ASSESSMENT OF THE EXPOSURE ASSOCIATED HEALTH EFFECTS TO HEXAMETHYLENE DIISOCYANATE (HDI) IN AUTOMOTIVE SPRAY PAINTING PROCESSES IN SMALL, MEDIUM AND MICRO ENTERPRISES

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A research report submitted to the Faculty of Health Sciences, University of the Witwatersrand, Johannesburg, in partial fulfilment of the requirements for the degree of Masters of Public Health in Occupational Hygiene

Johannesburg, 2006

DECLARATION

I, Adri Spies, declare that this research report is my own work. It is being submitted for the degree of Masters of Public Health in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at this or any other University.

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PUBLICATIONS AND PRESENTATIONS

- National Institute for Occupational Health. Research Day 2004 – Preliminary results to Hexamethylene diisocyanate exposure in automotive repair shops during spray-painting (oral presentation)
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ABSTRACT

During October 1996 to December 1999, isocyanates were the most frequently reported causative agent for occupational asthma cases (16.7% of all cases) submitted to the Surveillance of Work-Related and Occupational Respiratory Diseases in South Africa registry (SORDSA). Occupational disease surveillance registries in other countries also identified isocyanates as the most important occupational sensitiser. Asthma caused by isocyanates exposure may be severe and may persist even after exposure ceases. For this reason, it is important to identify the potentially hazardous isocyanate exposure settings, and to prevent sensitisation and asthma development where possible.

Auto body repair shops, typically small, medium or micro enterprises (SMMEs), were the focus group in this study. Due to the paucity of medical surveillance and occupational hygiene programmes, there is likely to be over-exposure to isocyanates in such workplaces. The aim of this study was to identify and quantify exposure to HDI in auto body repair shops, and secondly, to describe the control measures currently used in these repair shops.

The study investigated hexamethylene diisocyanate (HDI) exposure in the spray-painting processes of automotive repair shops in Gauteng. The repair shops were selected from the Highveld South African Motor Body Repairers' Association (SAMBRA) membership list. Ten repair shops were included in this cross sectional study. Twelve subjects directly or indirectly involved in spray-painting in each repair shop had HDI exposure measured, resulting in a total of

113 HDI measurements. HDI monomers, prepolymers and total isocyanates determined using the National Institute for Occupational Safety and Health (NIOSH) draft method 5525 for analysis of monomeric and TRIG aliphatic isocyanates.

Eighty one percent of workers were over-exposed to HDI monomers (exposure limit of 0.02mg/m^3) and 3.4% to HDI prepolymers (exposure limit of 0.5mg/m^3). Ninety percent of the establishments' HDI monomer airborne concentration exceeded the OEL and 30% the prepolymer HDI concentrations.

Workers were divided into 12 occupation categories according to the extent of their direct contact with the HDI-based paint and the three highest exposed groups were panel beaters, spray painters and dent-fillers. Workers directly and indirectly in contact with paint, in the auto body repair shops registered with SAMBRA were exposed to high levels of HDI during the spray painting operation. Insufficient and incorrect control measures were in place to control HDI exposure. The findings of this study confirm the risk of exposure to HDI in the automotive repair industry and the need for occupational hygiene control measures.

In conclusion, high concentrations of HDI were common and even indirectly exposed workers were at risk of excessive exposure to HDI. Inadequate exposure control methods were widespread

Keywords: *Hexamethylene Diisocyanate HDI, Spray painting, Auto body Repair shops*

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NOMENCLATURE

- 1,6 Hexamethylene diisocyanate (HDI),
- 4,4'-methylene bisphenyl diisocyanate (MDI)
- Chemical Agent Resistant Coating (CARC)
- Environmental Protection Agency (EPA)
- Forced Expiratory Volume expired in 1 second (FEV1)
- High Volume Low Pressure Spray Guns (HVLP)
- Low Volume Low Pressure Spray Guns (LVLP)
- Occupational Asthma (OA)
- Occupational Safety and Health Administration (OHSA)
- Parts per million (ppm)
- Recommended exposure limit (REL)
- Small, medium and micro enterprises (SMMEs)
- Surveillance of Work-Related and Occupational Respiratory Diseases in South Africa registry (SORDSA)
- The National Institute for Occupational Safety and Health (NIOSH)
- TLV (OHSA)
- Toluene diisocyanate (TDI)

DEFINITIONS

Definitions by National Institute for Occupational Safety and Health (NIOSH) and American Chemical Council's Diisocyanates Panel

Diisocyanates (Monomers):

A "monomer" is the starting unit from which the polymer is formed. An aliphatic diisocyanate monomer consists of an aliphatic hydrocarbon chain (straight-chained or cyclic) with two isocyanate groups.

Common examples of monomeric isocyanates include 1,6- hexamethylene diisocyanate (HDI), 2,4-and/or 2,6-toluene diisocyanate (TDI), 4,4'diphenylmethane diisocyanate (MDI), methylene bis (4-cyclohexylisocyanate) (HMDI), isophorone diisocyanate (IPDI), and 1,5-naphthalene diisocyanate (NDI).

Polyisocyanates: Species possessing free isocyanate groups and derived from monomeric isocyanates either by directly linking these monomeric units (homopolymer) or by reacting these monomers with di-or poly-functional alcohols or amines (copolymer).

The most important polyisocyanates based on HDI are:

- HDI trimer

- HDI biuret

- HDI uretdione

Prepolymers: The term “prepolymer ” is usually used to refer to short chain oligomers made from at least two different monomers, e.g. HDI with glycols.

For aliphatic diisocyanates, the term “prepolymer ” is also sometimes used to refer to what is technically a homopolymer, or polyisocyanate.

Oligomeric Isocyanates (Oligomers):

“Oligomer ” is used to refer to a substance in which each molecule is made up of several repeating structural units. It can be thought of as a start on a polymer, but it does not have enough repeating units to qualify as a polymer. Unlike the fully-reacted diisocyanate-based polymer, the oligomer molecules may still have reactive isocyanate units. