</b>	<b>55</b>
<b>8.</b>	<b>Appendix B .....</b>	<b>57</b>
<b>9.</b>	<b>Appendix C .....</b>	<b>59</b>
<b>10.</b>	<b>Bibliography &amp; Sitography .....</b>	<b>61</b>
<b>11.</b>	<b>Acknowledgments .....</b>	<b>63</b>

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## RIASSUNTO

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### INTRODUZIONE

MDI è l'acronimo del Metilene Difenil Diisocianato, un diisocianato aromatico. Fra tutti i diisocianati è quello prodotto in maggiori quantità ma anche il meno pericoloso. Viene utilizzato per la produzione delle resine poliuretatiche e degli adesivi ad elevata resistenza, ma anche schiume poliuretatiche (rigide o flessibili) ed elastomeri, poiché è un reagente necessario per la formazione del legame uretanico. Il difenilmetano diisocianato è considerato il meno pericoloso della sua famiglia grazie alla sua bassissima tensione di vapore (rispetto a quella degli altri diisocianati) e quindi alla sua capacità di essere disperso nell'aria circostante, ma ciò non lo rende innocuo, anzi! L'MDI, infatti, può causare molti problemi alla salute come: problemi respiratori e malattie delle vie respiratorie, reazioni allergiche della pelle ed è anche sospettato di causare il cancro.

Dal punto di vista della sicurezza chimica, il problema principale nell'azienda Adient Interiors d.o.o. Kragujevac è dovuto alla presenza dell'MDI, all'interno di un particolare adesivo, il poliuretano reattivo (PUR) hot melt, usato in un processo. Anche se l'MDI non è il componente principale, costituisce infatti solo il 5% della PUR hot melt, e le quantità processate giornalmente non sono elevate (20kg al giorno di adesivo), i rischi per la salute sono molto preoccupanti a causa dei limiti di esposizione professionali molto bassi. La Adient Interiors d.o.o. Kragujevac si trova, appunto, a Kragujevac, in Serbia, ed è una delle tante industrie della Adient sparse in tutto il mondo. Adient [1] è, indubbiamente, uno dei leader globali nel settore degli interni automobilistici, con 85000 dipendenti che operano nei più di 200 impianti collocati in oltre 30 Stati. L'azienda in cui è stato svolto questo lavoro di tesi è abbastanza grande, comprende più di 150 dipendenti e si occupa della produzione di interni automobilistici, come cruscotto, interni delle portiere, quadro strumenti ecc., ma non di sedili (poiché questi vengono prodotti in altri stabilimenti). Ci sono quindi molti processi differenti, in base al prodotto finale desiderato, ma in questa tesi verrà descritto quello svolto nella "Daimler Section", dove maniglie e pannelli interni delle portiere vengono rivestiti in pelle per ottenere il look degli interni delle automobili che tutti conoscono. Questa sezione è relativamente piccola, confrontata ad altri processi che avvengono nell'industria, e conta poco meno di venti dipendenti per turno di lavoro. Il processo, iniziato a Luglio del 2018, può essere definito ancora nella fase iniziale, o di test, con un basso consumo giornaliero di PUR hot melt.

L'obiettivo di questo lavoro di tesi è quello di identificare tutti i possibili rischi per la salute, connessi alla presenza del MDI, all'interno del processo e proporre delle soluzioni per eliminarli o, comunque, ridurli al minimo possibile per poter salvaguardare al meglio la salute dei lavoratori. Dopo aver discusso delle proprietà di questa sostanza, e della sua presenza nella PUR hot melt, verranno spiegati più a fondo i problemi di salute connessi ad essa, preceduti dalla Classificazione Europea in merito alle sostanze pericolose per l'uomo e l'ambiente. Successivamente verrà descritto il processo che avviene nella "Daimler Section" così da poter identificarne al meglio le criticità e capire dove bisogna intervenire per migliorare la protezione dei lavoratori. Infine, l'ultimo capitolo verterà sul metodo utilizzato per le valutazioni, sui risultati ottenuti dalle misurazioni sul campo e sulle soluzioni proposte.

Sfortunatamente non sarà possibile confermare l'effettiva efficacia delle soluzioni proposte poiché queste saranno installate a partire dagli inizi di Aprile 2019 (con annesse nuove misurazioni dell'aria). Grazie a questo studio, l'azienda sarà a conoscenza di tutti i rischi per la salute presenti nella "Daimler Section", dovuti alla presenza del MDI, ed avrà nozioni importanti sul come prevenire malattie, anche piuttosto gravi, per i propri dipendenti.

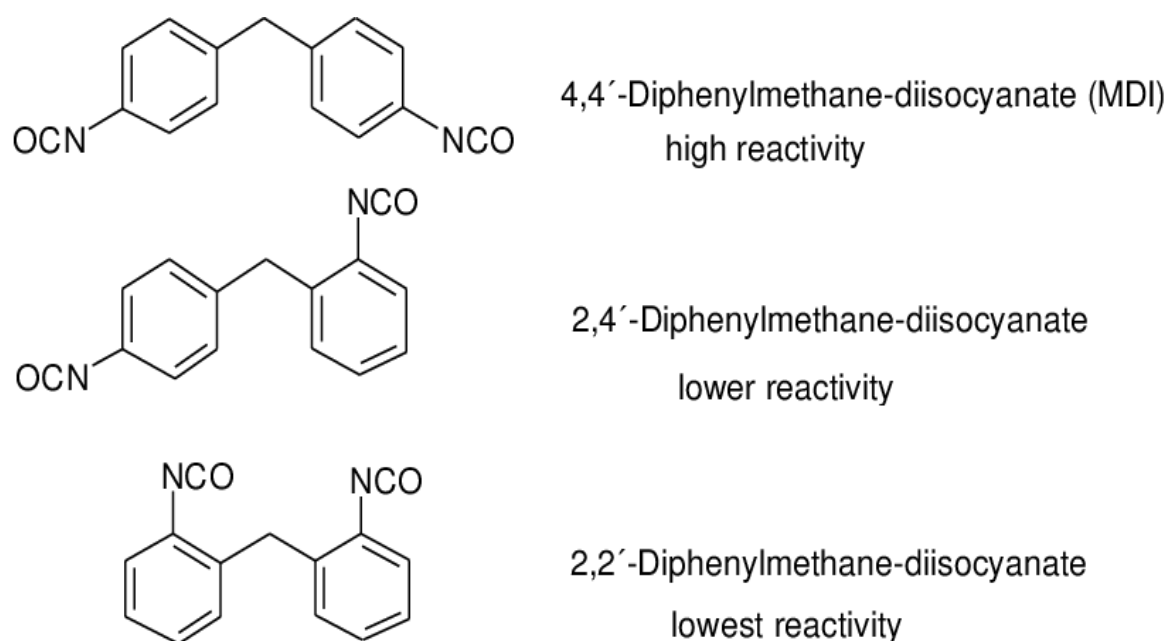
## PROPRIETÀ e REAZIONI

In Tabella 1 sono mostrate le principali proprietà del Metilene Difenil Diisocianato [2], mentre in Figura 1 sono rappresentati i tre isomeri della molecola con le rispettive reattività [3].

**Tabella 1** Proprietà principali del MDI.

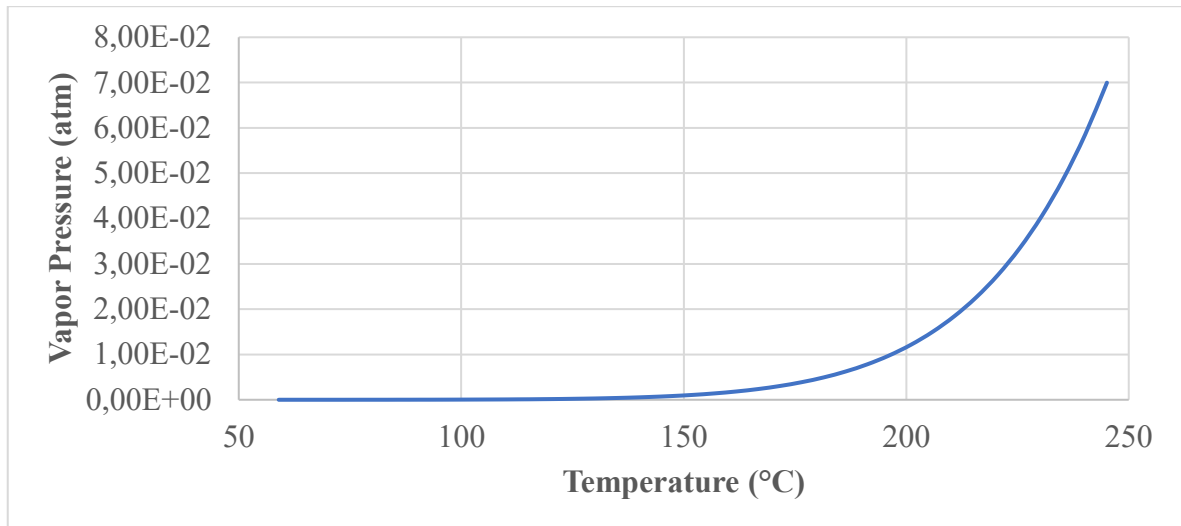
Aspetto	Peso Molecolare (u)	Densità (g/cm <sup>3</sup> )	Punto di Fusione (°C)	Punto di Ebollizione (°C)	Punto di Flash (°C)
Solido bianco	250,25	1,23	40	314	212

La diversa reattività dei tre isomeri dipende dalla posizione dei due isocianati (il gruppo funzionale NCO). Maggiore è lo spazio libero intorno a loro, maggiore sarà la reattività della molecola. In posizione 2, l'isocianato ha una reattività quattro volte inferiore a quella che ha in posizione 4; il 2,2'-Difenilmetano-diisocianato, infatti, è il meno reattivo a causa dell'ingombro sterico causato dai vicini anelli aromatici.



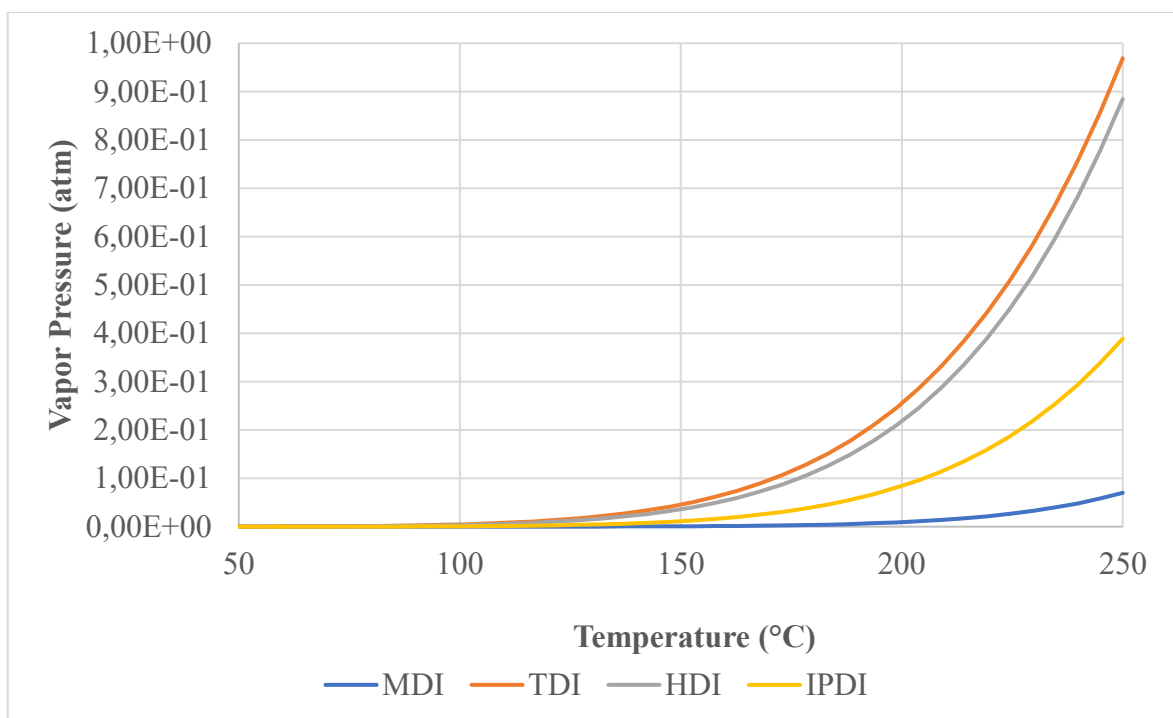
**Figura 1** I tre isomeri del MDI.

Pur non essendo applicabile in questo processo, il comportamento della sua tensione di vapore con l'aumentare della temperatura, raffigurato nella Figura 2, mostra come sempre più MDI passa in fase vapore ad elevate temperature (anche se non viene raggiunto il punto di ebollizione).



**Figura 2** Andamento della tensione di vapore del MDI al variare della temperatura.

Se però questa viene confrontata con la tensione di vapore degli altri diisocianati (toluene diisocianato TDI, esametilene diisocianato HDI e isoforone diisocianato IPDI), si può notare, da Figura 3, come il metilene difenile diisocianato, a parità di temperatura, è quello che tende di meno a passare in fase vapore.

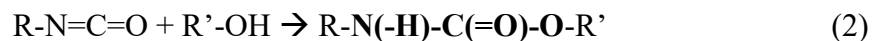


**Figura 3** Andamento della tensione di vapore dei diisocianati al variare della temperatura.

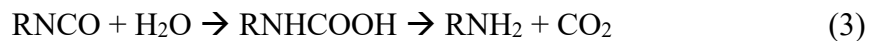
Tutti i diisocianati sono molto reattivi per la presenza dei due gruppi funzionali NCO, dato che ognuno di loro può reagire con nucleofili, grazie alla carica positiva sull'atomo di carbonio. Questo gruppo può reagire con molti componenti contenenti idrogeno, tramite la rottura del doppio legame fra carbonio ed azoto, portando alla formazione di derivati dell'acido carbammico [4].



Fra questi componenti troviamo: acqua, alcoli, ammine ed acidi carbossilici. La reazione tra un isocianato e un alcol, porta alla formazione di un **legame uretanico**.



Visto che il presente lavoro di tesi si concentra sulla sicurezza chimica, una reazione importante a cui prestare attenzione è quella dell'isocianato con l'acqua. Questa può essere vista come due step successivi: nel primo, l'isocianato reagisce con l'acqua per formare l'acido carbammico che, data la sua instabilità, si separa in ammina e diossido di carbonio, mentre nel secondo step l'isocianato reagisce con l'ammina appena formata per produrre urea sostituita.



Quindi, sarebbe buona pratica evitare di maneggiare acqua nelle vicinanze della PUR hot melt, per prevenirne il contatto, data la reazione velocissima che avverrebbe con conseguente formazione di CO<sub>2</sub> e placche di urea sulla colla, che ne comprometterebbe le proprietà meccaniche. La reazione con l'acqua è molto rapida e violenta, anche per questo l'MDI è idrofobico ed insolubile in acqua.

L'MDI, presente nella hot melt poliuretana, serve per garantire maggiore forza adesiva grazie alla sua reazione con l'umidità, presente nell'aria, che porta alla formazione di nuovi legami. Questi legami si formano anche fornendo calore, per questo motivo si dice che l'adesivo si "attiva" raggiungendo una determinata temperatura (per la PUR hot melt in questione, la temperatura di attivazione è 75 °C). Gli adesivi che hanno completato il processo di "curing" possono essere considerati inerti e non tossici, ma le fasi intermedie possono essere tossiche, irritanti e/o carcinogene.

## EFFETTI SULLA SALUTE

Dati i molteplici possibili effetti dannosi per la salute causati dalla presenza del metilene difenil diisocianato, nel regolamento CLP (CE n. 1272/2008, Classification, Labelling, and Packaging), ad esso, sono state assegnate diverse frasi di pericolo (più comunemente note come "frasi H"), oltre alle molte frasi di sicurezza (denominate "frasi P").

Le più rilevanti sono:



- H317 – Può provocare una reazione allergica cutanea.
- H334 – Può provocare sintomi allergici o asmatici o difficoltà respiratorie se inalato.
- H351 – Sospettato di provocare il cancro.

Oltre a questo tipo di frasi, nel CLP sono stati introdotti i nuovi pittogrammi di pericolo (che sostituiscono quelli della vecchia Direttiva per le Sostanze Pericolose 67/548/CEE) ed al MDI sono stati assegnati:



Pericolo per la salute: carcinogeno, sensibilizzante respiratorio e tossicità per inalazione (GHS08).



Punto esclamativo: irritante (per pelle ed occhi), sensibilizzante per la pelle ed irritante per le vie respiratorie (GHS07).

Gli effetti del MDI sui lavoratori dipendono da molti fattori come: la quantità di diisocianato rilasciata nell'aria, la durata della loro esposizione, la distanza fra loro e la fonte di rilascio ecc. I problemi per la salute possono manifestarsi quasi immediatamente oppure nel lungo periodo (anche se il lavoratore non è più esposto), ma la gravità dipende fortemente dalla quantità di MDI presente nell'ambiente lavorativo.

In generale, i limiti di esposizione professionali (Occupational Exposure Limit, OEL) rappresentano la massima concentrazione di una sostanza tossica, nell'aria, alla quale i lavoratori possono essere esposti, in un determinato periodo di tempo, senza incorrere in ripercussioni per la loro salute. Questi limiti vengono stabiliti da delle associazioni di professionisti del settore come la ACGIH (American Conference of Governmental Industrial Hygienists) che definisce tre categorie di valori limite, denominati Threshold Limit Value [9]:

Threshold Limit Value – Time-Weighted Average (TLV-TWA): è la concentrazione di una sostanza pericolosa, mediata su 8 ore lavorative giornaliere (o 40 ore settimanali), al di sotto della quale si ritiene che i lavoratori possano essere esposti, giorno dopo giorno, durante la loro vita lavorativa senza incorrere in nessun effetto collaterale per la loro salute.

Threshold Limit Value – Short-term exposure limit (TLV-STEL): è il valore di concentrazione massimo consentito per brevi esposizioni con durata fino a 15 minuti, al di sotto della quale le persone esposte possono stare senza avere conseguenze dannose a breve periodo. I lavoratori non dovrebbero essere esposti più di quattro volte al giorno a concentrazioni comprese fra TLV-TWA e TLV-STEL; dovrebbe, comunque, passare almeno un'ora tra esposizioni consecutive. Questo valore limite è stato adottato per tenere in conto gli effetti acuti delle sostanze che hanno effetti cronici sulla salute.

Threshold Limit Value – Ceiling (TLV-C): è la concentrazione che non dovrebbe essere mai superata durante qualunque parte della giornata lavorativa. Queste esposizioni a concentrazioni elevate dovrebbero essere sempre controllate.

I TLV per l'MDI sono:

- TLV-STEL 0,2 mg/m<sup>3</sup> (0,02 ppm)
- TLV-TWA 0,05 mg/m<sup>3</sup> (0,005 ppm)

La Tabella 2 riporta i risultati dello studio del Dott. Bernhard Brandt della BG RCI Mainz (2012), in cui viene mostrato come le varie concentrazioni di MDI nell'aria possono causare diversi effetti dannosi per la salute [10].

**Tabella 2** Effetti sulla salute umana a diverse concentrazioni di MDI nell'aria.

<b>Concentrazione</b>	<b>Effetti</b>
< 0,02 ppm	Possibili reazioni asmatiche per persone sensibilizzate
> 0,05 ppm	Irritazione degli occhi
> 0,1 ppm	Lieve irritazione di naso e gola
> 0,5 ppm	Bruciore di gola
> 1,3 ppm	Tosse, bronchite reversibile
> 10 ppm	Necrosi bronchiale irreversibile
> 50 ppm	Pericolo di vita

Dato che l'MDI non ha un odore caratteristico, è difficile che i lavoratori riescano a percepirlo; la soglia dell'odore è 0.4 ppm. Se confrontato con i valori della Tabella 2, questa soglia si trova ad una concentrazione maggiore di quella che causa lieve irritazione di naso e gola, quindi qualora qualcuno riuscisse a percepirne l'odore, si tratterebbe già di sovraesposizione!

## **SITUAZIONE IN ADIENT INTERIORS**

Il processo studiato in questo lavoro di tesi consiste nell'applicare un rivestimento, tramite la PUR hot melt, in pelle (per questioni estetiche) sulle parti in plastica, più precisamente polipropilene, che andranno poi a costituire gli interni delle automobili, in particolare gli interni delle portiere. Il processo è attivo 16 ore al giorno, suddiviso in due turni di lavoro, con circa 20 dipendenti coinvolti per turno. I prodotti finali, mostrati nelle Figure 4 e 5, sono maniglie e pannelli interni delle portiere, chiamati Centerfield. L'area di lavoro è divisa in cinque zone: adhesion, pre-fixing, pre-centerfield, centerfield e folding. Sia le maniglie che i centerfield subiscono pressoché lo stesso processo, le differenze dipendono, ovviamente, dalle loro diverse dimensioni (come si può notare anche dalle Figure 4 e 5). I rivestimenti in pelle, le parti di polipropilene e la PUR hot melt provengono da fornitori esteri.

Il processo inizia con il riscaldamento della hot melt poliuretanic, situata nel tank a lato della macchina che gestisce l'intera prima zona, la quale, raggiunti i 140 °C, passa allo stato liquido e viene mandata, tramite una pompa per fluidi viscosi, al rullo in movimento tramite cui viene distribuita sul retro delle parti in pelle. Successivamente, queste vengono portate nella zona consecutiva dove sono applicate, manualmente, sulle parti in polipropilene. Per favorire l'ulteriore attivazione della colla, prima che venga attaccata alla parte in plastica, questa viene riscaldata tramite una pistola termica che permette di raggiungere temperature oltre i 100°C in pochissimo tempo, così da assicurare la presa fra il rivestimento e la base. Per entrambi i prodotti, l'incollaggio viene fatto manualmente nelle zone di pre-fixing e

pre-centerfield, per maniglie e pannelli rispettivamente. Il riscaldamento dei rivestimenti in pelle, e quindi della PUR hot melt, porta all'evaporazione di una piccola quantità di MDI presente nella colla e quindi rappresenta una minaccia nascosta per gli operatori, per le possibili conseguenze discusse in precedenza.



**Figura 4** Maniglie rivestite in pelle, prodotto finale.



**Figura 5** Centerfield prodotto finale.

Maniglie e pannelli, dopo essere stati ricoperti con la pelle, vengono posti in dei sistemi di vuoto, all'interno dei quali viene migliorata l'aderenza fra plastica e pelle tramite, appunto, l'applicazione di una pressione inferiore a quella atmosferica per circa cinque minuti. Anche durante questa operazione i prodotti sono riscaldati, sempre per favorire l'attivazione della hot melt, fino a 130 °C per poter raggiungere la temperatura di attivazione della colla che si trova fra le due parti. Dopo di ciò, le maniglie vengono portate nell'ultima zona mentre i centerfield sono pronti e non devono subire ulteriori migliorie. Nella folding zone, l'ultima zona appunto, gli operatori verificano che il prodotto non abbia difetti o imperfezioni e ridefiniscono manualmente, tramite alcuni strumenti, gli ultimi dettagli (per esempio gli angoli o le parti interne della plastica). Inoltre, anche qui viene fornito del calore, sempre tramite pistole termiche, sempre con lo stesso obiettivo.

In ogni zona del processo, quindi, possono avvenire dei rilasci di MDI nell'aria a causa dell'aumento di temperatura, perciò tutti i lavoratori, chi più chi meno, saranno esposti ad un ambiente di lavoro contenente diisocianato. Risulta importante, allora, capire se sia necessario intervenire per migliorare la sicurezza del processo poiché l'inalazione, anche di bassissime quantità, potrebbe provocare effetti spiacevoli per la salute dei lavoratori.

All'interno dell'industria, questo processo è uno dei più recenti ma alcune misure di sicurezza fondamentali sono già state adottate per ridurre le emissioni di MDI e quindi i problemi derivanti da esse. Essendo basato principalmente sul lavoro manuale, con l'utilizzo di pistole termiche e strumenti come taglierini e similari, un'ottima misura di sicurezza, in uso sin dal primo giorno, è l'utilizzo di guanti protettivi; questi sono necessari per ridurre la possibilità di danni fisici per gli operatori, come tagli e ustioni, ma soprattutto per impedire il contatto diretto della hot melt con la pelle, visto che porterebbe a conseguenze non indifferenti (come orticaria e dermatite da contatto). Fra i tanti tipi di guanti protettivi esistenti, quelli usati nella "Daimler Section" sono quelli in schiuma di nitrile grazie alla loro ottima resistenza a tagli e forature, oltre alla loro elevata resistenza chimica. Sono particolarmente utili in questo processo poiché fungono da spugna per assorbire eventuali contatti con la hot melt e ne prevengono, quindi, il contatto diretto con la pelle.

Un'ulteriore misura preventiva adottata è la presenza di un sistema di aspirazione locale dell'aria esausta, contaminata dalla presenza dell'MDI evaporato, nella parte superiore della macchina da cui parte l'intero processo. Uno dei modi migliori per prevenire l'esposizione dei lavoratori, è quello di eliminare dall'ambiente di lavoro l'aria contenente il contaminante e ciò è ottenuto tramite l'utilizzo di questo sistema. È installato in prossimità del rullo, e dei rivestimenti in pelle sui quali viene applicata la hot melt, così da catturare il contaminante prima che possa disperdersi in tutto l'ambiente di lavoro. L'aria, contenente MDI, viene rimossa dall'incollatrice tramite un aspiratore (collegato ad un motore) e mandata fuori dall'impianto, in atmosfera, all'altezza del tetto così da prevenirne l'eventuale ricircolo. Il motore garantisce una velocità di 4 m/s in modo da impedire l'accumulo di MDI nel sistema di aspirazione e nell'interno dell'incollatrice.

Questa misura preventiva ha dimostrato di essere molto importante ed efficace dai risultati del campionamento dell'aria; in entrambe le misurazioni fatte finora, infatti, la concentrazione di MDI nell'aria è risultata trascurabile! I vapori di MDI presenti nell'aria immessa nell'atmosfera al di fuori dall'impianto, vengono abbattuti rapidamente grazie all'attacco dei radicali idrossilici, quindi non c'è pericolo di accumulo nell'ambiente circostante.

Discreta importanza hanno anche i controlli medici periodici. È sempre bene monitorare la salute dei lavoratori, soprattutto nei casi come questi in cui il rischio, dovuto ad agenti

chimici, potrebbe essere non trascurabile. Data la natura sensibilizzante, verso le vie respiratorie, del MDI, i migliori test a cui sottoporre i lavoratori esposti sono quelli respiratori (anche perché, grazie all'utilizzo dei guanti, è possibile trascurare i pericoli legati alle malattie cutanee), chiamati test di funzionalità polmonare. Il più comune fra questi è la spirometria che permette di tenere traccia della funzione polmonare. Essa viene determinata misurando la quantità di aria inspirata ed espirata in un certo periodo di tempo, ottenendo così un diagramma flusso-tempo che rappresenta il movimento dell'aria nel tempo. Dal diagramma emergono due parametri, FEV<sub>1</sub> e FVC, che consentono di rivelare l'insorgere dell'asma professionale e malattie simili. Il primo (Forced Expiratory Volume in the 1<sup>st</sup> second) è il volume, di aria, espirato alla fine del primo secondo di espirazione forzata. Il secondo (Forced Vital Capacity), invece, corrisponde al volume totale di aria che può essere espirata col massimo sforzo, dopo aver preso un bel respiro.

Tenendo sotto controllo la funzione polmonare di ogni singolo lavoratore e confrontandone l'andamento con tabelle ed equazioni, ottenute dall'esperienza nel corso degli anni passati, è possibile identificare condizioni pericolose come: asma, malattie respiratorie, fibrosi polmonare ed altri problemi delle vie respiratorie.

## **APPROCCIO E SOLUZIONI PROPOSTE**

L'approccio utilizzato per determinare le zone del processo più esposte a rischio chimico è basato sul modello della valutazione del rischio chimico (noto come "chemical risk assessment"). In base ai risultati del modello, si è proseguito con le misurazioni della concentrazione di MDI nell'aria all'interno Daimler Section per confermare, o smentire, i giudizi emersi. Una volta ottenuti i risultati di tali misurazioni, è stato possibile trovare le soluzioni più adatte per migliorare la sicurezza del processo. Risulta necessario menzionare il fatto che Adient non è proprietaria della "gluing machine", la macchina principale del processo tramite la quale la PUR hot melt viene distribuita sulle parti in pelle, quindi non è possibile modificarne alcuna parte o aggiungere componenti esterni.

### *Chemical risk assessment*

La valutazione del rischio chimico è un modello utilizzato per valutare il rischio chimico in un'industria; esso si basa su correlazioni matematiche che attribuiscono valori numerici ad una serie di fattori, pesati in base alla loro importanza, che influiscono nella determinazione del valore numerico del rischio chimico presente. Il rischio calcolato sarà poi paragonabile con dei valori numerici, riportati in una tabella, corrispondenti a diversi livelli di rischio.

Fra i tanti metodi esistenti per la determinazione del rischio chimico, quello utilizzato in questo lavoro di tesi è "MoVaRisCh" [14]. Questo modello è stato adottato in tre regioni italiane: Lombardia, Toscana ed Emilia-Romagna.

È importante ricordare le definizioni di rischio e pericolo, poiché spesso vengono confuse o scambiate:

- Il rischio è la probabilità che un lavoratore venga ferito o si ammali in seguito ad una esposizione al pericolo. Dipende dalla probabilità di accadimento e dalla gravità del pericolo.
- Il pericolo è qualunque potenziale fonte di danno e/o malattie ed è indipendente dal livello di esposizione dei lavoratori. È quindi una proprietà intrinseca della sostanza/miscela.

Il chemical risk assessment mira ad identificare i pericoli, dovuti alla presenza di agenti chimici, ed i rischi ad essi connessi che potrebbero causare danni ai lavoratori, ma anche analizzare e determinare dei metodi per prevenirli (o ridurli quando non possono essere eliminati del tutto).

In questo modello, il rischio R è calcolato tramite il prodotto fra due fattori P ed E che rappresentano, rispettivamente, il pericolo della sostanza e l'esposizione dei lavoratori. P è l'indice di pericolosità della sostanza, o della miscela, determinato in base alle frasi H ad essa associate; ad ogni frase H, infatti, è stato attribuito un valore numerico, compreso fra 1 e 10 (con 1 livello minimo di pericolosità e 10 livello massimo). L'indice E, invece, rappresenta il livello di esposizione dei lavoratori perciò dipende da molti fattori, quali: durata, modalità di esposizione, quantità di sostanza pericolosa in uso, tipo di sostanza ed efficacia delle misure preventive e protettive adottate.

Il rischio chimico può essere calcolato per esposizioni inalatorie e cutanee, ma in questo lavoro di tesi solo le prime saranno considerate grazie all'ottimo utilizzo di guanti protettivi da parte dei lavoratori coinvolti nel processo (è possibile, quindi, considerare trascurabile il rischio di esposizione cutanea). Il valore di R può essere compreso fra 0,1 e 100.

Per sostanze, o miscele, con più di una frase H, come nel caso della PUR hot melt contenente il metilene difenil diisocianato, per la scelta del valore da assegnare all'indice P si prende il valore più alto. In Tabella 3 sono riportate le frasi H, coinvolte nel processo, ed i valori corrispondenti dell'indice P.

**Tabella 3** Valori dell'indice P associati alle frasi H della PUR hot melt.

<b>Frasi H associate alla PUR hot melt</b>		<b>Valore indice P</b>
H317	Può provocare una reazione allergica cutanea.	6,00
H334	Può provocare sintomi allergici o asmatici o difficoltà respiratorie se inalato.	<b>9,00</b>
H351	Sospettato di provocare il cancro.	8,00

Da questi valori si evidenzia come i possibili problemi alle vie respiratorie, come asma o difficoltà nel respirare, sono considerati più gravi rispetto alla possibilità di causare il cancro. Comunque, considerando che 10 è il valore massimo, la presenza dell'MDI conferisce, alla PUR hot melt, caratteristiche molto pericolose per la salute.

La determinazione del valore di E non è immediata come per P, ma è il prodotto fra due sottoindici, d ed I. Il primo tiene conto della distanza fra i lavoratori e la fonte dei possibili pericoli; può variare fra 0,1 ed 1, come mostrato nella Tabella 4. Aumentare la distanza dalla fonte di pericolo, quindi, rappresenta uno dei modi per ridurre (anche di molto) il valore di E.

**Tabella 4** Valori del sottoindice d.

<b>Distanza (m)</b>	<b>Valori di d</b>
Meno di 1	1
Da 1 a 3	0,75
Da 3 a 5	0,5
Da 5 a 10	0,25
Più di 10	0,1

Il secondo sottoindice, I, corrisponde all'intensità dell'esposizione e, a sua volta, dipende da cinque fattori:

- Proprietà chimico-fisiche.
- Quantità in uso.
- Tipologia d'uso.
- Tipologia di controllo.
- Tempo di esposizione.

Questo metodo utilizza quattro matrici, da usare consecutivamente, per ottenere il valore di I con cui calcolare E e, infine, R. In ogni matrice vengono presi in considerazione due fattori, fra quelli elencati sopra o fra i nuovi sotto-fattori (D, U e C), restituendo come output un sotto-fattore o, nel caso dell'ultima matrice, il valore di I. I sotto fattori D, U e C, corrispondenti a disponibilità dell'aerodispersione, uso e compensazione, sono necessari per tenere conto di tutte le variabili che influiscono sulla sicurezza chimica. Le matrici sono da utilizzare in consecuzione poiché, dalla seconda in poi, uno dei due input è sempre il sotto-fattore ottenuto da quella precedente.

Una volta ottenuto il valore di R, è possibile confrontarlo con i valori in Tabella 5 per conoscere lo stato di sicurezza del processo. La tabella è divisa in due zone principali: "rischio irrilevante per la salute", con valori di R compresi fra 0,1 e 21, e "rischio superiore all'irrilevante per la salute" attribuito a valori superiori a 21.

È necessario calcolare il rischio chimico per ogni lavoratore coinvolto nel processo e per ogni sostanza/miscela pericolosa, perciò, in questo caso studio, è stato fatto cinque volte (una per ogni zona della Daimler Section).

**Tabella 5** Valutazione del rischio chimico di un processo.

Valori di Rischio (R)	Classificazione
$0,1 \leq R < 15$	Rischio irrilevante per la salute
$15 \leq R < 21$	Intervallo di incertezza
$21 \leq R \leq 40$	Rischio superiore all'irrilevante per la salute
$40 < R \leq 80$	Zona di rischio elevato
$R > 80$	Zona di grave rischio

Dai valori di R in Tabella 6, si può notare come tutte le zone, tranne quella del centerfield (cioè quella in cui viene utilizzato il vuoto per favorire l'adesione fra plastica e pelle), il rischio derivante da agenti chimici sia superiore all'irrilevante per la salute.

**Tabella 6** Risultati della valutazione del rischio chimico prima dell'implementazione delle soluzioni proposte.

ZONA	A	U	C	I	d	E	Valore P	R
Adhesion zone	1	1	1	7	0,75	5,25	9,00	47,25
Pre-fixing zone	1	1	2	10	1	10	9,00	90
Pre-Centerfield	1	1	2	7	0,75	5,25	9,00	47,25
Centerfield	1	1	1	3	0,75	2,25	9,00	20,25
Folding zone	1	1	1	7	1	7	9,00	63

Oltre alla pericolosità intrinseca della hot melt, uno dei fattori che influisce di più sul valore di R è il tempo di esposizione. Nell'azienda, infatti, ogni turno dura 8 ore, perciò il valore di I risulterebbe elevato anche nell'ipotesi della presenza delle migliori condizioni di controllo ed utilizzo. Ovviamente non basta soltanto ridurre questo valore, ma è necessario cercare di portare ad 1 il fattore di compensazione C nelle due zone in cui è 2. Questo perché l'obiettivo è quello di ridurre al minimo il valore di R in ogni zona, o comunque renderlo irrilevante per la salute (cioè minore di 21). La pre-fixing zone presenta un rischio di 90, quindi si trova nella zona di grave rischio, come era previsto, a causa di alcuni fattori, quali:



- Breve distanza fra le vie respiratorie dei lavoratori e la sorgente del pericolo durante i compiti lavorativi.
- Il calore fornito alla PUR hot melt tramite le pistole termiche porta al rilascio di MDI nell'aria.
- Essendo la seconda zona del processo, spesso i pezzi di pelle ricoperti di adesivo vengono processati dopo qualche minuto dalla fuoriuscita dalla prima zona, quindi la quantità di MDI che non ha ancora reagito è maggiore e la quantità che può essere rilasciata in aria è più elevata.

### *Campionamento dell'aria*

Prima di proporre una soluzione, è necessario verificare se realmente questi risultati, ottenuti con un modello puramente teorico, siano attendibili. Perciò sono state effettuate delle misurazioni dell'aria, nella Daimler Section, per conoscere la concentrazione di MDI nell'ambiente di lavoro. Queste misurazioni sono state fatte da una compagnia esterna, con sede a Belgrado, in due periodi dell'anno differenti (agosto e novembre) principalmente perché le prime constatarono solamente il fatto che le concentrazioni di MDI, in ogni area, fossero inferiori ai limiti consentiti dalle leggi nazionali (uguali a quelle Europee). Per avere delle informazioni aggiuntive sull'effettivo valore delle concentrazioni in ogni sezione del processo, è stata richiesta un'analisi più dettagliata, con risultati mostrati in Tabella 7.

Sono state utilizzate tre pompe per il campionamento dell'aria, ognuna collegata ad una provetta contenente carboni attivi (con la funzione di raccolta del campione), mentre per le analisi di laboratorio è stato usato un gas cromatografo con analizzatore di massa a triplo quadrupolo.

**Tabella 7** Risultati delle seconde misurazioni dell'aria.

<b>Zone</b>	<b>MDI's concentration (mg/m<sup>3</sup>)</b>	<b>Sampling time (hour)</b>
Adhesion	< 0,0015	8
Worker in adhesion	< 0,0015	8
Pre-fixing	0,00313	0,5
Pre-centerfield	< 0,0015	0,5
Centerfield	< 0,0015	0,5
Folding	< 0,0015	0,5

Ricordando che i TLV-STEL e TLV-TWA sono, rispettivamente, 0,2 mg/m<sup>3</sup> e 0,05 mg/m<sup>3</sup>, si può notare come la concentrazione di MDI, in ogni zona, sia inferiore ad entrambi i limiti (di breve e lungo periodo). Queste misurazioni, comunque, confermano come la pre-fixing zone sia quella con il maggiore contenuto di MDI nell'aria, mentre smentiscono l'attribuzione di "altamente pericolosa" alla folding zone. Il valore così basso nella prima zona è molto rassicurante, poiché ci permette di capire che il sistema di estrazione dell'aria presente svolge egregiamente il suo lavoro e non rilascia quantità notevoli di MDI in fase vapore in uscita dalla gluing machine. Non avendo un laboratorio interno all'azienda, però, non si hanno ulteriori informazioni sull'unico valore differente dagli altri. Soltanto con quel numero si può, per esempio, ottenere, in maniera banale, la concentrazione su 8 ore

moltiplicandolo per 16; così facendo si otterrebbe un valore molto prossimo al TLV-TWA, ma non si dovrebbe dare molta importanza a questo risultato poiché:

- Visto che non sono noti i valori di concentrazione nelle ore precedenti al campionamento, non è possibile dire come la concentrazione ottenuta sia cambiata nel tempo, cioè se sia, per esempio, aumentata di molto in mezz'ora oppure sia rimasta pressoché simile.
- Il campionamento in questa area è stato effettuato intorno alle 17:30, quindi è possibile che i vapori di MDI si siano accumulati dall'inizio del primo turno di lavoro (ore 6:00).

### *Soluzioni proposte*

Ci sono molti modi per ridurre il rischio, dovuto ad agenti chimici, nell'ambiente di lavoro, dalla sostituzione della sostanza pericolosa con una innocua (o comunque meno pericolosa per la salute), all'adozione di controlli ingegneristici. Nel caso in questione, non è possibile sostituire la PUR hot melt principalmente perché non è ancora disponibile un adesivo che garantisca le stesse, o molto simili, performance in termini di forza adesiva, resistenza termica e chimica. Quindi, il metodo più efficace per ridurre il rischio consiste nell'implementazione di nuovi sistemi e nell'ottimizzazione di quelli già presenti per proteggere al meglio la salute dei lavoratori.

La soluzione principale corrisponde all'installazione di un sistema di ventilazione locale (in inglese local exhaust ventilation LEV) nella pre-fixing zone, che è risultata quella più pericolosa data la concentrazione di MDI più elevata rispetto a tutte le altre. Ciò consentirà di ridurre la quantità di MDI inalabile da parte dei lavoratori, grazie al fatto che sarà installato in prossimità dei banchi di lavoro. Il sistema di ventilazione sarà connesso anche al banco di lavoro della pre-centerfield zone così da ridurre, anche lì, il valore del rischio chimico. L'aria, che può essere definita contaminata, sarà poi espulsa dall'impianto, ad altezza tetto, così come già accade per quella prelevata dal sistema di ventilazione locale installato nella prima zona. Le altre soluzioni materiali proposte sono:

- Filtri per l'aria.
- Misuratori di portata d'aria.
- Umidificatori locali.

Un altro fattore importante nella riduzione del rischio è, come visto precedentemente, la diminuzione del tempo di esposizione dei lavoratori; ha una grande influenza sul valore finale e non dovrebbe essere sottovalutato.

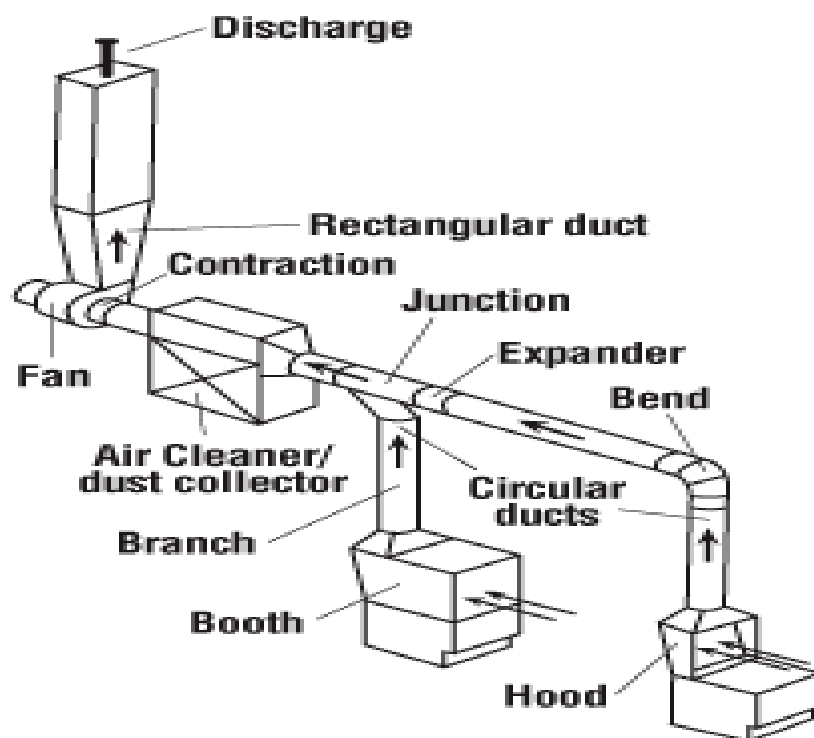
Il progetto del nuovo LEV è stato assegnato ad una compagnia esterna e l'installazione è prevista per la fine di marzo 2019; per questa ragione, in questo lavoro di tesi non saranno presenti i risultati delle nuove misurazioni dell'aria (per confermare l'efficacia dell'investimento effettuato) che saranno eseguite nel mese di aprile.

Il sistema di ventilazione locale può essere un'ottima soluzione per ridurre la concentrazione di vapori di MDI nell'aria nella pre-fixing zone, soprattutto considerata l'efficacia dimostrata da quello già presente nella prima zona del processo, dove viene raggiunta la temperatura maggiore. Grazie alla nuova unità, l'accumulo di MDI nelle zone respiratorie dei lavoratori sarà ridotto considerevolmente, o addirittura eliminato, e con esso i problemi di salute a lungo periodo. Oltre alla rimozione dell'aria contaminata, il LEV provvederà a mantenere umidità e temperatura a livelli confortevoli, abbassando così anche i pericoli legati a potenziali incendi o esplosioni. È importante, però, che il prelievo dell'aria contaminata venga fatto il più vicino possibile (ovviamente senza intralciare il lavoro dei

dipendenti) alla fonte di rilascio dei vapori, così da poterli catturare prima che diffondano nell'ambiente circostante e quindi anche nelle altre zone del processo.

Nel LEV, l'aria viene aspirata tramite delle cappe, come mostrato in Figura 6 [18], o aperture, grazie al gradiente di pressione generato fra il tavolo di lavoro e, appunto, la cappa che ha una pressione minore di quella atmosferica. L'aria contaminata fluisce così attraverso dei condotti e, prima di essere espulsa all'esterno del sito grazie al lavoro fatto dal motore, passa attraverso dei filtri per catturare la colla che condensa a causa dell'abbassamento della temperatura. Il design della rete dei condotti dovrebbe essere il più semplice possibile, evitando: curve ad angolo retto, connessioni dei rami a forma di T, ostruzioni del flusso d'aria, lunghezze elevate di tratti orizzontali e, in generale, punti dove potrebbero accumularsi i residui di colla condensati. Ogni raccordo e giunzione aumenta la resistenza al flusso d'aria quindi, quando possibile, sarebbe meglio evitarli così come i cambi di direzione.

Per questo tipo di applicazioni, la velocità consigliata all'interno dei condotti del LEV è di 5 m/s quindi, il motore del ventilatore, o qualunque altro dispositivo utilizzato per produrre il movimento dell'aria, deve essere abbastanza potente per poter garantire questa velocità in ogni tratto dei vari condotti (tre nel caso in questione). Fra i vari tipi di ventilatori, l'ideale per questo processo sarebbe quello assiale per il suo minore volume occupato, compattezza e quindi la possibilità di essere installato direttamente all'interno del condotto.



**Figura 6** Componenti del sistema di ventilazione locale (LEV).

Da non sottovalutare è l'importanza dei filtri dell'aria, necessari per evitare la condensazione della colla sulle pale del ventilatore. Questo fenomeno comporta un'eccessiva riduzione della vita utile dei dispositivi per la movimentazione dell'aria, richiedendo così costi elevati per comprare, ogni due o tre mesi, un nuovo dispositivo.

I filtri più adatti per il LEV di questo processo sono quelli a griglia, che essenzialmente vengono utilizzati come unità sacrificali, dato il loro bassissimo costo (se confrontato con quello dei ventilatori), per prevenire l'intaccamento delle pale e la riduzione delle prestazioni del ventilatore. Non appena la griglia sarà quasi o totalmente piena di colla, verrà sostituita con una nuova e la sostituzione potrebbe avvenire fra un turno e l'altro oppure prima dell'inizio del primo turno lavorativo poiché è richiesta, ovviamente, la fermata del sistema di aspirazione.

Risulta difficile, tuttavia, notare visualmente quando un filtro è saturo, cioè completamente ricoperto da hot melt condensata, poiché si trova all'interno di un condotto. Per questo motivo, ma anche per essere sicuri che l'unità stia funzionando correttamente è utile installare dei misuratori della velocità dell'aria. In caso di misuratori dotati di display, il valore misurato sarà visibile a tutti, così anche i lavoratori potrebbero notare un malfunzionamento dell'unità semplicemente leggendo un valore molto diverso da quello nominale. Altrimenti è buona prassi collegarlo ad un allarme di portata che dia un segnale, luminoso e/o acustico, nei momenti in cui il valore misurato non corrisponda a quello desiderato.

Per questo processo, i misuratori di portata (e quindi di velocità) dell'aria più indicati sono: a strozzamento o a pressione differenziale (a diaframma, a boccaglio, tubo di Venturi) e tubo di Pitot. Gli altri tipi, come l'anemometro per esempio, potrebbero alterare i reali valori a causa dei possibili depositi di colla che si potrebbero formare sulle superfici dei misuratori.

Gli umidificatori locali, invece, servono per garantire un livello adeguato di umidità in ogni zona del processo per garantire un ambiente di lavoro salutare. Data la grandezza dello stabile in cui è ubicato il processo e considerato il fatto che non è svolto in una zona isolata, risulterebbe molto costoso e non efficiente l'utilizzo di un umidificatore globale. È fondamentale mantenere il livello di umidità compreso fra il 40% ed il 70% per il confort dei lavoratori, ma soprattutto per prevenire l'ulteriore diffusione di MDI nell'aria. Durante il processo di curing della PUR hot melt, infatti, l'MDI reagisce con l'umidità presente nell'aria per formare ulteriori legami molto forti, migliorando così le sue caratteristiche adesive, quindi, qualora l'umidità dell'aria non sia sufficiente, il gradiente di concentrazione porterebbe l'MDI verso le zone respiratorie dei lavoratori dove la quantità di acqua presente sarebbe maggiore.

La soluzione organizzativa proposta, invece, riguarda il tempo di esposizione dei lavoratori coinvolti nelle zone più critiche del processo. La gluing machine processa 8 rivestimenti in pelle per volta per le maniglie, mentre soltanto uno nei casi dei centerfield, quindi quando viene processato un tipo di prodotto, gli operatori assegnati all'altro hanno una sorta di pausa pur essendo comunque esposti all'MDI presente nella loro zona (dovuta al riscaldamento dei pezzi precedenti). Per questo, nell'arco di un turno lavorativo, si verificano molti tempi morti, seppur di breve durata, che potrebbero essere eliminati al fine di ridurre il tempo che spendono nell'area di lavoro. Si potrebbe, per esempio, fare per 4 ore consecutive soltanto centerfield, facendo lavorare i rispettivi operatori, e le restanti 4 soltanto maniglie così da ridurre il tempo di esposizione di ognuno di loro. Sono partiti da poco degli studi di ottimizzazione delle effettive ore lavorative di ogni dipendente coinvolto nel processo così da poter organizzare al meglio il lavoro e diminuire, di molto, il valore del rischio chimico presente.

Dopo questi cambiamenti, è necessario eseguire nuovamente i calcoli della valutazione del rischio, dovuto ad agenti chimici, per verificare di quanto effettivamente possono ridurre il valore di R. In Tabella 8 sono riportati i dati ottenuti. Le celle a sfondo azzurro contengono

i valori cambiati rispetto a quelli di Tabella 6 grazie alle soluzioni fisiche proposte, quelle a sfondo verde, invece, mostrano i nuovi valori ottenuti con la riduzione del tempo di esposizione dei lavoratori.

**Tabella 8** Risultati della valutazione del rischio chimico dopo l'implementazione delle soluzioni proposte.

ZONA	A	U	C	I	d	E	Valore P	R
Adhesion zone	1	1	1	3	0,75	2,25	9,00	20,25
Pre-fixing zone	1	1	1	3	1	3	9,00	27
Pre-Centerfield	1	1	1	3	0,75	2,25	9,00	20,25
Centerfield	1	1	1	3	0,75	2,25	9,00	20,25
Folding zone	1	1	1	3	1	3	9,00	27

Con questi cambiamenti, la prima e la terza zona adesso rientrano nel range di incertezza (con valore di R compreso fra 15 e 21), rispetto al precedente 47,25.

La zona più pericolosa, invece, è passata da 90 a 27, valore ancora superiore al rischio irrilevante per la salute, tramite l'implementazione del sistema LEV. Risulterebbe molto difficile ridurre ulteriormente il valore di I in questa zona principalmente per il valore P di 9 (assegnato alla frase H334) e per la breve distanza, corrispondente al valore del fattore d, tra lavoratore e fonte del pericolo. Per evitare di ridurre il tempo di esposizione ad un massimo di due ore per turno (soluzione troppo estrema in termini di ore lavorative), un buon accorgimento da adottare sarebbe quello di evitare di avvicinarsi con la faccia al prodotto durante le fasi di riscaldamento del prodotto per controllarne i dettagli. Eventuali imperfezioni possono essere controllate più in sicurezza quando il prodotto ha raggiunto nuovamente temperatura ambiente (temperatura alla quale la PUR hot melt presente risulta innocua per la salute umana). Quasi lo stesso discorso può essere fatto per la Folding zone, anche se qui la riduzione del valore di R da 63 a 27 è attribuibile al cambiamento del tempo di esposizione dei lavoratori.

## CONCLUSIONI

Nel corso degli ultimi venti anni, la popolarità della PUR hot melt è cresciuta di molto, così come i processi che la coinvolgono, grazie alle sue ottime prestazioni in termini di forza adesiva, resistenza termica e chimica superiori a quelle dei comuni adesivi e colle. La presenza dell'MDI al suo interno, tuttavia, introduce problemi per la sicurezza dei lavoratori, in termini di malattie con effetti più o meno gravi, che in alcuni casi sono completamente sconosciuti a chi gestisce il processo o addirittura vengono ignorati per la bassa quantità presente. I limiti nazionali di concentrazione ammissibile nell'ambiente di lavoro variano di paese in paese; per esempio, in Inghilterra sono molto più bassi rispetto a quelli dei paesi dell'est Europa, come la Serbia, quindi molti leader mondiali del settore hanno impianti di produzione in questi luoghi. Spesso, però, i rischi chimici e per la salute,

connessi al rilascio dei vapori di MDI nell'aria, vengono sottovalutati per la bassa concentrazione, ma soprattutto per la mancanza di laboratori, specializzati, in grado di effettuare dei test specifici per la misurazione dei diisocianati nell'aria. Dato che la quasi totalità degli impianti del settore non possiede un laboratorio interno per il campionamento dell'aria, le compagnie sono costrette a rivolgersi a gruppi esterni per poter ottenere i dati sulle concentrazioni e ciò comporta un costo non indifferente.

L'MDI non è benigno affatto e, di conseguenza, anche la PUR hot melt che lo contiene non lo è, confermato anche dalle frasi H presenti nella relativa scheda di sicurezza. Tutti questi problemi, però, sorgono soltanto quando il diisocianato è allo stato vapore, poiché se solido o liquido non comporta nessun problema di inalazione (sempre considerando trascurabili i rischi legati al contatto cutaneo), quindi bisognerebbe prestare molta attenzione nei processi che coinvolgono temperature superiori ai 100 °C.

È necessario, perciò, prevenirne il più possibile l'evaporazione in ogni zona del processo tramite la rimozione dell'aria contaminata nelle prossimità delle varie fonti di rilascio. Il sistema di ventilazione locale (LEV) adempie perfettamente a queste richieste poiché preleva l'aria dai tavoli di lavoro e la scarica fuori dall'impianto, così da non avere ricircoli. In generale, i lavoratori dovrebbero prestare molta attenzione durante le operazioni giornaliere che coinvolgono il riscaldamento dell'adesivo, specialmente perché l'MDI è pressoché inodore quindi risulta difficile identificarne il pericolo e quando si riesce a percepirlo si è già in sovraesposizione. Se non controllato, l'MDI può diffondersi nell'ambiente di lavoro e può colpire anche altri lavoratori dei processi vicini o comunque personale non coinvolto nel processo.

I controlli medici periodici hanno un ruolo fondamentale nella prevenzione poiché possono mostrare eventuali peggioramenti di salute, di funzione polmonare principalmente, e segnalare che quindi le misure preventive presenti non sono abbastanza efficaci. Quando sono presenti sostanze, o miscele, che possono causare problemi di questo genere, è molto importante avere dei riscontri continui con il medico (interno o esterno all'azienda che sia) poiché l'obiettivo principale è, ovviamente, salvaguardare la salute dei dipendenti.

Sostituire la PUR hot melt con un adesivo meno pericoloso sarebbe un grande cambiamento, seppur riducendo le performance adesive. Sul mercato c'è già qualche nuova PUR hot melt meno pericolosa, con contenuto di MDI inferiore allo 0,1%, che non è nemmeno classificata come pericolosa (a differenza di quella utilizzata in questo processo), quindi gli studi verso questo tipo di prodotti proseguono. Un altro tipo innovativo di colla è quello basato sull'acqua, formulate da polimeri naturali o sintetici solubili, che necessitano di essere miscelati con acqua, appunto, prima dell'applicazione, anche se i processi di incollaggio in cui viene utilizzato sono diversi da questo.

EU-OSHA ed agenzie simili sono sempre pronte ad aiutare le aziende, dalle piccole imprese alle grandi multinazionali, per comprendere a fondo tutti i rischi per la salute legati ai componenti chimici presenti nei vari processi ed aumentare la consapevolezza su quello con cui i lavoratori hanno a che fare otto ore al giorno, così da poterne prevenire tutti i tipi di malattie professionali. La salvaguardia della salute dei dipendenti dovrebbe essere uno degli obiettivi principali di ogni azienda, anche perché, dal punto di vista economico, un lavoratore infortunato o ammalato non potrà svolgere al meglio i suoi compiti e quindi anche lo stesso processo di produzione ne risentirà!

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## 1. INTRODUCTION

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MDI is the acronym for the Methylene Diphenyl Diisocyanate, an aromatic diisocyanate. It is by far the most produced diisocyanate and it is also the least dangerous between of all the diisocyanates. It is used in the production of polyurethane resins and high-strength adhesives. MDI is also one of the main components in the processes to produce a lot of different polyurethanes (like rigid or flexible foams, low density structural foams and elastomers), as it is a necessary reagent in the formation of the urethane linkage. It is the low vapor pressure that makes it the least hazardous, when compared to the other diisocyanates, but it can affect human health in terms of breathing problems, allergic skin reactions and it is suspected of causing cancer. MDI has three isomers but the most worrying for the health is surely the 4,4'-MDI.

The main chemical safety problem in Adient Interiors d.o.o. Kragujevac is related to the usage of a Polyurethane Reactive (PUR) hot melt that contains around 5% of MDI. Even though the MDI is not the main component and it is not present in high amount, the health risks are very worrisome due its low occupational exposure limits. It is an asthma sensitizer, it can cause light symptoms as well as acute long-term effects on the respiratory system, it can also cause allergic skin reactions in case of contact and it is suspected to be carcinogenic.

Adient Interiors d.o.o. is located in Kragujevac (Serbia) and it is one of the many Adient industries present all over the world. Adient [1], in fact, is a global leader in the automotive seating sector, with 85000 employees operating in more than 200 plants distributed in more than 30 countries; every year they supply automotive seats and components for more than 25 million vehicles.

The industry where this work of thesis has been done is a manufactory facility and it produces many kinds of car interiors like dashboard, or instrument panel, car doors, grab handles and so on. The factory itself is very big and there are around 150 employees. There are a lot of different processes but here it will be only described the "Daimler Section" that is where grab handles and internal panels of the car door are covered with the aesthetic skin. In the whole picture of the factory, this section is relatively small and only 20 employees per shift work there. This process has started in July 2018 and it is still in the beginning phase, where low amounts of glue are consumed daily.

The grab handles and the internal panels of the car are made in similar ways. The first ones are way smaller than the second ones but they both undergo almost the same process. It will be explained in detail in the fourth chapter but, essentially, it is about sticking leather on the plastic parts to obtain the finished products that we can see in our cars. This is achieved using a particular glue that is the Polyurethane Reactive (PUR) hot melt. The process consists in many phases, done in the respective zones, and the workers are divided into groups. From the chemical safety point of view, the PUR hot melt is the most dangerous substance in the process due to the presence of methylene diphenyl diisocyanate. In the last years, the use of this hot melt as an adhesive has gained a lot of popularity, thanks to its peculiar characteristics, so the awareness about the presence of diisocyanates inside them should be raised to effectively protect workers.

This work of thesis focuses on how to deal with MDI, starting from knowing what it is and how it affects the workers, in terms of safety and health prevention, then deciding the best way for the industry to reduce its emissions in the working environment and the employees' exposure to it.

Hence, here will be described properties and reactions of this diisocyanate, as well as its presence in the used glue; then all the health-related risks will be analysed (with examples of possible consequences due to the exposure to MDI), with a closer look on the European Classification of the substance/mixture and all the hazard statements associated it.

After these general concepts regarding this diisocyanate, there will be an introduction of the dangerous substances used in the everyday life within the industry, followed by the full description of the process where it is involved. With a detailed picture of what happens in the "Daimler Section", it is possible to understand which the most dangerous zone, from a chemical point of view, are and where the improvements in safety should be done. These areas needing safety implementations will also be highlighted by a chemical risk assessment and two air samplings (performed in different months). Then a suggested solution to reduce the chemical risk in the working area will be explained, coupled with some other little implementations and a look at the future. Unfortunately, it will not be possible to confirm if the suggested solutions effectively achieve the desired results because the equipment will be installed at the end of March 2019, with the new air sampling scheduled for the start of April.

Thanks to this study, the company will be fully aware of the health risks connected to the presence of MDI. Since this process is still in the early stages, where a lot of things are being tested, this work of thesis could result useful for the present and for a possible future scale-up of the process.



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## 2. MDI's properties

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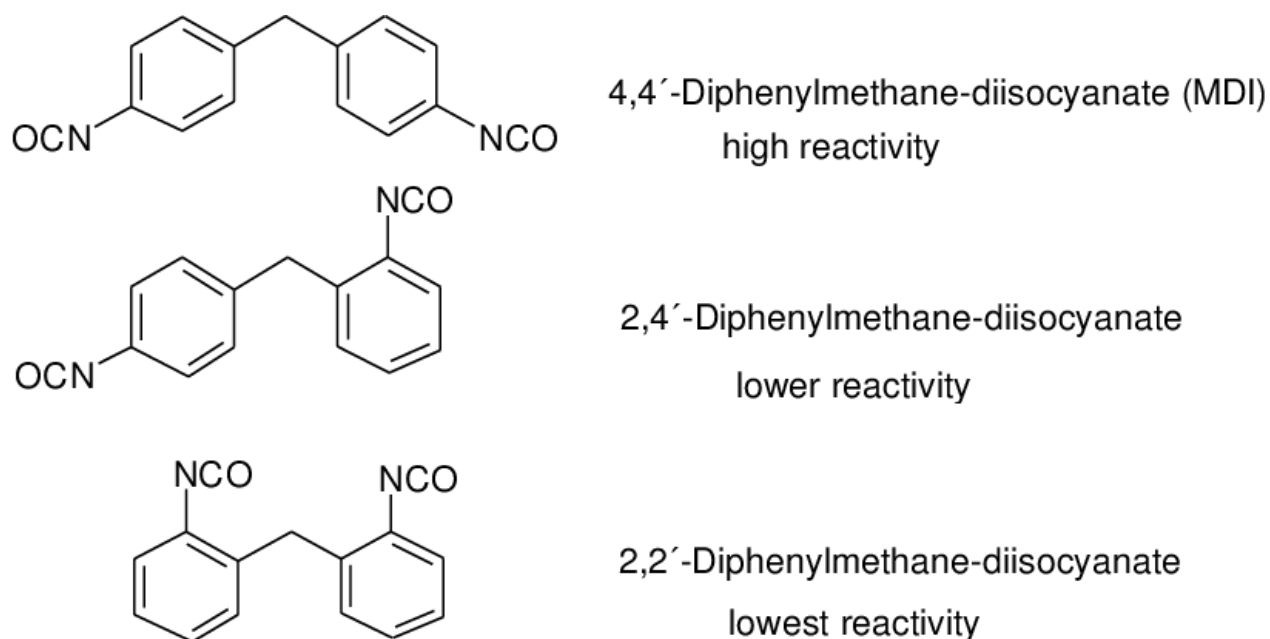
The diphenylmethane diisocyanate is the most produced and the least hazardous of all the diisocyanates. The main other ones are: toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI).

In the Table 2.1 are presented the MDI's main properties [2].

**Table 2.1** Main properties of MDI.

Aspect	Molecular Weight (u)	Density (g/cm <sup>3</sup> )	Melting Point (°C)	Boiling Point (°C)	Flash Point (°C)
White Solid	250,25	1,23	40	314	212

There are three isomers of MDI and they differ in reactivity due to the position of the isocyanate groups. In Figure 2.1 are shown the three MDI isomers and the scale of their reactivity.



**Figure 2.1** The three MDI isomers.

Image taken from the article from Dirk Grunwald [3]

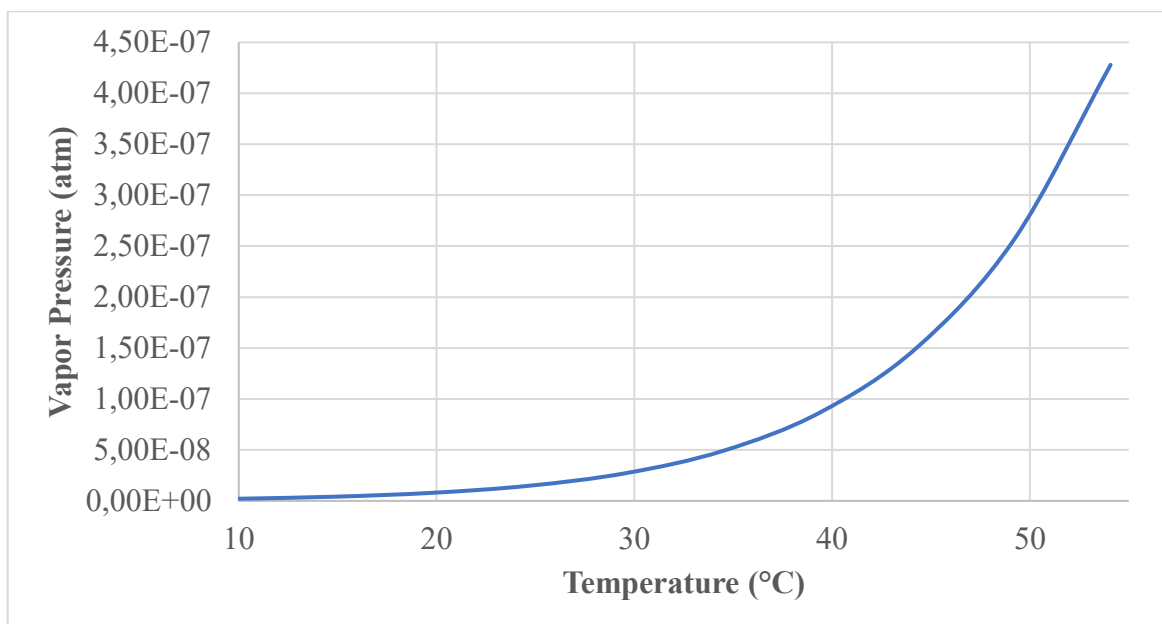
[https://www.researchgate.net/publication/256088991\\_New\\_Analytical\\_Methods\\_as\\_Tools\\_for\\_the\\_Determination\\_of\\_Resin\\_Properties](https://www.researchgate.net/publication/256088991_New_Analytical_Methods_as_Tools_for_the_Determination_of_Resin_Properties).

The position of the isocyanate group highly influences the reactivity of the molecule. The ones that are in position 2 are less reactive than the ones in position 4 due to steric hindrance (specifically they are four times less reactive).

### 2.1 Vapor Pressure

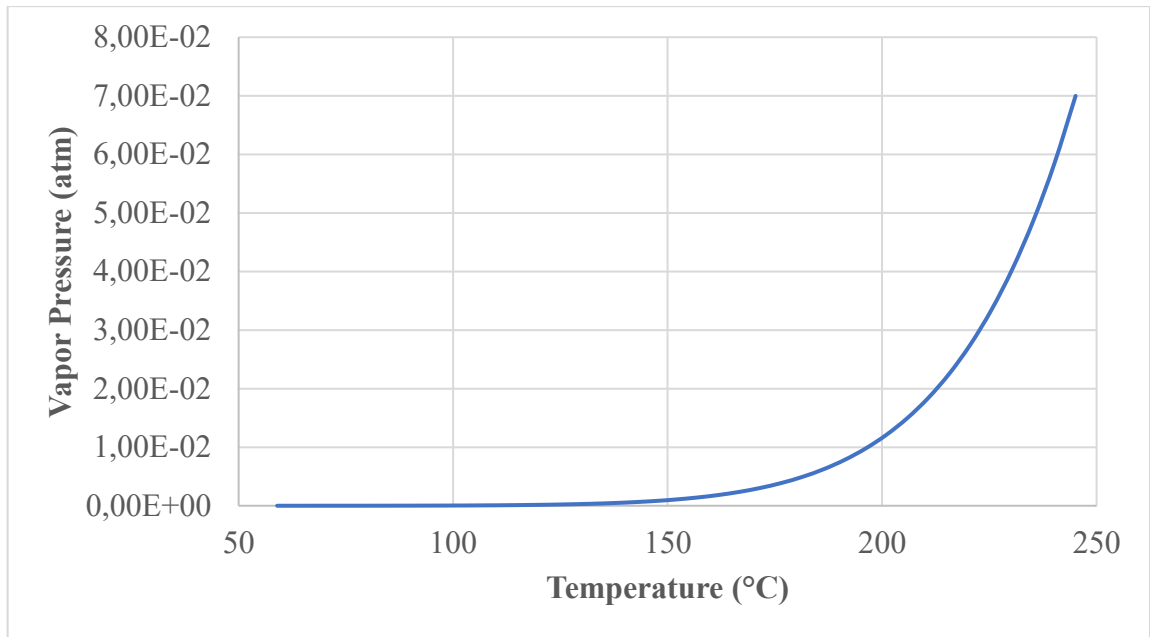
In this case of study, it is hard to reach the thermodynamic equilibrium between the solid/liquid phase and the vapor phase due to the wide and open system, the low amount of MDI present in the glue and the ventilation system. The vapor pressure, nevertheless, can help understanding why the glue, containing MDI, can be dangerous for the workers that work in close contact with it. MDI is not harmful for human's health when it is in the solid or liquid state, but it is in the vapor phase; the vapor pressure shows the tendency of particles to escape from a liquid or solid.

Since the glue, during its use, is used between 10 °C and 250 °C, it is useful to separate the vapor pressure values in two different diagrams to perfectly see them. Figure 2.2 and 2.3 show the behaviour of the vapor pressure with the temperature.



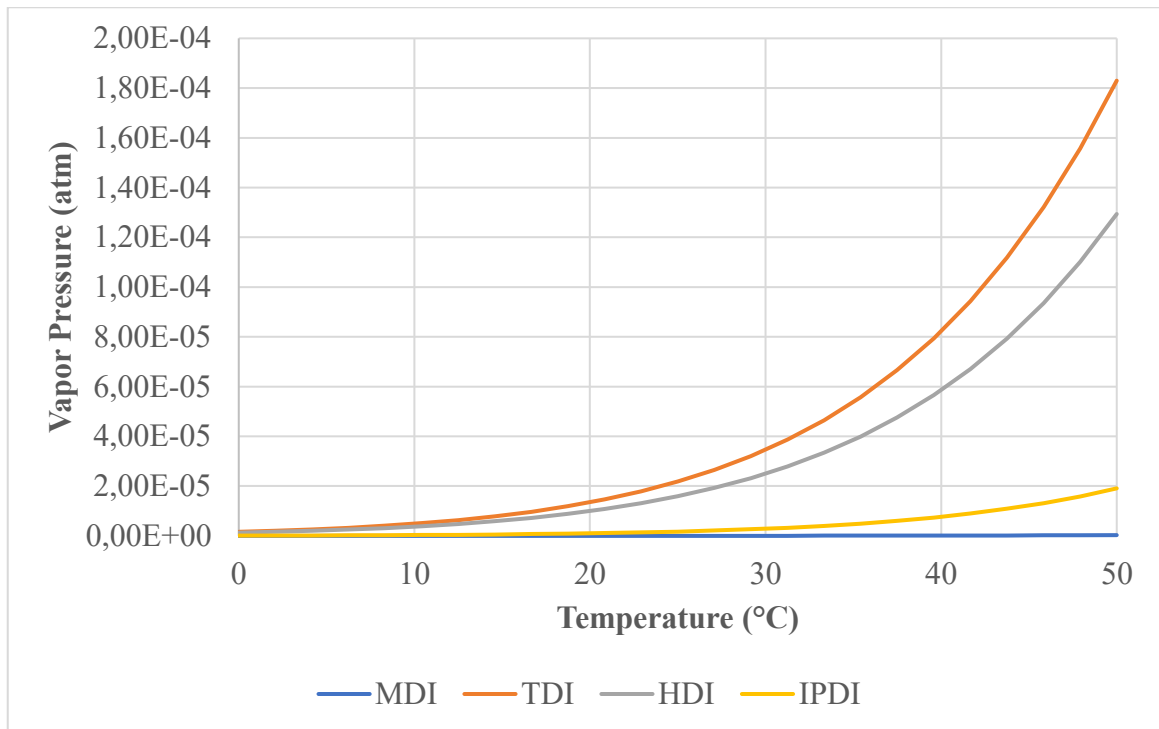
**Figure 2.2** Variation of MDI's vapor pressure with the temperature.

When the glue is activated by a heat gun, it reaches 180-200°C, for less than one second, and then it goes down to 50-60°C. Even though the boiling temperature is never reached, these graphics show that some MDI is released in the atmosphere. This is also confirmed by the MDI's flash point temperature, that is 212 °C. The flash point is the lowest temperature at which the vapours of the material will ignite when given an ignition source, so a fraction of MDI should be expected to change phase to vapor during the heating of the glue.



**Figure 2.3** Variation of MDI's vapor pressure with the temperature at high temperatures.

When comparing MDI's vapor pressure with the other diisocyanates, it comes clear why MDI is considered the least dangerous diisocyanate. It has the lowest volatility between all the compounds of this group and this can be seen in Figure 2.4 and 2.5.

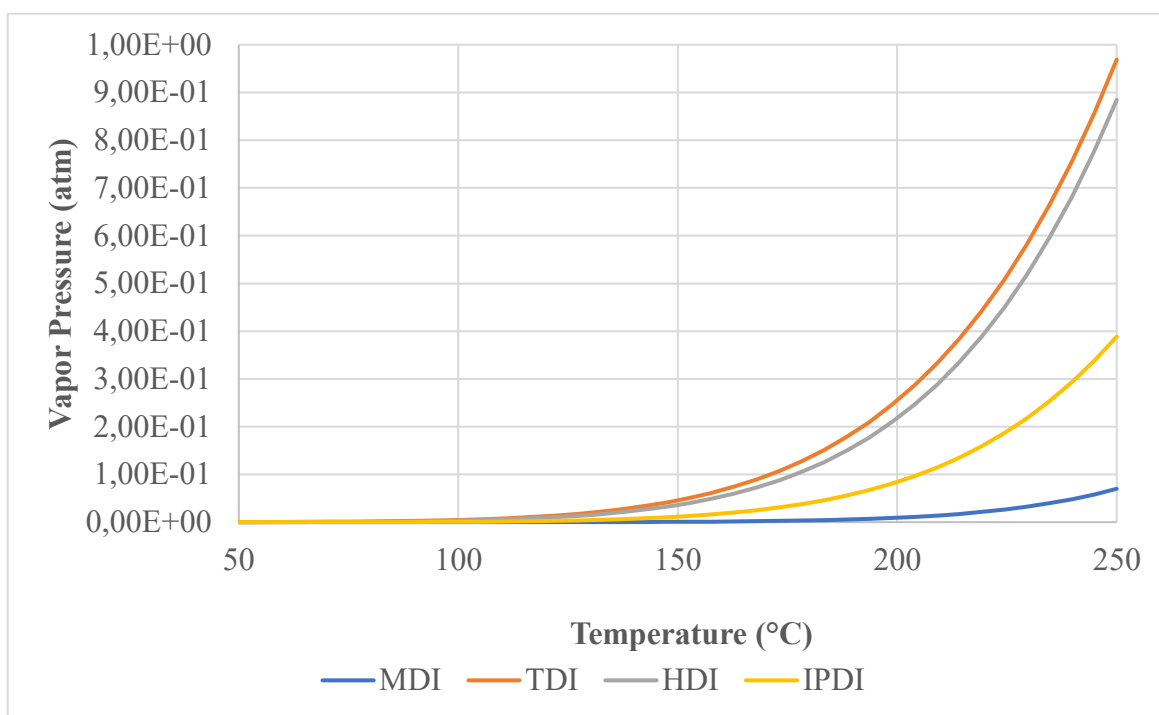


**Figure 2.4** Comparison of the Vapor Pressure of diisocyanates.

The TDI is the most volatile between them due to its chemical structure, followed by the HDI. Comparing these data with the ones in Figure 2.2, it is possible to confirm that MDI

is the least volatile among all diisocyanates: at 25 °C, MDI has a vapor pressure about 1400 times lower than the TDI's one. This ratio, however, gets lower with increasing temperature. At 50 °C, for example, it is less than the half of the previous one (around 655 times).

In Figure 2.5, when reaching relatively high temperatures, the vapor pressure of all diisocyanates becomes almost 1 atm due to the proximity to their respectively boiling point, except for MDI. As stated in Table 2.1, MDI's boiling point is 314 °C but at 250 °C its vapor pressure is 0.07 atm and it only 13 times lower than the TDI's one.

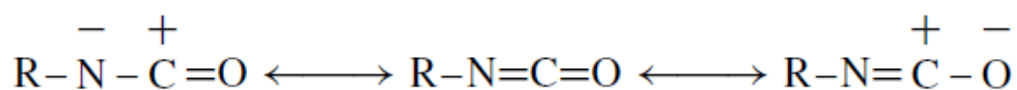


**Figure 2.5** Comparison of the Vapor Pressure of diisocyanates at high temperatures.

All these data were calculated via Aspen Plus, a software of the Aspen Technology, Inc. known as AspenTech, analysing the properties of the substances as pure and using the UNIFAC method.

## 2.2 Reactions

All diisocyanates are very reactive due to their two isocyanate groups, as every group can react with nucleophiles, thanks to the positive charge on the carbon atom as shown in Figure 2.6.



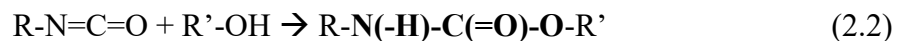
**Figure 2.6** Isocyanate group resonance structure.

The isocyanate group can easily react with many compounds containing an active hydrogen, by adding across the Nitrogen and Carbon double bond to form derivatives of the carbamic acid [4].

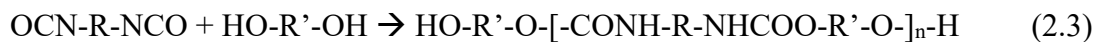


Those compounds can be: water, alcohols, amines and carboxylic acids.

The reaction of an isocyanate with an alcohol gives the formation of a **urethane linkage**.



Specifically, the reaction between a diisocyanate and a polyol is one of the most common way to produce polyurethanes (including PUR).



Since the present work of thesis focuses more on the safety and MDI's effects on health, an important reaction to be looked at is the reaction between MDI and water. It can be seen as two consecutive steps: in the first step, the isocyanate reacts with water to form a carbamic acid but, since this compound is not stable, it separates itself into an amine and carbon dioxide; in the second step, the remaining isocyanate reacts with the new amine formed to produce a substituted urea.



So, it would be a good practise to avoid using water near the PUR hot melt to prevent the contact between the two, because it could lead to the formation of carbon dioxide and plaques of polyurea on the glue. This last effect can cause a malfunction in the usage of the glue and it can greatly reduce its adhesive/mechanical properties.

The methylene diphenyl diisocyanate is hydrophobic and insoluble in water. Part of the latter is due to the fact that when it gets in contact with water, MDI readily reacts to produce the compounds seen in the step 1 of the reactions above.

### 2.3 Presence in PUR hot melt

The Polyurethane Reactive (PUR) hot melt is an innovative kind of binder that presents better physical and mechanical properties than the classic glues and adhesives. As the words "hot melt" suggest, the PUR is a solid but it is used in the liquid state hence it gets melted, in the process, before the application and then it will solidify and react with the moisture in

the air. These bonds are very strong and they ensure that the glue will not re-melt in case of high temperatures. Usually, PUR have very low setting times and their bonds get stronger and stronger as the time passes because of its reaction with the moisture; it is possible to say that they undergo curing, or they polymerize, to strengthen their bonds with the objects.

PUR have lower temperature range (85 to 140 °C) than the traditional thermoplastic hot melt adhesives. They also have lower volatile organic compound (VOC) content as well as polycyclic aromatic hydrocarbons (PAH) levels. The PUR hot melt used in the “Daimler Section” has 0% of VOC.

MDI is often one of the main reagents in the production of polyurethanes and a fraction of non-reacted reagent can be found in the final glue. In general, the isocyanate groups grant the additional chemical crosslinking in ambient humidity hence why, in many of the PUR hot melts, the presence of the methylene diphenyl diisocyanate is intended because every molecule has two free isocyanate groups ( $\text{-N=C=O}$ ).

Completely cured products are fully reacted, so they can be considered inert and non-toxic, but the intermediate phases are toxic, irritating and/or carcinogenic.

In the process object of this work, the PUR used is the Technomelt PUR 6220 UV LV which its main component is, of course, the polyurethane but the concentration of MDI in it is not negligible and it is reported in the Table 2.2.

**Table 2.2** Presence of MDI in the PUR used in the process.

Name	CAS Number	Concentration %
4,4'-methylenediphenyl diisocyanate	101-68-8	1-3 %
o-(p-Isocyanatobenzyl) phenyl isocyanate	5873-54-1	1-3 %
Diphenylmethane diisocyanate, isomers and homologues	9016-87-9	0,1-1 %
2,2'-Methylenediphenyl diisocyanate	2536-05-2	0,1-1 %

The second component in the Table 2.2 is the 2,4'-diphenylmethane diisocyanate (there are many names to address the same substance, as it is for the 4,4'-MDI), it has lower reactivity than the 4,4' but higher than the 2,2'. This means also that the dangerous, for the health, properties are lower than the 4,4'-MDI ones. To take the safest way of approaching the safety and health problems, related to these components, it has been assumed that all the MDI components are 4,4' so, this work will deal with a composition of around 5% of 4,4'-methylenediphenyl diisocyanate.

The polyurethanes are combustible and they can be ignited if exposed to open flames. Decomposition, that starts at around 600 °C, from fire can produce CO, HCN, NO<sub>x</sub>, isocyanates and other toxic products.

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### 3. EFFECTS ON HEALTH

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The methylene diphenyl diisocyanate, as well as the toluene diphenyl diisocyanate, is known to be harmful for the human health. It mainly affects the respiratory tract and system, it is a sensitizer and it can cause: asthma (better defined as occupational asthma), nose and throat irritations, lung fibrosis and alveolitis, hypersensitivity pneumonitis and this kind of problems. Unfortunately, it does not end here because the MDI is also a skin sensitizer and it is even suspected to be a carcinogenic substance [5].

The most worrying problems are the breathing difficulties ones, as it is way easier to prevent skin contact rather than inhalation, while, for the cancer part, there are not direct confirmations of it causing cancer yet. MDI can affect workers (and people in general) mainly as a vapour so, at room temperature, it is not that frequent to have detectable airborne concentrations thanks to its very low vapor pressure (when compared to the other diisocyanate). It is easy to understand, then, that the danger comes when the MDI is heated because its vapor pressure increases with the increase of temperature and it is progressively more likely to release some dangerous vapours in the air.

Obviously if someone inhales a very low quantity of MDI vapours, he will not get asthma in the next few hours or days but, if a worker spends 8 hours per day, 5 days a week, in a factory where there is a not so low concentration of it in the air, then he is likely to get irritation of throat first and then, eventually, occupational asthma. This happens for almost every dangerous chemical: there are short-term effects and long-terms effects.

Since the MDI has so many dangerous effects for the human health, it has been included in the CLP, REACH and GHS regulations.

#### *3.1 European Regulations*

REACH [6] is the European Regulation EC n. 1907/2006. It came into force in the European Union on the 1<sup>st</sup> June 2007 and it is related to Registration, Evaluation, Authorisation and Restriction of Chemicals. REACH addresses the production and use of chemical substances, as well as their potential impacts on both human health and the environment, imposing on every producer and importer (from extra EU countries) of chemical substances the obligation of registering these substances at the European Chemicals Agency (ECHA). The registration is about submitting a lot of information on the characteristics of the substances and on their uses. For some particularly dangerous substances, ECHA imposes on more obligations of authorisation or restrictions of use.

CLP is the European Regulation EC n. 1272/2008 about Classification, Labelling and Packaging of chemical substances and mixtures. It came into force in the European Union on the 20<sup>th</sup> January 2009 and it introduced in Europe a new system for the classification and labelling of hazardous substances and mixtures, based on the UN global harmonized system (GHS). It complemented the REACH and it introduced new classification criteria, the European hazard symbols (pictograms) and Risk and Safety Statements for labelling. It also replaced the old system contained in the Dangerous Substances Directive (67/548/EEC). In the Appendix A it is possible to find all the “old” and “new” hazard pictograms.

Every dangerous chemical substance belongs to a Hazard Class and it is associated to one or more (depending on the substance) Hazard statements and Precautionary statements, the so-called H-phrases and P-phrases. Whenever a H-phrase is present on a Material Safety Data Sheet (MSDS) or on a Safety Data Sheet (SDS), it will be joined by a hazard pictogram to easily understand what the main safety issues of the substance are.

The Hazard Classes [7] can be grouped in 3 main categories: physical hazards, health hazards and environmental hazards. In the first category there are the hazard classes related to the substances' physical-chemical properties, like explosives, flammable, oxidising, self-reactive, corrosive to metals and so on. The second one involves the classes connected to the toxicological properties like skin corrosion, toxicity, respiratory sensitisation, mutagenicity, carcinogenicity etc. The last category comprehends hazardous to the aquatic environment and to the environment in general.

Hazard statements are intended to form a set of standardized phrases about the hazards of chemical substances and mixtures that can be translated into different languages. They replace the previous well-known R-phrases. Precautionary statements, instead, are intended to form a set of standardized phrases giving advice about the correct handling of chemical substances and mixtures, which can also be translated into different languages. They replace, as the H-phrases for the R-phrases, the previous well-known S-phrases.

Each hazard statement is designated a code, starting with the letter H and followed by three digits. Each precautionary statement is also designated a code, this time starting with the letter P and followed by three digits. Statements which correspond to related hazards are grouped together by code number, so the numbering is not consecutive. The code is used for reference purposes, but it is the actual phrase which must appear on labels and safety data sheets. Some precautionary phrases are combinations, indicated by a plus sign "+".

### *3.2 MDI's H-phrases, P-phrases and pictograms*

Since it has a lot of different dangerous effects for human health, MDI has been classified, by the CLP regulation, with many H-phrases. Mainly it is identified as a respiratory sensitizer, skin sensitizer and possible cause of cancer.

Here are listed all the H-phrases, P-phrases and hazard pictograms associated with the methylene diphenyl diisocyanate [8].

Hazard Statements:

- H315: Causes skin irritation.
- H317: May cause an allergic skin reaction.
- H319: Causes serious eye irritation.
- H332: Harmful if inhaled.
- H334: May cause allergy or asthma symptoms or breathing difficulties if inhaled.
- H335: Causes respiratory irritation.
- H373: May cause damage to respiratory system through prolonged or repeated exposure by inhalation.
- H351: Suspected of Causing Cancer.



#### Precautionary Statements:

- P260: Do not breathe dust / fume / gas / mist / vapours / spray.
- P264: Wash skin thoroughly after handling.
- P271: Use only outdoors or in a well-ventilated area.
- P272: Contaminated work clothing should not be allowed out of the workplace.
- P280: Wear eye protection/ face protection and protective gloves.
- P284: Wear respiratory protection.
- P301 + P352: IF ON SKIN: Wash with plenty of water.
- P304 + P340: IF INHALED: Remove person to fresh air and keep comfortable for breathing.
- P305 + P351 + P338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
- P333 + P313: If skin irritation or rash occurs: Get medical advice / attention.
- P337 + P313: If eye irritation persists: Get medical advice / attention.
- P342 + P311: If experiencing respiratory symptoms: Call a POISON CENTER or doctor.
- P362 + P364: Take off contaminated clothing and wash it before reuse.
- P403 + P233: Store in a well-ventilated place. Keep container tightly closed.
- P405: Store locked up.
- P501: Dispose of contents / container to an approved waste disposal plant.

#### Hazard Pictograms:



Health hazard: carcinogen, respiratory sensitizer and aspiration toxicity.



Exclamation mark: irritant (skin and eye), skin sensitizer and respiratory tract irritant.

### *3.3 Occupational Exposure Limits*

The consequences of the exposure of workers to MDI depend on various factors: its quantity released in the air, the time of the exposure, the distance between them and the substance that releases these vapours and so on. The problems for the health can happen immediately or after a long period of time (even after the exposure has stopped) but their severity mainly relies on the quantity present in the atmosphere.

In general, the occupational exposure limit (OEL) represents the maximum airborne concentration of a toxic substance to which a worker can be exposed over a period of time without suffering any harmful consequences. These limits are set out by many professional organizations around the world, such as the American Conference of Governmental Industrial Hygienists (ACGIH) and the National Institute for Occupational Safety and Health (NIOSH) in the United States. They are established based on the chemical properties of the substance, experimental studies on animals and humans, toxicological and epidemiological data. Different organizations may use different terminology for the OEL.

For example, the ACGIH term for OEL is "Threshold Limit Value" (TLV)<sup>®</sup> while the NIOSH term is "recommended exposure limits" (REL). In this work, the term TLV, or OEL, will be used from now on.

The ACGIH recognizes that there are a lot of different variations in the level of the biological answer to a particular chemical substance hence, the TLV does not represent a net line between a safe work environment and a dangerous one or the exact point at which the damages to health start to happen. These limits do not protect adequately every employee! Someone, in fact, can show more or less serious symptoms even with concentrations lower than the established ones. There are a lot of possible reasons for an increase of susceptibility to chemical substances: age, gender, ethnicity, genetic factor (predisposition), life styles, personal habits, medical care or previous illnesses. It is necessary to say that these limits are only referred to the inhalation exposure because, compared to the skin exposure, it is more dangerous and way easier to happen.

ACGIH defines three categories of threshold limit values [9]:

**Threshold Limit Value – Time-Weighted Average (TLV-TWA):** the concentration of a hazardous substance in the air averaged over an 8-hour workday and a 40-hour workweek to which it is believed that workers may be repeatedly exposed, day after day, for a working lifetime without adverse effects.

**Threshold Limit Value – Short-term exposure limit (TLV-STEL):** a 15-minute time weighted average exposure that should not be exceeded at any time during a workday. Workers should not be exposed more than four times per day to concentrations between TLV-TWA and TLV-STEL. There should be at least a 60 minutes interval between exposures. The short-term exposure threshold has been adopted to account for the acute effects of substances that have primarily chronic effects.

**Threshold Limit Value – Ceiling (TLV-C):** this is the concentration that should not be exceeded during any part of the working exposure. Peak exposures should be always controlled. For substances that do not have TLV-TWA or TLV-C established, the maximum admissible peak concentrations must not exceed:

- Three-times the value of the TLV-TWA for no more than 15 minutes, no more than four times per workday. Consecutive exposures must be at least 1 hour away from each other during the workday.
- Five times the TLV-TWA under any circumstances.

If any of these limits is exceeded, it is assumed that a potential risk exists.

The units of measurement for the threshold limit values are ppm and mg/m<sup>3</sup>. The TLVs for aerosols are expressed usually in mg/m<sup>3</sup>. The TLVs for gases and vapours are expressed in ppm or mg/m<sup>3</sup>. The expression (3.1) to convert the TLV from mg/m<sup>3</sup> to ppm is:

$$TLV \left( \frac{mg}{m^3} \right) = TLV (ppm) * \left( \frac{MW}{24,45} \right) \quad (3.1)$$

where MW is the molecular weight of the substance and 24,45 is the molar volume of air, in litres, in normal conditions (25 °C and 1 atm).

The established Threshold Limit Values for MDI are:

- TLV-STEL 0,2 mg/m<sup>3</sup>
- TLV-TWA 0,05 mg/m<sup>3</sup>

These values can vary from country to country: for example, the STEL for all isocyanates in the United Kingdom is only 0,07 mg/m<sup>3</sup>.

Since MDI's molecular weight is 250,25 g/mol, it is easy to see that its TLV in mg/m<sup>3</sup> is approximately 10 times higher than the ppm one (0,02 ppm and 0,005 ppm respectively).

The Table 3.1 reports the results of Dr. Bernhard Brandt of the BG RCI Mainz (2012), it shows how the various quantities of MDI in the air can cause different harmful problems [10].

**Table 3.1** Effects on human health at various concentrations of MDI.

Concentration	Effects
< 0,02 ppm	Possible asthmatic reactions in sensitized person
> 0,05 ppm	Eye irritation
> 0,1 ppm	Slight irritation of nose and throat
> 0,5 ppm	Burning throat
> 1,3 ppm	Cough, reversible bronchitis
> 10 ppm	Irreversible bronchial necrosis
> 50 ppm	Life-threatening

Since the MDI has not a characteristic odour, it is hard for workers to sense it; the odour threshold for MDI is 0.4 ppm. Compared to the values in table 3.1, this odour threshold is higher than the concentration causing nose and throat irritation meaning that if someone can smell it, over-exposure is already occurring.

### 3.4 Main consequences

Now that all the possible problems caused by the MDI are acknowledged, it is possible to group them in 3 categories: respiratory hazards, skin hazards and cause of cancer.

#### 3.4.1 Respiratory hazards

The most common health problem related to the methylene diphenyl diisocyanate is surely the occupational asthma. It is called "occupational" because almost every asthma caused by the MDI develops during workers' everyday life. All the diisocyanates, in general, can generate asthma in sensitized people also at very low concentrations. Since the MDI is dangerous only in the vapour phase, its airborne concentration should be a parameter to monitor. Other respiratory hazards linked to the exposure of workers in "contaminated" air, containing not so low concentration of MDI, are: irritation of the airways, dryness of the

throat, acute bronchial irritation and difficulty in breathing, tightness of the chest, shortness of breath and bronchospasm.

Asthma is a chronic inflammatory disorder of the respiratory tract for which the airways narrow, swell and produce more mucus; asthmatic attacks involve coughing, wheezing, tightness of the chest, difficulties in breathing. It has not to be underestimated because it could, eventually, have some life-threatening attacks!

Occupational asthma is, asthma of course, caused by workplace irritants such as chemical fumes, gases, vapours or dusts. In this case however, asthmatic attacks can be triggered by exposures to even very low concentration of the generating chemical substance.

For a healthy, non-sensitized person, without previous asthma history, repeated exposure to airborne concentration of MDI higher than 20 ppb (0,02 ppm) represents a health risk.

### 3.4.2 Skin hazards

Out of the three, this category is the least worrying due to the “low” impact on health and to the usage of Personal Protective Equipment (PPE) almost world widely nowadays; however, it has not to be underestimated. Within the skin irritations and the allergic skin reactions caused by the contact of MDI with the skin, we can find urticaria (also called hives) and contact dermatitis.

One of the causes of urticaria is the reaction of the skin with a chemical substance and it is mainly manifested by the appearance of an itchy rash, sometimes associated with a burning or tingling sensation. Depending on the time of contact and on the amount of diisocyanate, the urticaria can become more serious in the acute (less than six weeks) or chronic form.

Contact dermatitis is an inflammation of the skin caused by direct contact skin/irritant (non-allergic, irritant contact dermatitis) or skin/allergens (allergic contact dermatitis). In the car interiors field, where a lot of rubbers and adhesives are used, the latter is the most likely to happen. It manifests with itchy rash, red skin and skin lesions, but the particular phenomenon is that these lesions can also manifests in different places on the body from where the contact happened.

As highlighted above, it is very hard for the MDI, or the glue containing it in our case, to get in contact with human skin, hence the skin hazards are caused almost all the times by inadequate occupational hygiene and/or human distractions.

### 3.4.3 Cause of cancer

The methylene diphenyl diisocyanate is linked to cancer in an indirect way. Since MDI was acknowledged as a harmful chemical substance, in fact, no strictly direct connection between lung cancer and MDI has been found but that does not exclude it from the carcinogenic category. In the last 60 years, there have been a lot of lung cancer cases in the polyurethane industries and in the ones that use many polyurethanes everyday so there are not enough proofs to identify MDI as a sure cause of cancer neither as a certainly not carcinogenic substance. This is why, it was classified as Category 2 in the Dangerous Substances Directive (67/548/EEC) where the three categories are:

- Category 1: Substances known to be carcinogenic to humans.
- Category 2: Substances which should be regarded as if they are carcinogenic to humans.

- Category 3: Substances which cause concern for humans, owing to possible carcinogenic effects but the available data are not sufficient for making a satisfactory assessment.

With the new European Regulation, MDI is identified, from the carcinogenic point of view, with the hazard statement H351 that means it is “suspected” of causing cancer. The International Agency for Research on Cancer (IARC), instead, has it in the Group 3. The groups listed by the IARC are:

- Group 1: Certain carcinogenic substances for people.
- Group 2a: Probable carcinogenic substances for people.
- Group 2b: Possible carcinogenic substances for people.
- Group 3: Substances that are not classified as carcinogenic for people.
- Group 4: Probably not cancerogenic substances for people.

The type of cancer most often related to MDI is, of course, the lung cancer (or lung carcinoma) as it primarily affects the respiratory tract. It is a malignant tumour characterized by uncontrolled cell growth in tissues of the lungs; this growth is not limited to the lungs, but it can reach also nearby tissues or even other parts of the human body. Signs and symptoms which may suggest lung cancer include: coughing, coughing up blood, wheezing, shortness of breath, weight loss, weakness, fever, chest pain, bone pain, superior vena cava obstruction, or difficulty swallowing. If the cancer grows in the airways, it may obstruct airflow, causing breathing difficulties.

Many of these symptoms are similar to the ones of the respiratory hazards, so employees should consider calling a doctor whenever they have one or more of these symptoms because, otherwise, it is possible that they could degenerate very badly, especially if they keep working in the contaminated work environment.



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## 4. SITUATION IN ADIENT INTERIORS

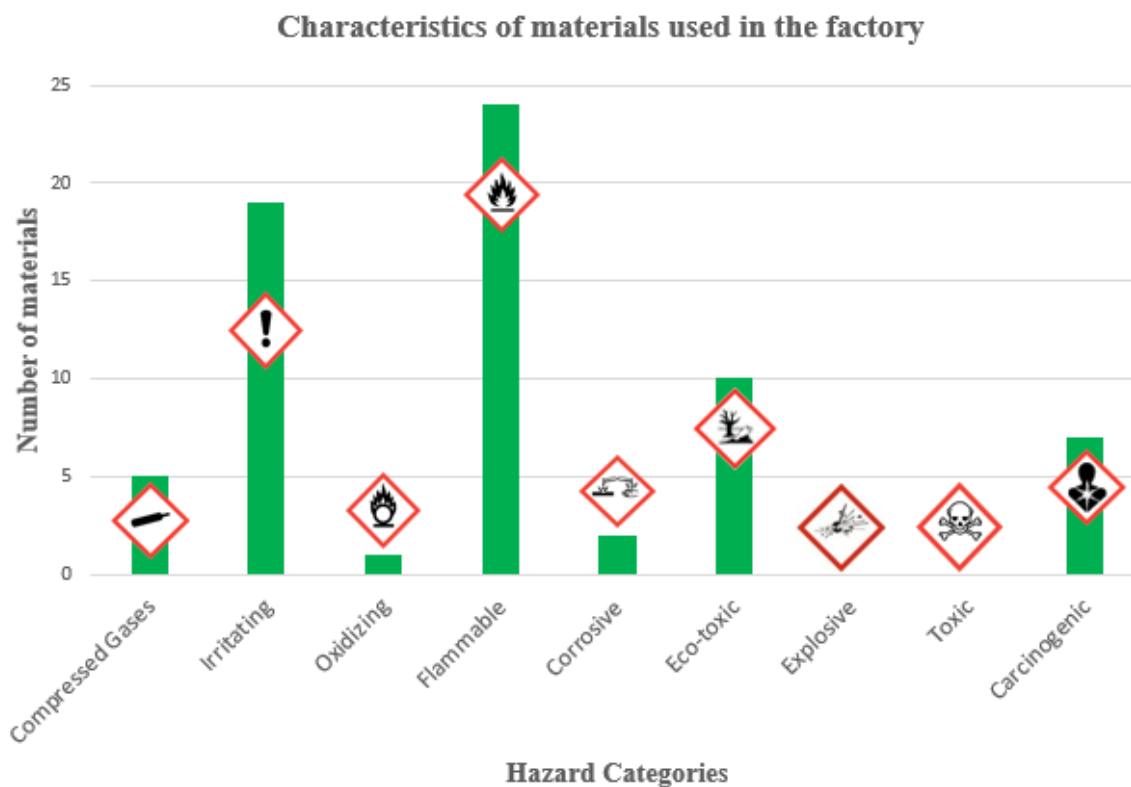
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Adient Interiors d.o.o. Kragujevac was established in 2011 by Johnson Controls Automotive and Plastic Components and fully became Adient in 2016. This plant is engaged in the manufacture and sale of interior parts for the automotive industry (Figure 4.1 is an example) and produces parts for Fiat, Mercedes and many more car companies. In the industrial building there are a lot of sections where different processes happen and various products are produced; some of them operate at high temperature, others involve the usage of huge robotic industrial arms but almost all work on plastic pieces, like polypropylene, polyethylene and polyurethanes.



**Figure 4.1** Example of products in Adient Interiors d.o.o Kragujevac.

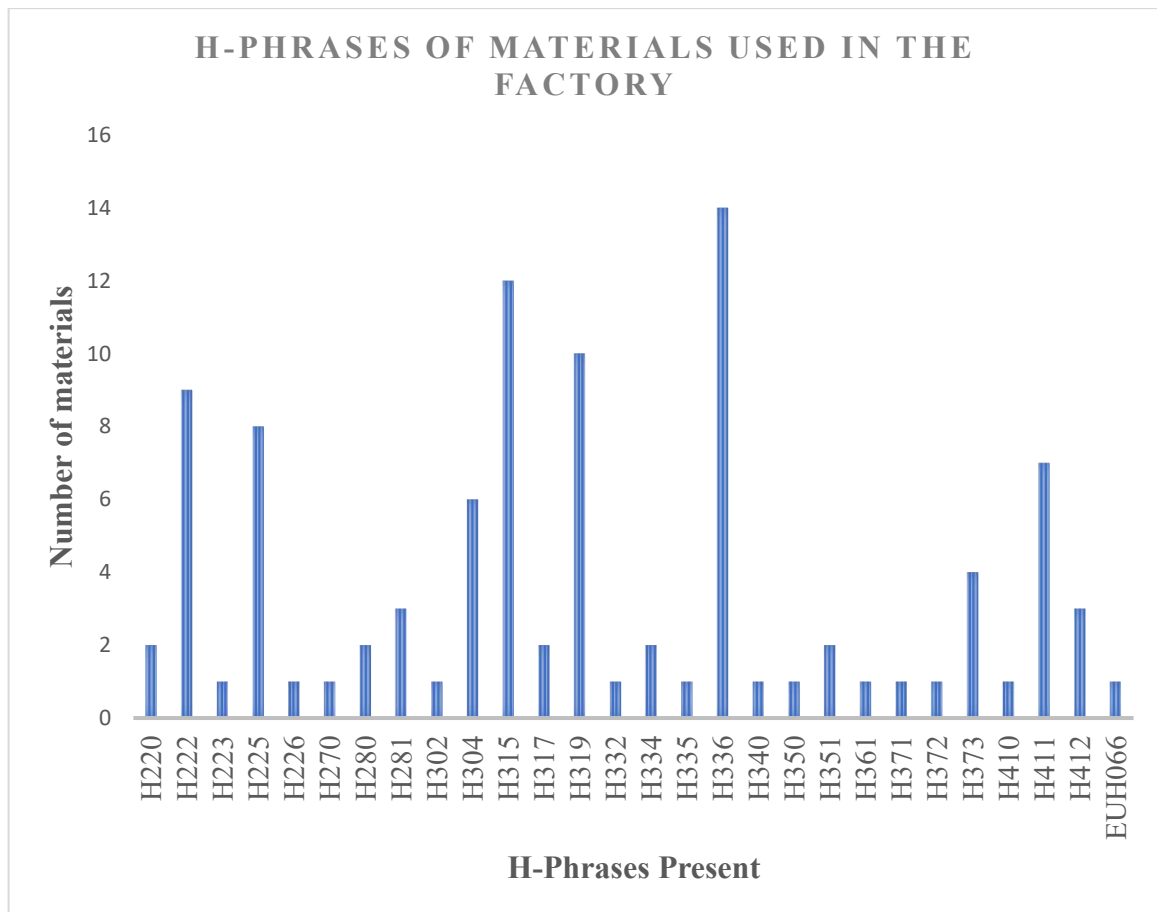
It is easy to assume, then, that in the industry it is frequent to encounter every kind of material (from liquid solvents to glues and combustible gases) and every physical phase; this comprehends also dangerous and harmful to human ones. In Figure 4.2 are shown the characteristics of these materials; many have multiple hazard pictograms associated to them like, for example, the glue containing MDI. The most common characteristic is the flammability, represented by 24 materials (out of 32), followed by the irritant with 19; until now, no explosive and highly toxic substances are used. The last pictogram on the right does not refer only to carcinogenic substances, but also to mutagenic, respiratory sensitizer, toxic for reproductivity and aspiration toxicity ones (as explained in the Appendix A). The polyurethane reactive hot melt, object of this study, has associated to it one pictogram: the health hazard (the last on the right). It was pretty much expected because its dangerous properties derive from the MDI's presence and the diisocyanate, as seen in the previous chapter, has the same pictogram.



**Figure 4.2** Statistic on the characteristics of the materials used in the factory.

This statistic can be done also with the hazard statements (H-phrases) associated to these dangerous materials and it is reported in Figure 4.3. In the previous chapter, we have already seen H315, H317, H319, H332, H334, H335, H351 and H373 while the full text of the other phrases can be found in the Appendix B. It is right to mention the H336 since it is the most common: “may cause drowsiness or dizziness”. For the cancer related ones, there are two materials suspected to be causes (H351) and one that may cause it (H350). The absence of the phrase H360 ensures that there are no materials that may damage fertility or the unborn child but there is one (H361) that is suspected to; same speech for the damage to organs, with only one to be suspected (H371). H372 and H373 are also damage to organs but through prolonged or repeated exposures, they follow the same rule (the first one is confirmed to cause damage while the second is only suspected to do so).





**Figure 4.3** Statistic on the hazard statements of the materials used in the factory

#### 4.1 The process involving MDI

The process performed in the Daimler Section is about applying a cosmetic cover onto some plastic pieces, more specifically polypropylene, which will constitute the interior of the car door panel. About 20 employees, per shift, work on this process and it is active 16 hours per day (divided into two shifts: morning and afternoon). The cosmetic cover of the plastic parts is leather, in different colours depending on the job request, and it is applied using a glue. The final products of this process are grab handles covered with leather and interior panels of the car door, called Centerfield, also covered with leather but this one requires a way bigger piece of leather as shown in Figure 4.4. The process is divided into 5 zones: adhesion, pre-fixing, pre-centerfield, centerfield and folding. Both grab-handles and centerfield undergo almost the same process, the differences depend, of course, on their different dimensions. Plastic parts and leather pieces come from external suppliers as well as the PUR hot melt (the glue).

The process starts with the heating of the polyurethane reactive hot melt, done in the adhesion zone, followed by its distribution, through a roller, onto the leather parts; then the glued leather, after some minutes, goes into the pre-fixing zone where two operators stick them on the black plastic parts. To further promote the bond between the plastic and the leather, they use heat guns to reach higher temperature (to further activate the glue) and avoid detaching. For the grab handles, there are two tables (pre-fixing zone 1 and 2) where four operators perform these actions, plus using some tools to manually ensure the contact

in every part, while for the centerfield there is a shelf similar to a table where an employee, with the help of a machine, attaches it on the plastic part (this is the pre-centerfield).



**Figure 4.4** Grab handle (on the left) and Centerfield (on the right) leather cover.

Both products are now ready to go into the next zone, that is the centerfield, where they undergo vacuum for approximately five minutes to further ensure the intimate contact between leather and plastic. They are placed in a vacuum machine, that has moulding sets to keep them fixed during the operation, covered with a foil then heated and depressurized. After the operation is finished, the fans are activated to cool down the inner part of the machine and the pieces. The central door panels are now finished and ready to go in the quality control, while the grab handles need to go into the last zone (folding area). In this area 8 operators work manually with the correct tools and perform the last adjustments on the edges or on the inner parts of the grab handles; eventual defected pieces are placed away. The final products look like the ones in Figure 4.5 and 4.6.

Since the PUR hot melt contains MDI, all the workers working on this process will have to deal with it and someone, more than some others, may enter in contact with it (mainly by inhalation) so this thesis aims to protect them and prevent potentially harmful consequences. From the MDI's properties, described in the second chapter, it is clear that at room temperature this particular glue is not dangerous at all, but the real problems arise when it gets heated. Heat is supplied in every zone of the process, different temperatures are reached in each zone, so the concentration of MDI in the air will surely be not negligible.

Now every zone will be described in detail to fully understand which the safety issues are, related to the methylene diphenyl diisocyanate, of the process and where are the critical points. The block diagram of the process and the scheme of the disposition of the working tables and machinery can be found in Appendix C.



**Figure 4.5** Grab handles, finished product.



**Figure 4.6** Centerfields, finished product.



#### 4.1.1 Adhesion zone

The adhesion zone is where everything starts and it is the first zone of the process. Everyday are processed 20 kg of polyurethane reactive hot melt. The glue machine, shown in Figure 4.7, does most of the job while the only operator working in this zone needs to follow some simple tasks and he must make sure that everything operates correctly. The machine is constituted by: a tank for the glue, a pump, a heating system, a rotating roller, a conveyor belt and an automatic control system, for the glue's temperature, connected to some procedural lights. The operator at the start switches on the machine and puts on the plate, that will run on the conveyor belt, one very big piece of leather (needed for the centerfield) or eight little small ones (four left hand grab handles and four right hand grab handles). After it has been switched on, the machine will provide heat to the glue until its lower part in the tank melts (around 140 °C); then the glue, in the liquid form, is pumped through an heated tube, to prevent solidification, to the rotating roller that, based on the program chosen on the machine (between centerfield and grab handles), will distribute the glue over the eight leather pieces or the big one. Since there is no more heat provided in this section, the glue will start to cool down as soon as it gets deposited on the leather. The diisocyanate groups start to react with the air, more specifically with the moisture of the air, to consolidate the bond just formed with the cosmetic cover. Then, at the exit of the machine, there is a UV lamp to check the quality of the glue on the leather and after that the pieces are removed from the plate and from the table to go into the other zones. The extraction system connected to the top of the machine will be explained in the paragraph 4.2.



**Figure 4.7** Gluing machine in the adhesion zone.

#### 4.1.2 Pre-fixing zone

In this zone there are four operators, divided in two tables, that manually attach the glued leather pieces onto the plastic parts but it is only for grab handles. The plastic parts are locally heated to 80 °C through usage of heat guns to further promote the gluing with the leather parts; the heat guns are also used to heat the glued leather pieces with the same aim before the attachment between the two pieces because the PUR hot melt is activated around 73 °C. Since the plastic parts are not made only of planar surfaces, the operators need to use some hand tools to ensure the correct connection of every part. It is important to respect the order of arrival of the glued leather parts because after two hours they lose a lot of their gluing power and it can result in unfavourable conditions or mechanical characteristics. When eight grab handles, four left and four right, are collected, they can go into the following zone where they will undergo vacuum.

As it is possible to see from Figure 4.8, operators work very close to the products and the heating of the glue, given the reached temperatures, may generate some MDI vapours!



**Figure 4.8** Pre-fixing zone tables.

#### 4.1.3 Pre-centerfield zone

This is the corresponding zone for the centerfields, where the big glued leather pieces are bound to the plastic part of the same dimension. The table for this area, shown in Figure 4.9, is different because it is connected to a laser machine that guides the operator in putting the cosmetic skin over the plastic to avoid making mistakes in the process. It is very important that the leather is positioned very precisely, in particular on the edges. In these same points, the operator uses the heat gun to heat the glue present on the leather before proceeding. After this, the interior door panels of the cars are ready to undergo vacuum in the next and last zone (for them).

For the workers that are not particularly tall, the heating of the superior edges happens close to their face or neck, so they may be exposed as well to MDI vapours.



**Figure 4.9** Pre-centerfield zone table.

#### 4.1.4 Centerfield zone

This zone is also called vacuum due to the presence of the vacuum machines, because they have a key role in the process as they promote even further the attachment between plastics pieces and leather parts. The pieces are positioned on the white table, as shown in Figure 4.10, and then the operator covers them with a foil to apply vacuum. After the system products-foil is ready, the lid of the machine is lowered, locked and the heating will start. The two machines reach similar conditions: temperature (135 °C for the grab handles and 130 °C for the centerfield), overall time for cycle that is warming up and cooling down (around 10 minutes) and produce similar vacuum (-0,050 bar the small pieces and -0,150 bar the big one). The heating is required to activate the glue, but reaching 73 °C would not be enough because of resistances to the heat transfer, this is why higher temperatures are required. After the first five minutes, the lid is lifted, the fans are switched on and the cooling phase starts; only after another five minutes the foils get removed. Now the products are ready to go into the next zone: the centerfields are finished and ready to go in the quality control while the grab handles still need some manual work.

It is safe to say that this area looks the less dangerous, than the other ones, in terms of MDI releases in the air mainly thanks to the vacuum machine, because here, even if the pieces are heated up, the coverage with the foil and the vacuum make it like a close system, which does not happen in other zones.





**Figure 4.10** Grab handles (on the left) and Centerfield (on the right) vacuum machines.

#### 4.1.5 Folding zone

This area is where the grab handles are refined by manual work. Depending on the amount of work, here are present six to twelve (in two tables like in Figure 4.11) operators per shift. The last details are refined through hand tools and heat guns. For a short period of time, the products go up to 80 °C. The safety problem here could be the accumulation of MDI vapours right on top of the heat guns because they are used as a fixed source of heat (they are not moved around the pieces like in the pre-fixing or pre-centerfield zones) and every operator, once or twice per piece, put their pieces on top of it to make them hotter and easier to refine.



**Figure 4.11** Folding zone table.

## 4.2 Existing preventive measures

The possibility of methylene diphenyl diisocyanate releases in the air are not negligible in the “Daimler Section”, especially knowing the temperatures that are reached in every zone of the process. The PUR hot melt was classified, in the CLP classification, as a: respiratory sensitizer, skin sensitizer and suspected cause of cancer. So, the related hazard statements and pictogram are:

- H317: May cause an allergic skin reaction.
- H334: May cause allergy or asthma symptoms or breathing difficulties if inhaled.
- H351: Suspected of Causing Cancer.



GHS08 (see Appendix A).

They are some of the MDI's ones, so it is easy to say that the dangerousness for the health of the PUR is attributable all to that 3-5% concentration of MDI.

In the industry, this process is one of the newest, as it was established in July 2018, but they have already set some good practise rules and some preventive measures to reduce the emissions and the health problems connected to them.

### 4.2.1 Protective gloves

The process is about sticking together plastic parts and leather pieces, using glue, heat guns and some machines and hand tools so it is mandatory to use protective gloves to avoid skin cuts, direct contact of the materials with the skin, hot burns etc. In the industry world, a lot of different kind of protective gloves are used by workers, but here, mainly due to the presence of the glue and the heat guns, are used nitrile foam gloves (like the one in Figure 4.12).

Nitrile is becoming the coating of choice for most jobs because it protects from many hazards. They offer a very good puncture and tear resistance, they can be used in a wide temperature range (-5 °C to 120 °C) and they have superior strength and chemical resistance to oils and acids than natural rubbers. They are particularly good in this context because the foam nitrile functions as a sponge to absorb the eventual contact with the glue.



**Figure 4.12** Nitrile foam gloves used in Adient Interiors d.o.o Kragujevac.



#### 4.2.2 Local exhaust ventilation system

The first way to prevent health problems for the workers is to avoid releasing any vapour of MDI. This is mostly achieved through a local exhaust ventilation system that removes the air containing the diisocyanate vapours. It is installed right on top of the roller in what seems like a closed system (see the upper part in Figure 4.7). Through an extractor fan motor, the air contaminated by the MDI's releases is sucked from the top of the machine and it is sent directly into the atmosphere, outside the plant, at roof height. The motor, positioned at the same height, grants an air speed of 4 m/s to avoid accumulations of MDI inside the top of the gluing machine. This has proven to be very important and very efficient because from the air measurements (that will be discussed in chapter 5) that was performed until now, both times it resulted that the concentration of MDI, in the air next to this ventilation system, was negligible!

When released into the air outside the plant, MDI vapours are broken down quickly to common air constituents thanks to hydroxyl radicals attack present in the atmosphere. The tropospheric half-life of MDI is around one day and therefore there is no long-term accumulation of MDI in the environment.

#### 4.2.3 Medical checks

Periodical medical examinations are planned to start very soon to monitor the health trend of workers involved in this process. They focus exclusively on the respiratory tract because, due to the extensive and accurate usage of protective gloves, the skin hazards can be neglected. The most important parameter to monitor during these checks is surely the lung function. Most of the times, it is determined by measuring rate and extend to which the lungs can move air in and out of the respiratory system and then making a flow-time curve that represents the movement of the air over time. Between the possible tests (called pulmonary function tests) to gather these data, spirometry is one of the most common.

Spirometry is very helpful in assessing breathing patterns that identify conditions such as asthma, respiratory diseases, pulmonary fibrosis and other problems regarding the respiratory tract. With a spirometer, it is possible to create a volume exhaled-time diagram on which there can be identified two main parameters: FEV<sub>1</sub> and FVC. By monitoring them, it is easy to reveal the generation of occupational asthma or other problems related to the emissions of MDI.

FEV<sub>1</sub> (Forced Expiratory Volume in the 1<sup>st</sup> second) is the volume that has been exhaled at the end of the first second of forced expiration.

FVC (Forced Vital Capacity) is the total volume of air that can be exhaled using maximum effort, following a full breath.

Standard prediction equations and reference tables for different group of people have been developed over the years through experience and can be very useful during the interpretation of the spirometry data.

It is important to say that in the industry a lot of good practices are carried out:

1. Usage of PPE (Personal Protective Equipment) like protective gloves and safety boots.
2. Washing hands with water and soap after work and before eating/drinking.
3. Use of disposable towels.
4. Not reutilization of contaminated gloves.
5. Keeping work area clean and tidy.

### 4.3 Healthy workplaces

The European Agency for Safety and Health at Work (EU-OSHA) is an agency of the European Union [11], founded in Bilbao in 1994, with the task of collecting, analysing and spreading relevant information for the people working in the field of health and safety at work. It works with governments, employers and workers' representatives but also with public and private companies of all over Europe. EU-OSHA aims to create a culture of risk prevention and is involved with designing practical instruments that can be used by companies of micro, small and medium sizes that will help them to assess workplace risks and to share knowledge and good practices on safety and health.

Adient Interiors d.o.o Kragujevac adhere to the latest EU-OSHA's campaign called "healthy workplaces, manage dangerous substances" [12]. Even Serbia, as a nation, has joined this campaign and on the 30<sup>th</sup> October 2018 a conference was held in Belgrade to raise awareness on managing dangerous substances at work. The one shown in Figure 4.13 is the cover image of this campaign.



Figure 4.13 EU-OSHA's campaign on healthy workplaces.

This campaign aims to raise awareness about the exposure of workers to dangerous substances and the risks associated with them, because most of the time they are ignored or underestimated. The exposures to such substances are very common and they can cause a lot of different occupational diseases, health problems and safety risks.

The occupational diseases negatively impact on workers' quality of life and work performances so, other than the risks for the health, they also represent significant costs to business. Workplace exposure to dangerous substances must be eliminated or at least effectively managed to ensure the safety and health of workers and the economic success of businesses and society.

This EU-OSHA's campaign also promotes the sharing of "good practices" between companies to manage effectively dangerous substances in the workplace. The campaign started in April 2018 and the motto is "Safety and health at work is everyone's concern. It's good for you. It's good for your business".

In a company, everyone, in different ways, needs to deal with the presence of dangerous substances, from the employers to the workers. Employers are **legally obliged** to carry out risk assessments to identify all potential hazards associated with dangerous substances. Managers should communicate well with workers to share the culture of safety in the

workplace and they should also ensure that workers receive specific training to be aware of the risks that could happen within the area where they work. Workers should understand the potential risks, be well informed of any preventive measures, feel comfortable pointing out or discovering possible safety concerns and be encouraged to actively participate in finding solutions.

Establishing a prevention culture is key to avoid possible occupational diseases or, even worse, fatal accidents. Through strong leadership and commitment to occupational safety and health, employers and managers can create a working environment that encourages everyone to take safety and health very seriously and cooperate in identifying and tackling risks.

Risk assessment can be the first step towards prevention and everyone in the industry should be involved. The risks posed by dangerous substances are often complex, sometimes not so clear and many factors must be considered when identifying them. Risk assessments should be updated every time there is a considerable change in the process because whenever something is changing with materials, tool, machines, process parameters, also the risk for exposure to dangerous substances change.

The main aim of occupational risk assessment is to protect workers' health and safety. Risk assessment helps to identify all possible hazard risks related to working activities.

EU-OSHA offers a free and easy to use online tool for the risk assessment to help micro and small companies to be able to make the risk assessment themselves. It is called OiRA (Online interactive Risk Assessment) [13] and it offers a step-by-step approach to the risk assessment process, beginning with the identification of workplace risks, then taking the user through the process of implementing preventive actions, and finally to monitoring and reporting risks.



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## 5. APPROACH AND SUGGESTED SOLUTION

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Since there were not many actual data available, the approach was based on the chemical risk assessment. Later, to confirm the emerged critical issues of the process, air measurements were performed in all the zones of the “Daimler Section” and, once these data were collected, it was possible to figure out the best way to improve the safety of the process. It is necessary to mention that the gluing machine, the core part of the process, is not propriety of Adient but it is rented from an external company, so it is not possible to modify any part of it, neither to add some new components. The suggested solutions will take into consideration this obligation and it will be focused on how to prevent the inhalation of MDI vapours from the workers, based on the data from the air measurements and on the results of the chemical risk assessment.

In the next years the process, if it will be considered very profitable and safe enough for the workers, could be scaled-up to increase the number of products and/or the amount of the current ones. In the scale-up, the amount of glue used per day will be obviously increased so an input in the chemical risk assessment will inevitably change (that is the amount of MDI in use) and the results could differ from the current ones. Also, data from the air measurements might change and there could be more emissions of diisocyanate vapours due to the increase in the amount of glue used. This will be taken into account in the “possible future implementations” paragraph, where different ways of reducing the emissions of MDI into the atmosphere will be explained.

### *5.1 Chemical Risk Assessment*

The chemical risk assessment is a system to evaluate the risk, in an industry, based on mathematical correlations called algorithms. These are procedures that assign a numerical value to a series of factors that act in the determination of risk, then they weight the importance of these factors on the final value. The output is an index (more specifically a number) that allows to compare the situation with a numerical scale of risk to understand the importance of the calculated value of the index.

There are a lot of different methods and algorithms to define the chemical risk and to classify it above or below the “Risk irrelevant to health” threshold, but the one used in this study is “MoVaRisCh” [14]. This is the model for the evaluation of chemical risk used in three regions of Italy: Lombardy, Tuscany and Emilia-Romagna.

It is important to present the definitions of risk and hazard because they are often confused:

- Risk is the probability that a worker will be harmed or experience an adverse health effect if exposed to a hazard. It is also the combination of the likelihood of the occurrence of a harm and its severity.
- A hazard is any source of potential damage, harm or adverse health effects on something or someone. It is independent from the levels of exposure of the workers.

The chemical risk assessment aims to identify chemical hazards and risk factors that could cause harm to employees, analyse and evaluate the risks associated with these hazards and determine ways to prevent them or contain them (when they cannot be fully eliminated).

In the model used here, the risk R, due to exposure to dangerous chemical agents, is calculated by multiplying the hazard H per the exposure E as in (5.1).

The hazard H represents the index of dangerousness of a substance, or of a mixture, determined by the hazard statements (H-phrases) linked to the substance subject of study; to each H-phrase is assigned a score based on the CLP's dispositions. According to common sense, the hazards related to the ingestion of the chemical substance, object of this study, are neglected also due to the very low probability of occurrence.

The exposure E represents the level of exposure of the workers, so it depends on various factors including: type, time and modality of exposure, the amount of dangerous substance in use, the effectiveness of the adopted preventive and protective measures.

$$R = H * E \quad (5.1)$$

The risk can be calculated for inhalation exposures and cutaneous exposures, but in this thesis only the first ones will be taken into account due to the extensive use of protective gloves from the workers. So, it is possible to say that the cutaneous exposures are negligible seen the workers' attitude to the usage of gloves.

R can range between 0,1 and 100.

If a substance, or a mixture, has more than one dangerous property (corresponding to more than one hazard statements), for the choice of the value of the index H it is taken the highest value between them.

Before explaining how to calculate E, there will be listed the values of H corresponding to the hazard statements of the PUR hot melt containing MDI.

As discussed in paragraph 4.2, the glue used in this process has three hazard statements (according to the CLP regulation), so it will have three different scores for the index H, as shown in the Table 5.1, and only the highest is going to be taken for the calculations.

**Table 5.1** Scores of H index of the PUR hot melt.

H-phrases of the glue		Score
H317	May cause an allergic skin reaction.	6,00
H334	May cause allergy or asthma symptoms or breathing difficulties if inhaled.	9,00
H351	Suspected of Causing Cancer.	8,00

The values assigned to the hazard statements of the glue, confirm that the possible problems to the respiratory tract (with asthma or breathing difficulties) are considered worse than the suspected cause of cancer. However, considering that the index H ranges from 1 to 10, this mixture is reputed as very dangerous for human health.

It is not that immediate, instead, to determine the value of the index E (5.2). It, in fact, is the product between two subindexes: I and d.

$$E = I * d \quad (5.2)$$

The subindex d expresses the distance from the exposed workers to the source of the possible dangers; it can then assume different values from 0,1 up to 1 as presented in the Table 5.2.

**Table 5.2** Values of the sub-index d.

<b>Distance (m)</b>	<b>Values of d</b>
Less than 1	1
From 1 to 3	0,75
From 3 to 5	0,5
From 5 to 10	0,25
More than 10	0,1

So, the intensity of exposure I can be reduced up to ten times if the workers operate far from the chemical mixture.

The second subindex is, indeed, the intensity of exposure I that, in turn, depends on five factors:

- Physical-chemical properties.
- Amount in use.
- Type of use.
- Type of control.
- Exposure time.

This method of chemical risk assessment uses four matrixes to determine the final value of I and each of them is a combination between two of the factors listed above. To be more precise, only the first matrix is a combination of two pure factors, while the other ones link one factor to an index obtained from the previous matrix. The first three matrixes give three correspondent intermediate indexes, while the last one has as output, of course, the value of I that is needed to finally calculate E.

These matrixes here will be presented as tables.

The first one, Table 5.3, relates to the amount that could be dispersed into the air by considering the physical-chemical properties and the amount in use. It gives back the intermediate index A that is availability.

**Table 5.3** First matrix of the chemical risk assessment.

Physical-Chemical Properties	Amount in use				
	< 0,1 kg	0,1 - 1 kg	1 - 10 kg	10 -100 kg	> 100 kg
Solid or fog	Low	Low	Low	Medium/ Low	Medium/ Low
Low volatility	Low	Medium/ Low	Medium/ High	Medium/ High	High
Medium/ High volatility and fine powders	Low	Medium/ High	Medium/ High	High	High
Gaseous state	Medium/ Low	Medium/ High	High	High	High

Every colour of the matrix is linked to a value of the index A:

- Low                    A = 1
- Medium                A = 2
- Medium/Low        A = 3
- Medium/High        A = 4

The second matrix, Table 5.4, includes this potential availability in the air A and the type of use, to give back the index U corresponding to usage. The type of use of the dangerous chemical substances can greatly influence their presence in the surrounding working area but, often, it is not possible to intervene on this parameter on an existing process or the economic investments would be much higher compared to the possible other modifications.



**Table 5.4** Second matrix of the chemical risk assessment.

A	Type of use			
	Closed System	Inclusion in matrix	Controlled use	Dispersive use
1	Low	Low	Low	Medium
2	Low	Medium	Medium	High
3	Low	Medium	High	High
4	Medium	High	High	High

The index U, unlike the index A, can assume only three values:

- Low            U = 1
- Medium        U = 2
- High            U = 3

This index identifies the effective availability of the dispersion of the dangerous chemical substance in the air.

From this and the type of control of the process is built the third matrix, Table 5.5, that provides the intermediate index C as compensation. The type of control consists in the preventive measures that can be applied to avoid the exposure of the workers. As happened in the type of use, the term on the left is the safest while the one on the left is the most dangerous.

**Table 5.5** Third matrix of the chemical risk assessment.

U	Type of control				
	Complete Containment	Local Aspiration	Segregation/ Separation	General Ventilation	Direct Handling
1	Low	Low	Low	Medium	Medium
2	Low	Medium	Medium	High	High
3	Low	Medium	High	High	High

This intermediate index, as the previous one, can assume three values:

- Low            C = 1
- Medium        C = 2
- High            C = 3

The last matrix, described in Table 5.6, takes into consideration C and the time of exposure of the workers and it yields the value of the intensity of exposure I. The time of exposure is evaluated on a daily basis and it is independent from the frequency of usage of the substance/mixture on higher periods of time.

**Table 5.6** Fourth matrix of the chemical risk assessment.

C	Exposure Time				
	< 15 min	15 min - 2 hours	2 - 4 hours	4 - 6 hours	> 6 hours
1	Low	Low	Medium/ Low	Medium/ Low	Medium/ High
2	Low	Medium/ Low	Medium/ High	Medium/ High	High
3	Medium/ Low	Medium /High	High	High	High

Finally, the values of the subindex I correspond to:

- Low                    I = 1
- Medium/Low        I = 3
- Medium/High      I = 7
- High                    I = 10

Then, obtained this value, by multiplying it for the value of d, the result is E.

So, from the H score and the value for the exposure, it is now possible to calculate the chemical risk R.

Once R is obtained, it can be compared to the values in Table 5.7 to understand in which case the situation is. The table is divided into two main zones: “Irrelevant risk for health” and “Higher risk than irrelevant for health”, respectively corresponding to  $0,1 < R < 21$  and  $R > 21$ .

**Table 5.7** Chemical risk evaluation.

<b>Risk Values (R)</b>	<b>Classification</b>
$0,1 \leq R < 15$	Irrelevant risk to health
$15 \leq R < 21$	Uncertainty range
$21 \leq R \leq 40$	Risk higher than the irrelevant risk to health
$40 < R \leq 80$	High risk zone
$R > 80$	Serious risk zone

The chemical risk R has to be calculated for every worker involved in the process and for every dangerous substance/mixture so, in this case of study, it will be done for the glue containing MDI for every zone (hence 5 times).

First up is the Adhesion Zone, described in paragraph 4.1.1, where the glue is introduced into the process; since 20 kg per day are used, the amount of MDI put in this zone, and in all the other zones, can be considered a bit less than one kilogram per day. Regarding the physical state, the PUR hot melt solidifies in a very short period of time, so it can be treated as a solid even in this stage of the process. Entering in the first matrix with these two inputs, the corresponding A index is 1. For the type of use, it is not wrong to say that in this zone the glue is spread on precise parts inside the gluing machine, thanks to the program behind the whole machine, but it is not a closed system nor included in a matrix. Then the controlled use and value of A being equal to 1 result, from Table 5.4, in a low usage factor ( $U = 1$ ). This zone is the only one, up until now, that has a local exhaust system installed right on top of the gluing machine to prevent the diffusion of MDI vapours into the work

environment, so it leads to a compensation factor of 1 using the third matrix of this chemical risk assessment method. So far everything seems going well with all the calculated indexes being equal to one, but now it is where the risk R escalates the most, thanks to the exposure time. Every employee working in this process, spends around seven hours in the “Daimler Section” because of the shift being eight hours (minus the time spent for two small breaks and the main meal break), reason why the last matrix yields an intensity factor of 7. This has to get multiplied for the distance factor  $d$ , that in this case is 0,75 because the worker usually is within 3 meters from the glued parts once they get out of the machine, to obtain the exposure factor  $E$ . Now it is all about multiplying  $E$  for the index  $H$  representing the hazard of a substance/mixture, but, how was shown in Table 5.1, its value is 9,00 corresponding to the highest score between all the hazard statements linked to the PUR hot melt. Hence, the final result that is the risk  $R$  is 47,25, a high value if compared to the ones in Table 5.7.

The second zone to be addressed in the chemical risk assessment is the Pre-fixing zone where the glued leather pieces arrive right after exiting from the gluing machine. Here they are heated before being attached to the plastic parts, but the heat is not enough (or not given for long enough) to consider the glue a low volatility liquid, so also in this zone, as in every other zone, the physical state corresponds to solid. The amount of PUR hot melt does not change in this zone because it is emitted only from the gluing machine, which lead to an  $A$  factor of 1. Also, in this zone, the type of use corresponds to the controlled one hence, the  $U$  factor is 1 as well. The main difference between the Pre-fixing zone and the Adhesion zone is the absence of the local exhaust ventilation system which can cause an accumulation of MDI vapours nearby the workers of this area; for this reason, the compensation factor  $C$  of this zone is 2. This value, combined with the hours spent working in this environment, leads to an intensity factor  $I$  of 10, that is the maximum achievable. It gets worse when the distance factor is considered: the workers are in close contact with the pieces that they have to link together so the distance between them and the source of possible MDI vapour releases is less than one meter. All things considered, this zone is the most dangerous one with a calculated risk of 90.

The next zone is the Pre-centerfield where, this time, are the centerfield pieces getting prepared for the vacuum machine instead of the grab handles. The values of the corresponding variables are pretty much the same as the previous zone, the only difference is in the exposure time because daily are produced more grab handles than centerfield hence a lower amount of them are processed in the pre-centerfield zone. For this reason, the worker in this area spends 4-6 hours working there while in the remaining time he helps other zones. The intensity factor  $I$  is 7 because of  $C (= 2)$  but  $d$  is 0,75, for the same reason explained in the Adhesion zone, with a final result of  $R$  equal to 47,25.

Next up is the Centerfield zone, it is considered to be the safest in terms of chemical exposure thanks to the vacuum machine that prevent the MDI vapours to be released into the air. The first two factor assume value equal to 1 and the complete containment during the functioning of the machines, as the type of control, allow the compensation factor to be 1 as well. The working time here, as in the previous zone, can be assumed 4 to 6 hours because it is possible to process multiple pieces at once in the vacuum machines with different tasks. They are two: in one can be fitted two centerfields while, in the other one, are put sixteen grab handles (eight left and eight right). The workers here are around two meters away from the products, so the obtained value of  $R$  is 20,25. This is the first, and only, area to be in the “Irrelevant risk for health” range at the current state of things.

The last zone in the chemical risk assessment is the Folding zone that concerns only grab handles. Here the output of the first two matrix is the same as the previous zones ( $A = 1$  and  $U = 1$ ), but it is important to notice that the type of use can be considered “inclusion in matrix”, as the leather and plastic parts joint together can be seen as a matrix that envelops the PUR hot melt. For the type of control it is possible to assume it as segregation/separation in this zone because the workers are aware of the possibility of releasing some MDI vapours in the air and they try to avoid working that close to the products, trying not to have them right under their chest. The distance factor  $d$ , still, is 1 because they are closer than one meter to the products and the calculated risk factor  $R$  is 63.

All these calculated factors and final results are reported in Table 5.8 to clearly highlight the critical aspects of each zone.

**Table 5.8** Chemical risk assessment results before any implemented solutions.

<b>ZONE</b>	<b>A</b>	<b>U</b>	<b>C</b>	<b>I</b>	<b>d</b>	<b>E<sub>inh</sub></b>	<b>H-Score</b>	<b>R</b>
Adhesion zone	1	1	1	7	0,75	5,25	9,00	47,25
Pre-fixing zone	1	1	2	10	1	10	9,00	90
Pre-Centerfield	1	1	2	7	0,75	5,25	9,00	47,25
Centerfield	1	1	1	3	0,75	2,25	9,00	20,25
Folding zone	1	1	1	7	1	7	9,00	63

The Pre-fixing zone, as expected, results the most dangerous zone in the entire process, followed by the folding zone, while the Centerfield zone, instead, is the safest. One of the main problems for these high values coming from this method of chemical risk assessment is the exposure time, in most cases  $> 6$  hours, that leads to an elevated intensity factor  $I$ . A key for solving part of the issue could be some exchanges of workers between different zones. The score 90, obtained as the calculated risk in the Pre-fixing zone, is mainly due to the type of control that it is not safe enough and it awards the higher compensation factor ( $C = 2$ ).

These results will be compared with the ones obtained by the air measurements, discussed in the following chapter, and both of them will be taken into account for the suggested safety solutions. The aim of these solutions is to lower the values of  $R$ , in each zone, to be conformed with the definition of “Irrelevant risk for health”.

## 5.2 Air measurements

To enter a bit more into the details of what is the real situation in the working area during the process, air measurements are necessary to see effectively how much of MDI is released, from the polyurethane reactive hot melt, in the surrounding air. They are required in most of the industrial realities, involving dangerous chemical substances, to check if the chemical safety limits for health prevention are respected.

Since there is not a chemical laboratory inside the Adient Interiors d.o.o. Kragujevac, the air samplings were committed to an external company. Up until the end of February 2019, the concentration of MDI in air in the working areas were measured two times: the first one was performed at the start of August 2018, while the most recent was done in the middle of November. Before describing how these measurements were done and how the results were calculated, it must be said that the one performed in August have been done before my arrival in Serbia (and so in the industry) and the description of the sampling techniques will be based on the second measurements where myself was present as well.

In both occasions, of course, the air measurements were performed in every zone of the process because the possibility of having MDI vapours in the air is higher than zero everywhere in the process, due to the heat given to the glue.

The used equipment is:

- Pump for sampling air with constant flow.
- Sorbent tubes used as sample media to collect the sample.
- Pump for air sampling.
- Digital handheld battery pump for personal air sampling.
- Gas chromatograph with triple quad-weight detector.

It was decided to take use three different pumps, shown in Figure 5.1, to perform the measurements in the key areas of the process. The personal pump for air sampling was placed onto the worker in the Adhesion zone to monitor MDI's concentration in the air that he breathed for the entire eight hours of the working shift; personal sampling, in fact, is done by putting the sample media, connected with the battery pump, in the worker's breathing zone. The sorbent tubes are composed of a charcoal (with a cylindrical shape) and a sealed glass tube which contains the adsorbing material. These are the standard sorbent tubes, they are used for monitoring levels of hydrocarbons, alcohols and organic vapours in the air. The tube is inserted into a holder, then a protective cover is installed to prevent its breaking and the holder gets clipped into the worker breathing zone.

The pump for air sampling with constant flow was placed in the Adhesion zone, the sampling sorbent tube connected to it was placed just below the UV lamp, right at the exit of the gluing machine to capture the eventual MDI vapours releasing from the glued leather parts (the sampling time for this pump was also eight hours).

The remaining pump was used for short-time measurements (30 minutes each) and it was moved into the following zone to measure every time that one sampling finished. The sampling media, different for each zone of course, was always placed as closer as possible to the glued products to catch the harmful released vapours.

In general, after a sampling was completed, the ends of the sorbent tubes were covered by sealing caps to prevent contamination, labelled and stored to be lately analysed in the laboratory.



**Figure 5.1** The three pumps used for the air measurements in Adient Interiors d.o.o. Kragujevac: digital handheld battery Casella (left), pump for sampling air with constant flow QB1 Dadolab (centre), pump for air sampling Bravo M plus (right).

Images taken from: [15] <https://www.casellasolutions.com>; [16] <https://www.dadolab.com/en/products/ambient-samplers/qb1>; [17]

<https://www.tcr-tecora.com>.

So now it should be clear that the air sampling consists in three phases:

1. Setting and placing the equipment on the interested zones.
2. Collecting samples for a determined amount of time.
3. Analysing the samples in a laboratory of analysis.

Not having seen personally the performed analysis on the collected samples, puts many limits on the description of the third point of the above list, hence, in the following paragraph will be explained, in general, the gas chromatography as a standard analysis technique commonly used to establish the concentration of harmful chemical vapours in the air.

### 5.2.1 Gas chromatography

The chromatography is a laboratory technique used to separate a homogeneous mixture. The separation is based on the distribution of the components of the mixture between two phases: the stationary (usually solid or viscous fluid) and the mobile phase that is a fluid which runs across the capillary or packed column. The stationary phase is present throughout the whole structure of the column, allowing the separation of the constituents of the mixture to separate and travel at different speeds. The output data from this kind of analysis are represented in a diagram, called chromatogram, that has the retention time on the x-axis and the signals of the components, registered by the machine, on the y-axis. The retention time is the time required for a component to pass through the entire system, while

the signal depends on the type of detector and it is proportional to the concentration of the separated component.

The gas chromatography is one of the most used type of chromatography and it was the one used to perform the calculations for this air measurements. The mobile phase in this specific technique is an inert gas, such as helium or nitrogen, while the stationary phase is a very thin layer of liquid on an inert solid support. Two notable characteristics of the gas chromatography are that the column, through which the gas phase passes, is located in an oven where the temperature of the gas can be controlled and the concentration in the mobile phase is only function of the vapor pressure of the gas.

In the chromatographic separation, the distribution of the components in the liquid phase follows the phenomenon described by the Henry's law (5.3):

$$C_i = K_H * P_i \quad (5.3)$$

where  $C_i$  represents the concentration of the  $i$  component in the liquid stationary phase,  $P_i$  is the partial pressure of the same component in the gas mobile phase and  $K_H$  is its Henry's coefficient.

There are a lot of different detectors, based on different functionalities, but the one used for our air measurements is the mass spectrometer that has high sensitivity also for small quantities of sample. The device used during this chromatography is more a GS-MS (Gas chromatograph - Mass spectrometer); it is mainly utilized for the identification of a specific substance thanks to a specific test. Hence, at the exit of the column, the mobile phase enters the mass spectrometer where it gets ionized and the ions are sorted by their mass-to-charge ratio. To quantify the amount of interested substance, the instrument compares the relative concentrations in the generated spectrum (that is a plot of the ion signal, function of the mass-to-charge ratio). Since the GS-MS is connected to a computer containing a list of substances, with their mass-to-charge ratio, it is easy to compare the obtained results from the analysis with the ones present in the library.

### 5.2.2 Results

Many of the results are in line with what was expected, while others disprove what emerged from the chemical risk assessment. In Table 5.9 and 5.10, respectively, are reported the air measurements results as they were sent from the external company that was in charge of them. Since they were performed in every zone, there are 5 sets of data composed of measurement time and concentration of MDI (in the second air measurements, done in November, there are six because two different pumps were used simultaneously in the Adhesion zone as explained at the start of this chapter). There are a lot of differences between the two air measurements but not in terms of actual results of MDI's concentration: in the first sampling only the pump for air sampling, Bravo M plus, was used, the sampling time was always 30 minutes and the final output results were only to check if every zone was within the national exposure limits (comply with the OEL).



**Table 5.9** First air measurements results.

<b>Zone</b>	<b>MDI's concentration (mg/m<sup>3</sup>)</b>	<b>Sampling time (min)</b>
Adhesion	< 0,05	30
Pre-fixing	< 0,05	30
Pre-centerfield	< 0,05	30
Centerfield	< 0,05	30
Folding	< 0,05	30

These results are good from the chemical safety point of view, but they are not detailed enough to make some more elaborated considerations or to think about possible changes in the process or in the workers' attitude to prevent harms from even lower exposure levels. In order to intervene on the more critical zones, emerged from the chemical risk assessment, new and more detailed measurements were required, also from a future prospective where the industry will, most likely, process more than 20 kg of PUR hot melt per day. This is why, in the second air samplings, there were used three different pumps with a focus on the adhesion zone because it is where all starts from.

**Table 5.10** Second air measurements results.

<b>Zone</b>	<b>MDI's concentration (mg/m<sup>3</sup>)</b>	<b>Sampling time (hour)</b>
Adhesion	< 0,0015	8
Worker in adhesion	< 0,0015	8
Pre-fixing	0,00313	0,5
Pre-centerfield	< 0,0015	0,5
Centerfield	< 0,0015	0,5
Folding	< 0,0015	0,5

It is clear that the results in Table 5.10 are a bit more interesting, they highlight something that was not possible to estimate solely with the data from Table 5.9. First of all, it is very reassuring that in 8 hours, the amount of MDI, present in the air, in the area around the exit of the gluing machine and in the breathing zone of the worker was less than 0,0015 mg/m<sup>3</sup>, even though the actual value is unknown for us. It can be 0,0013 as well as 0,00001 mg/m<sup>3</sup> but, being less than 0,0015 mg/m<sup>3</sup> means a lot in terms of chemical safety for the workers.

The other results come from the pump for air sampling, the same that was used for all the first measurements, that stayed for 30 minutes as close as possible to the glued products and then it was moved in the next zone.

In the Pre-fixing zone, it was registered the only different value from all the other zones (including the worker's breathing zone), that is 0,00313 mg/m<sup>3</sup> in half an hour. It was expected to have a higher value in this zone from what emerged in the chemical risk

assessment calculations and, in fact, this zone seems to be the most dangerous in the process. Knowing that the TLV-STEL is  $0,2 \text{ mg/m}^3$ , it is clear that there are no risks regarding the short exposure but there might be some problems when considering the TLV-TWA; through some basic calculations it is possible to see that in 8 hours, corresponding to the working shift, this value can reach the time weighted average threshold limit value of  $0.05 \text{ mg/m}^3$ . However, some considerations regarding this situation must be done:

- From the results we know that the concentration of MDI in air in that zone is  $0,00313 \text{ mg/m}^3$  but we don't know what was the value of the same parameter 30 minutes/1hour/2hours before the sampling.
- Since we don't know the values before the sampling happened, it could be that the concentration five hours before was similar to the obtained result and in only half an hour it increased by a very low amount.
- The sampling in this area was done around 17:30, so maybe MDI vapours were accumulated in the air since the start of the day (at 6:00).

At first impact, the concentration in the Pre-centerfield zone resulted weird because, since the heating operations are the same, it was expected to be around the same value as the ones from the Pre-fixing zone. Even though the quantity of glue per centerfield is way higher than on the grab handles, these big pieces are less produced than the little ones (with a ratio around 1/4), but an interesting detail is that in this zone the quantity of air "moved" is higher because the worker physically goes to take the piece next to the gluing machine, then he brings it in its area of competence and, after it is ready, he delivers it into the Centerfield zone. This kind of air movement does not happen in the Pre-fixing zone, where two consecutive tables receive one or two trays containing the glued leather and, when they are ready, only one of the four workers bring them to the next zone. So, in the Pre-centerfield the working operations are faster (even if they have to be more precise) and there is no accumulation of finished products, while in the corresponding zone for the grab handles, since they are produced in higher amount, more time per piece is required and up to 20 pieces can be accumulated in the trays. In the Centerfield zone MDI's concentration in air was confirmed not to be a problem, it was expected, even from the chemical risk assessment, thanks to the vacuum machine. The results in the last zone, instead, disagree with the model's calculation, showing that the accumulation of MDI vapours above the "fixed" heat guns is not so relevant and this zone is not so risky as it may look.

From the results in the last two tables, the analysis laboratory concluded that, of course, the working areas are in line with the permitted values imposed by the national regulations, regarding maximum permissible concentrations of harmful gases, vapours and aerosols in the atmosphere of work rooms and work sites.

### 5.3 Suggested solutions

There are many ways to reduce the chemical risks in a working environment, from replacing the hazardous substances, with a less harmful one, to adopting some engineering controls. It is not possible to replace the current polyurethane reactive glue, containing a 5% of MDI, yet because it has not been found another adhesive, less dangerous for the workers, that grants the same mechanical and chemical properties. There are some studies going on to find a good replacement for the glue, but they are not ready to be used in this kind of process.

The most effective way to reduce the risks, then, is to implement some engineering controls to further prevent chemical hazards for the workers and to optimize the useful life of some existing systems.

The main one is the local exhaust ventilation (LEV) system in the Pre-fixing zone, that resulted to be the most dangerous one, with the aim of reducing the concentration of MDI vapours released in the air and close to the workers' breathing zone. This ventilation system will collect also the vapours from the Pre-centerfield zone and throw them away into the atmosphere at a considerable height, as does the already existing ventilation system in the Adhesion zone. The other physical implementations will be:

- Air filters.
- Air flow meters.
- Local humidifiers.

In the process of reducing the risks, another factor to act on is the exposure time because, as shown in the fourth matrix of the chemical risk assessment, the higher its value the higher the corresponding risk will be. It weights a lot in the evaluation of the risk and it should not be underestimated.

All of those solutions are explained in detail in the following paragraphs.

A new risk assessment is required every time that there is a change in the interested variables, so the results will be presented also to directly see the effects of these changes.

The project for the new equipment has been assigned to an external company and they will install it around the end of March 2019, this is why, in this work, there will be no ulterior data about the concentration of methylene diphenyl diisocyanate in the air to prove that this solution was effective. After the new local exhaust ventilation system will be installed, in fact, new air samplings and a new set of analysis will be required to confirm and test the benefits for the quality of the air in the working environment. In general, for this process, it is a good practise to repeat the air measurements every time that there is:

- An increase in temperature higher than 10 °C or 160 °C exceeded for the first time.
- Change in exhaust system.
- Change of glue.
- Relocation of process.

#### 5.3.1 New LEV and the other minor solutions

A local exhaust ventilation (LEV) system can be a good solution to reduce the vapours of MDI released into the air, due to the heating of the glue during the process. It has already proven to be very effective in the Adhesion zone, where there is the highest quantity of glue, the highest reached temperature and still there is no considerable concentration of the diisocyanate in the air. Thanks to this new equipment, the accumulation of vapours, close

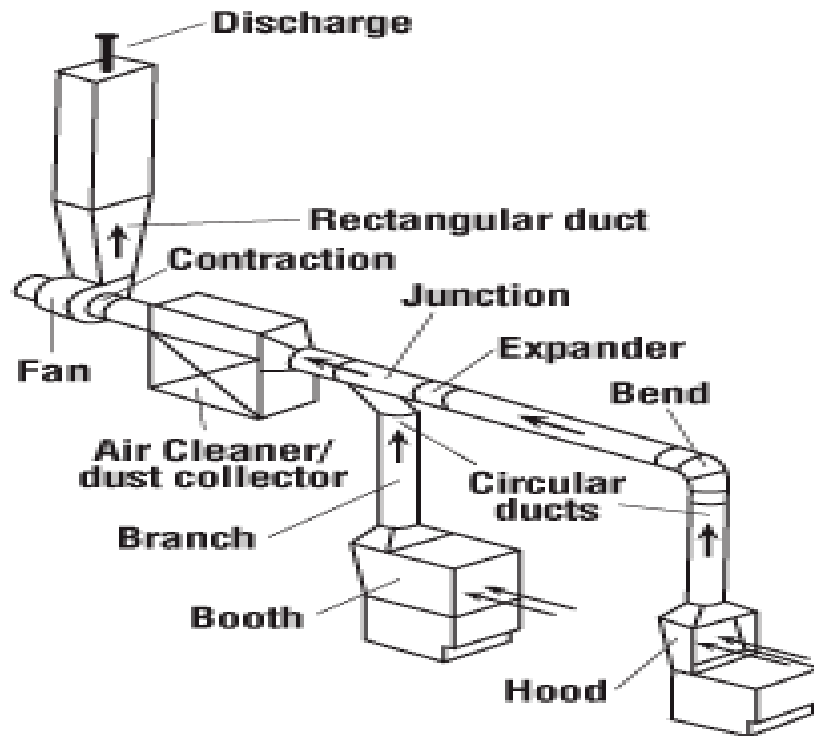
to the workers' breathing zone, will be avoided, hence, the long-term effects on human health will be greatly reduced. In the Pre-fixing zone, the employees operate at a very low distance, hence they are more exposed, and the chemical risk is higher in that zone; this is why the local exhaust ventilation (also called extraction) system is required, rather than the general ventilation.

The ventilation system is also a good way to keep temperature and humidity at comfortable levels, reduce potential fire or explosion hazards and remove other airborne contaminants. It is very important to place the LEV system as close as possible to the source of hazards, so it is easier to capture organic vapours from the working site and send them outside the plant.

The LEV system takes the contaminated air from the surrounding area through openings or hood. This phenomenon is granted from the pressure gradient between the working table and the hood, because this, as most of the system, is under negative pressure (compared to the workplace pressure). Then the exhausts flow into the ducts, away from the workers, and it goes to the fan. In some extraction system, before reaching the fan, the air passes into the air cleaner to remove some/all contaminants, for example in this new equipment that will be installed there will be an air filter to capture the condensing glue from the air (even if it is not present into the already existing system in the Adhesion zone). The fan, that is the most common unit used to move the air, draws the air from the duct after the hood and discharges it into the exhaust stack. This discharge section ends, very often, with an opening into the atmosphere outside the plant. A scheme for the LEV system could be the one presented in Figure 5.2.

The design of the ductwork should be as simple as possible, avoiding 90° angles in the ducts, T-shape connections of the branches, obstructions for the air flow, elevated length of the horizontal ducts and, in general, points where the condensed glue could accumulate. Every bend and junction will contribute to increase the resistance to the contaminated air flow, so they should be reduced in number (whenever possible), as well as the direction changes.

The recommended duct velocity for this application of the LEV is around 5 m/s, so the fan, or the air mover, must be powerful enough to grant this value in every duct, especially when there are multiple branches, for example three as in the case study. There are many types of fan but the chosen one for this system is the axial, thanks to its low occupied volume, it is very compact, and the fact that it, together with its motor, can be placed inside the duct. The whole design part and decisions about all the parameters has been assigned to an external company.



**Figure 5.2** Local exhaust ventilation (LEV) system components.

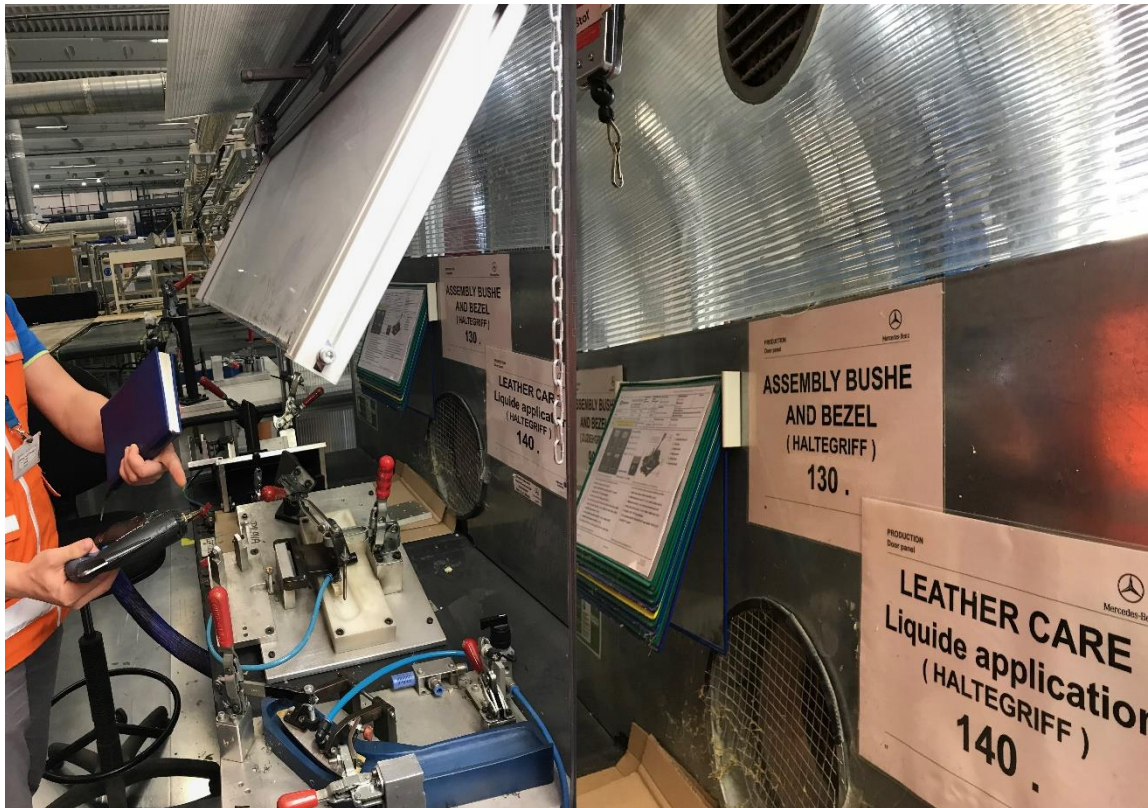
Image taken from [18]

<https://www.ccohs.ca/oshanswers/prevention/ventilation/introduction.html>

However the final look of the tables in the Pre-fixing zone should be something like Figure 5.3. The workers can still perform their tasks without any obstacle, they will have just a protective screen in front of them to further prevent the inhalation of the harmful organic vapours released during the process. As it is shown, the two openings are very close to the emission area, so they can easily catch any released vapour and, thanks to the difference in pressure, move them away from the workers' breathing zone. The screen will also help to redirect the vapours, flowing upward, towards the upper hole, obtaining a better removal.

This kind of system, unfortunately, requires regular cleaning, inspection and maintenance because it is very easy to have accumulation of condensed material on the planar surfaces or on the edges. Each of these solid piles opposes a resistance to the air flow, increases the pressure drop, hence, induces a higher requested power at the motor to maintain the normal specifics.

In the process, it has been proved that some of the released vapours tend to condense when reaching higher heights due to the lowering of temperature; this can be a huge problem for the fan because the condensed glue damages its blades, making them performing way worse than usual. For this reason, the fan has to be changed every two or three months and it is not a good thing because, usually, they have a higher useful life!



**Figure 5.3** Possible look of the tables, in the Pre-fixing zone, after the installation of the new LEV system.

The local exhaust ventilation systems for processes like this one, then, need to be coupled with air filters to prevent the depositing of glue on the fan's blades and, to do so, they must be placed before the fan. There are a lot of different air filters but, for this application, it is better to use a grid-like filters; they will essentially be used as sacrificial units because they are way less expensive than the fan, so, whenever they will be almost or fully covered by the condensed glue, they will just be removed and replaced by new ones.

Since it is hard to visually determine when a filter is saturated, it would be useful to install in the duct one, or more, air flow meters. They could be very vital in understanding when a filter is almost fully covered with condensed glue, thanks to the constant measurement of the velocity of air passing in the duct, but they can also indicate a malfunction of the fan, or the motor, because if the air velocity is much lower than the normal one, something is going wrong, and the malfunction of the air mover could be the cause. In general, they can be a visual signal for some fault in the process because any worker, just looking at the screen containing the air velocity value, can see if it is 0,7 m/s instead of 5 m/s and understand that the equipment is not working properly. If there is no screen connected to the air flow meter, or it is not so easy to instantly see the measured value, it can be connected to a flow-alarm that emits a sound or a light whenever the air velocity exits from a set range of values (for example it can have different sounds/lights for too low and too high values).

There are a lot of devices to measure the velocity of air, or its flow rate, in a duct but, for this application, the most suited are: throttling meters (diaphragm type, nozzle type and Venturi) and Pitot tube. The others would not perform very well due to the condensed glue that could deposit on them, for example on anemometers, turbine meters, rotameters, making the measurements distorted and untrusted.

Another small but important implementation would be the presence of small local humidifiers. Since the process is carried out in a very big industrial building, but it is not in an isolated room, it would be hard and way more expensive to install a global humidifier. There are many types of small local humidifiers, depending on how they actually humidify the surrounding environment. The percentage of humidity of the air is a very key factor to further prevent the inhalation of the harmful organic vapours, specifically MDI, because, in the curing process of the glue, the moisture of air is necessary to keep the reactions going. If the humidity percentage, in the working environment, goes below 30%, other than less comfort for the employees, the MDI will start diffusing in the workers' breathing zones, looking for the required amount of water to continue the ongoing reactions; hence, these local humidifiers will prevent this ulterior source of danger.

To further reduce the chemical risks, the time of exposure should be reduced. In this process, every worker has an eight-hours shift and they get paid to properly work this amount of time, but the exposure time could be lowered to 6 hours, or even less, with some little adjustments. In the "Daimler Section" are produced two different products, so if we consider only one we can say that the process is not continuous due to the alternation between the two. During the process for the Centerfields, for example, the workers in Pre-fixing might or not have some pieces to work on (depending on the quantity currently available in their trays) and vice versa. Hence, during a shift, there are some dead times, even if they are of a short duration, during which they can move away from the working zone. Optimization studies can be performed on this aspect to reduce as much as possible the dead times, still keeping the same amount of work, granting the workers continuous work and giving them larger breaks to lower their exposure time up to six hours, or even less in the days with a lower production. It is better to reduce the exposure times rather than letting the workers have many very small breaks in their working areas, because, even if the concentration of dangerous vapours does not increase during these times, the vapours accumulated previously can still diffuse into them.

### 5.3.2 Chemical risk assessment after the implementations

After such changes, it is necessary to perform new calculations, using the chemical risk assessment model, to understand and verify if they properly reduced the existing chemical risk and how impactful they were.

The presence of the new local exhaust ventilation system and the better organization of working time has led to a big reduction in the values of R, in almost every zone, as shown in Table 5.11. The light blue background is related to the changes in the equipment, hence in the type of control (in the third matrix of the chemical risk assessment), while the green one is about the optimization in the exposure times. The local aspiration obviously grants a way better control on the released organic vapours in the two interested zones, so the compensation factor C is reduced to 1. This, coupled with the lower exposure times, reduces the intensity factor I down to 3, the medium/low value in the fourth matrix of the model, allowing us to obtain a significant difference in the final value of R if compared to the original chemical risk assessment.

**Table 5.11** Chemical risk assessment results after the suggested solutions.

<b>ZONE</b>	<b>A</b>	<b>U</b>	<b>C</b>	<b>I</b>	<b>d</b>	<b>E<sub>inh</sub></b>	<b>H-Score</b>	<b>R</b>
Adhesion zone	1	1	1	3	0,75	2,25	9,00	20,25
Pre-fixing zone	1	1	1	3	1	3	9,00	27
Pre-Centerfield	1	1	1	3	0,75	2,25	9,00	20,25
Centerfield	1	1	1	3	0,75	2,25	9,00	20,25
Folding zone	1	1	1	3	1	3	9,00	27

In Tabella 8 sono riportati i dati ottenuti. Le celle a sfondo azzurro contengono i valori cambiati rispetto a quelli di Tabella 6 grazie alle soluzioni fisiche proposte, quelle a sfondo verde, invece, mostrano i nuovi valori ottenuti con la riduzione del tempo di esposizione dei lavoratori.

With these changes, Adhesion and Pre-Centerfield zones are now in the uncertainty range (with  $15 < R < 21$ ) that is more reassuring for the workers' health respect the previous 47,25. The Pre-fixing zone dropped from 90 to 27 but it is still in the range of risk higher than the irrelevant risk to health, mainly because MDI has 9 as the hazardous score (due to the H334 phrase associated to it) and the workers perform their task very close to the source of possible chemical danger. It would be impossible to further reduce the I index because it would mean to reduce the exposure time down to maximum two hours, so the best way to bring the R values in the irrelevant risk for the health range is to increase the distance from the workers and the glued leather. This is not an easy task because they use their hands to perform their working duties, so the best way would probably be to let them stay as far as possible from the products during the work and to avoid getting closer with their faces for any reason during the heating process. They can then check if something went wrong when the product has fully cooled down, avoiding the direct inhalation of MDI vapours.

Almost all said above for the Pre-fixing zone, can be applied in the Folding zone. Here the changes were only regarding the exposure times, but they were enough to reduce R from 63 to 27, but the low distance and the high hazard related to the presence of MDI make it hard to go further below this value. As described previously, being more careful during the heating of the product, that are the periods in which most of the dangerous vapours are released into the air, is the best way to prevent the inhalation of these vapours.

The real effectiveness of these changes will be demonstrated at the start of April 2019 when the new air samplings will be performed.



#### *5.4 Possible future implementations*

In the future, it is possible that the process will scale-up, corresponding also to an increase of production. This, however will lead to a higher consumption of glue per day, hence the vapours of MDI introduced in the air will be unavoidably higher. So, in the first matrix of the chemical risk assessment, we will move on the right compared to the current situation and the availability index could increase to two. This variation will make the following factor U higher, leading to a snowball effect on the final value of the chemical risk. For this reason, if the consumed glue will rise up to 200 kg per day (instead of the current 20 kg/day), some big changes, as equipment, will be required. To reach the same values of R, reported in the previous table (Table 5.11), a brand-new look will be needed in terms of making a complete containment of the process. The glued products coming out from the gluing machine, for example, should go onto a tray that transports them into the next zone, but all done under a close system in order to avoid dispersions of vapours in the surrounding environment. It could be done with a plexiglass route, with some openings for the hands to let the workers perform their tasks, coupled with the local extraction system right above it to draw the contaminated air away from the process.

The releases of MDI, at the end of the local exhaust ventilation system, outside the plant are very low but, most importantly, they are not persistent in the atmosphere because they are easily degraded by air and water. For this reason, this organic compound will most likely be removed from the list of the hazardous air pollutants, even because there are not emission limits (also due to the difficulty in measuring its concentration in air).

An ulterior preventive measure, however, could be adopted if the process will become big enough to release very high amounts of MDI in the air. Before releasing the exhausts into the atmosphere, it could be useful to remove this harmful component from the air because, in case of accidental release in the working environment (from the LEV system), its concentration in the working zone will rise to not acceptable levels. To accomplish this removal, an adsorption unit can be used. One of the best sorbents for removing organic vapours from the air is “active carbon”, thanks to its high surface area, selectivity and low cost. Hence, an adsorption unit, made of these active carbons, can be placed inside the local exhaust ventilation system (with all the adjustment necessary to do this modification) in the dedicated section. Of course, after some months, the carbons will be almost or full saturated and it will be necessary to change them, the same fate as the air filter discussed previously, but it can be done during the breaks of the process or when there are no shifts due to the fact that it is not a 24-hours continuous process.



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## 6. CONCLUSIONS

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During the last twenty years, the application of Polyurethane Reactive (PUR) hot melt, containing MDI, has gained a lot of popularity thanks to its high binding performances, its thermal resistance and, in general, superior characteristics compared to the commonly used glues and adhesives. The presence of MDI, however, discouraged the usage in some companies (located in West Europe) due to the very low national admissible concentration in the working areas. Since these limits vary from nation to nation, it is possible to find much higher allowable limits in other countries like, for example, most of the East Europe ones.

Most of the times, the chemical risks connected to the release of MDI vapours in the working areas are underestimated, mainly due to its low concentration in the PUR and the fact that not so many laboratories of analysis are able to perform this kind of test to actually attribute a precise value to its presence in the air. This happens because almost all the companies that carry out these types of processes do not have a chemical laboratory inside the plant and each air sampling, or MDI's concentration measurement, cost them a lot, often making them even reconsidering the necessity of performing these tests.

This diisocyanate is not benign at all, as demonstrated by the hazardous phrases linked to it, because it can have both short-term and long-term harmful effects on the workers with the possibility of causing occupational asthma or even more serious consequences. All these problems are related to the vapour phase of the MDI, not to its solid or liquid state, so much awareness must be raised when heat is involved in the process and temperatures above 100 °C are reached (also for short periods of time).

For this reason it is necessary to prevent as much as possible its releases into the surrounding air, also because inhalation is the most worrisome way of contact with human body; a good measure to take in cases like this is to remove the vapours directly from the source. The local exhaust ventilation fits very well the necessities of the process because it draws the contaminated air very close to the heated glued products, hence prevent the dangerous vapours from reaching the workers' breathing zones.

In general, workers must be very careful when they heat the glue containing MDI, especially because it is odourless and by the time they start to sense it, it is already late as the odour threshold limit is four times higher than the dangerous for health limit.

It is a real hidden menace because, due to thermal lift and aerosol formation, it can affect also other employees that are not involved in the process that work in the neighbouring areas.

Periodic medical checks also have a key role in the prevention because they can show, through the lungs function behaviour, if the workers' health is getting worse. The doctor help in these cases is always needed and very important because it can confirm that the adopted preventive measures are doing their job, or it can suggest that something more is needed to keep the employees safe.

EU-OSHA and similar agencies are always ready to help companies to fully understand all the risks related to these chemical components, to raise awareness on the things that workers daily enter in contact with and to prevent occupational diseases. Employees' health is very

important, so all the details should be observed with care, because it often happens that they are not aware of all the characteristics that some substances have, resulting in more frequent unexpected accidents or injuries.

A great change would be to replace this PUR hot melt with a less dangerous, for human health, glue or adhesive but with the same optimized characteristics. There are already some adhesives that have similar characteristics like the PUR hot melt with an MDI content of less than 0,1% that, for this reason, are not classified as dangerous substances. Another kind of innovative glue is the water based one, formulated from natural or soluble synthetic polymers that need to be mixed with water before application (but these adhesives are mostly used in processes very different from the one discussed in this work).

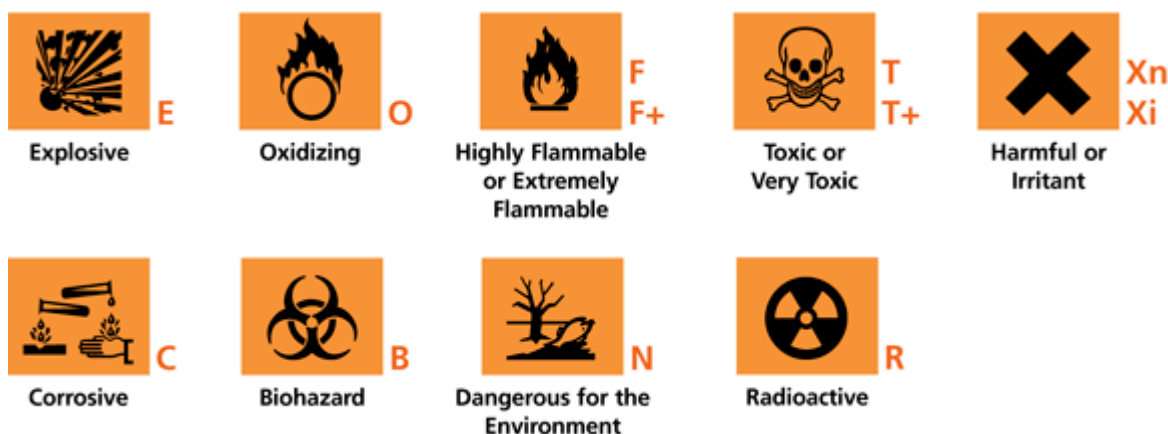
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## 7. APPENDIX A

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In the Dangerous Substances Directive (67/548/EEC), valid through 2015, dangerous chemical substances and mixtures were classified in categories. Almost all of them are associated with a symbol and a hazard pictogram, like the ones in Figure 7.1, while the remaining ones are: carcinogenic, mutagenic, toxic for reproduction and dangerous for the environment.

A hazard pictogram is an image on a label that includes a warning symbol and specific colours intended to provide information about the damage a substance, or mixture, can cause to human health or the environment.



**Figure 7.1** Dangerous Substances Directive (67/548/EEC) hazard pictograms.

Image taken from [19] <https://www.sigmaaldrich.com/safety-center/understanding-the-label.html>










Risk phrases and safety advices, respectively R-phrases and S-phrases, were part of this Directive and were, of course, assigned to dangerous substances.

The CLP Regulation has introduced a new classification and labelling system for hazardous chemicals in the European Union. The pictograms, shown in Figure 7.2, have also changed and are in line with the United Nations Globally Harmonised System (GHS). The new hazard pictograms are nine, rhombus shaped with red border, white background and black illustrations.

Every pictogram contains one or more group of dangerous substances:

- GHS01: Explosives, Self-Reactive, Organic Peroxides.

- GHS02: Flammables, Pyrophoric, Self-Heating, Emits Flammable Gas, Organic Peroxides.
- GHS03: Oxidizers.
- GHS04: Gases under pressure.
- GHS05: Skin corrosive, eye damaging, corrosive to metals.
- GHS06: Acute Toxicity (fatal or toxic).
- GHS07: Irritant (skin and eye), Skin Sensitizer, Acute Toxicity (harmful), Narcotic Effects, Respiratory Tract Irritant, Hazardous to Ozone Layer.
- GHS08: Carcinogen, Mutagenicity, Reproductive Toxicity, Respiratory Sensitizer, Target Organ Toxicity, Aspiration Toxicity.
- GHS09: Aquatic Toxicity.

GHS01 Explosive 	GHS02 Flammable 	GHS03 Oxidising 
GHS04 Gas Under Pressure 	GHS05 Corrosive 	GHS06 Acute Toxic 
GHS07 Harmful / Irritant / Skin sensitiser 	GHS08 Carcinogen / Germ cell mutagen / Reproductive toxin 	GHS09 Hazardous to the aquatic environment 

**Figure 7.2** CLP European Regulation hazard pictograms.

Image taken from [20] <https://www.york.ac.uk/biology/intranet/health-safety/chemical-safety-2/classification-of-chemicals/comparison-of-old-and-new/>

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## 8. APPENDIX B

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In this appendix are reported all the hazard statements related to the dangerous substances present in the Adient Interiors d.o.o Kragujevac.

This is a good example to understand the hazard classes and the division of the hazard statements into the three categories: physical hazards, health hazards and environmental hazards. The first category comprehends all the H-phrases from H200 to H290 related to the properties of the substances. The second one has the statements from H300 to H373 and is about the substances that represent danger for human health. The last one has very few statements (five to be precise) from H400 to H413 regarding the substances dangerous for the environment. Note that not every H + number corresponds to a hazard statement (the third category of the hazard classes is a clear example)!

EUH phrases are additional hazard statements and they are basically the equivalent of the previous R-phrases (they have the same numbers). On the implementation of the GHS through the CLP regulation, the European Union found out that many of the R-phrases did not have a precise corresponding statement, so they decided to introduce these EUH statements to cover all the possible dangerous properties of a substance.

**Table 8.1** Hazard statements for the other dangerous substances in Adient Interiors d.o.o Kragujevac.

H220-Extremely flammable gas
H222-Extremely flammable aerosol
H223-Flammable aerosol
H225-Highly flammable liquid and vapour
H226-Flammable liquid and vapour
H270-May cause or intensify fire; oxidizer
H280-Contains gas under pressure; may explode if heated
H281-Contains refrigerated gas; may cause cryogenic burns or injury
H302-Harmful if swallowed
H304-May be fatal if swallowed and enters airways
H336-May cause drowsiness or dizziness
H340-May cause genetic defects
H350-May cause cancer
H361-Suspected of damaging fertility or the unborn child
H371-May cause damage to organs
H372-Causes damage to organs through prolonged or repeated exposure

H410-Very toxic to aquatic life with long lasting effects
H411-Toxic to aquatic life with long lasting effects
H412-harmful to aquatic life with long lasting effects
EUH066 Repeated exposure may cause skin dryness or cracking

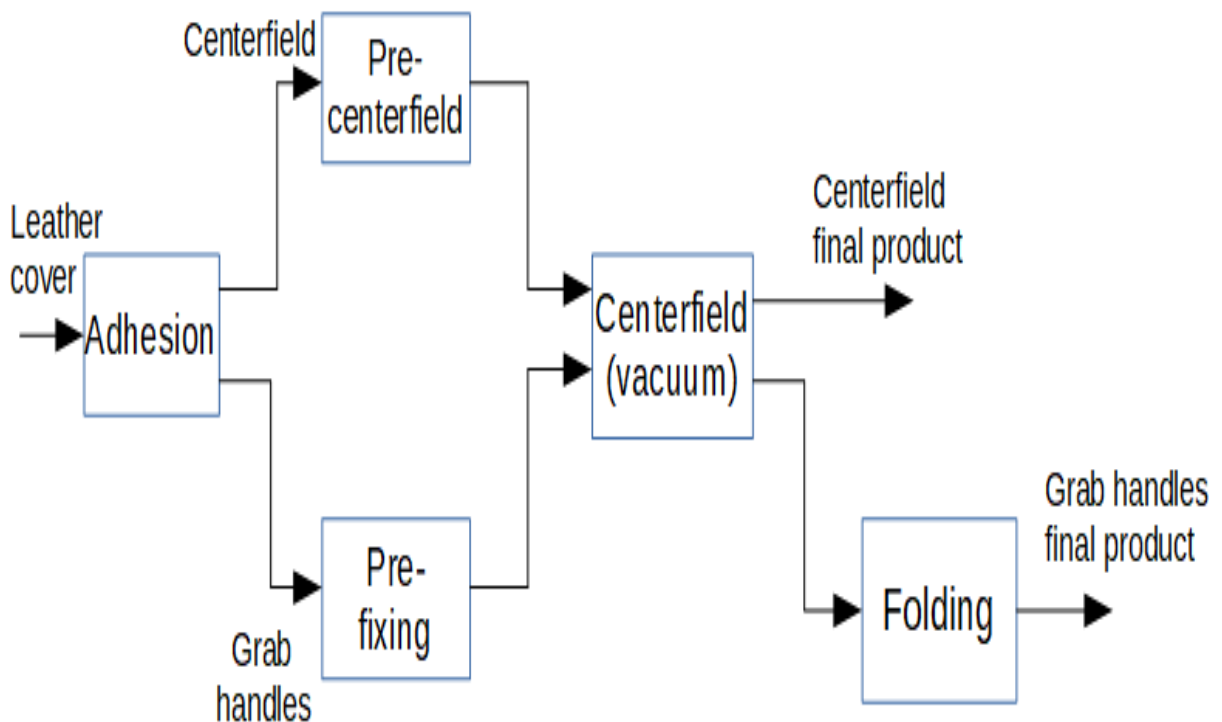


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## 9. APPENDIX C

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A schematisation of the process carried out in the “Daimler Section” can be represented by the block diagram shown in Figure 9.1.

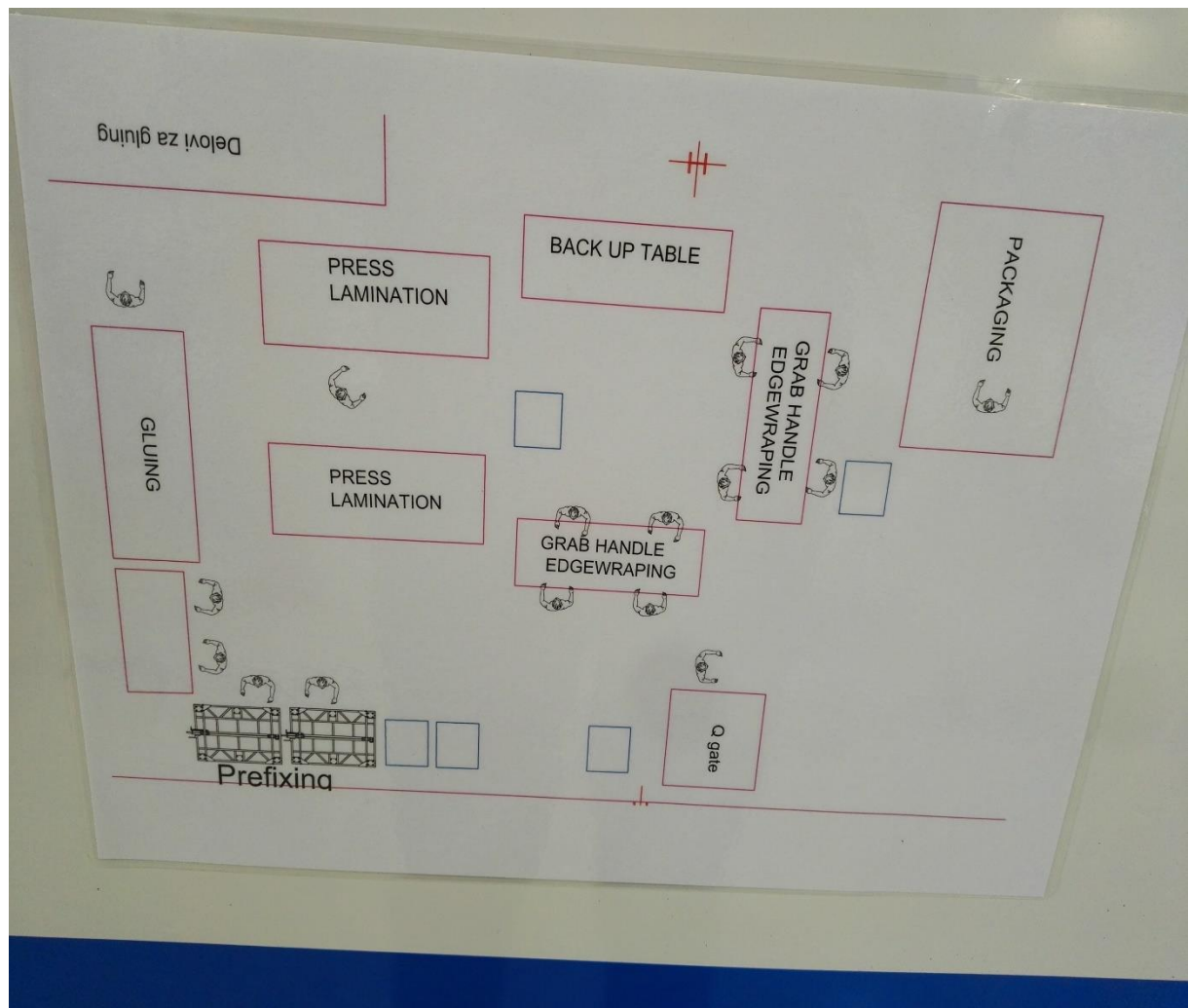


**Figure 9.1** Process block diagram.

The input of the glue is directly inside the gluing machine, in the adhesion zone, from a tank that is refilled every week more or less.

Both types of finished products go in the quality control zone before exiting from the “Daimler Section”, where the final verdict is given on the quality of the product.

While the exact disposition of the working tables and machinery is in Figure 9.2.



**Figure 9.2** Original disposition in the “Daimler Section”.

It has changed during the winter season due to the lack of a centralized heating system, hence most working tables were placed much closer to each other. During the cold months, then, workers were supposedly more exposed to MDI vapours, due to the fact that all the zones were closer and these vapours from one zone could diffuse to the workers of the other zones.

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## 10. BIBLIOGRAPHY & SITOGRAPHY

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- [1] [www.adiant.com](http://www.adiant.com)
- [2] <https://pubchem.ncbi.nlm.nih.gov>
- [3] Dirk Grunwald  
[https://www.researchgate.net/publication/256088991\\_New\\_Analytical\\_Methods\\_as\\_Tools\\_for\\_the\\_Determination\\_of\\_Resin\\_Properties](https://www.researchgate.net/publication/256088991_New_Analytical_Methods_as_Tools_for_the_Determination_of_Resin_Properties)
- [4] Allport D.C., Gilbert D.S., Outterside S.M., *MDI and TDI: Safety, Health and the Environment*, Chichester, John Wiley & Sons, 2003
- [5] <https://www.epa.gov/sites/production/files/2015-09/documents/mdi.pdf>
- [6] <https://echa.europa.eu>
- [7] [https://www.chemsafetypro.com/Topics/GHS/GHS\\_hazard\\_statement\\_h\\_code.html](https://www.chemsafetypro.com/Topics/GHS/GHS_hazard_statement_h_code.html)
- [8] Ashland LLC  
[https://www.ashland.com/file\\_source/Ashland/Documents/Sustainability/rc\\_Methylene\\_Diisocyanate.pdf](https://www.ashland.com/file_source/Ashland/Documents/Sustainability/rc_Methylene_Diisocyanate.pdf)
- [9] <https://www.acgih.org/tlv-bei-guidelines/tlv-chemical-substances-introduction>
- [10] Dr. Bernhard Brandt  
[https://www.bgrci.de/fileadmin/BGRCI/Veranstaltungen/Schlema\\_VII\\_2012/Isocyanatexpositionen\\_am\\_Arbeitsplatz\\_Dr.\\_Bernhard\\_Brandt.pdf](https://www.bgrci.de/fileadmin/BGRCI/Veranstaltungen/Schlema_VII_2012/Isocyanatexpositionen_am_Arbeitsplatz_Dr._Bernhard_Brandt.pdf)
- [11] <https://osha.europa.eu>
- [12] <https://healthy-workplaces.eu>
- [13] <https://osha.europa.eu/it/tools-and-publications/oira>
- [14] <http://www.ausl.mo.it/dsp/movarisch>
- [15] <https://www.casellasolutions.com>
- [16] <https://www.dadolab.com/en/products/ambient-samplers/qb1>
- [17] <https://www.tcr-tecora.com>
- [18] <https://www.ccohs.ca/oshanswers/prevention/ventilation/introduction.html>
- [19] <https://www.sigmaaldrich.com/safety-center/understanding-the-label.html>
- [20] <https://www.york.ac.uk/biology/intranet/health-safety/chemical-safety-2/classification-of-chemicals/comparison-of-old-and-new/>



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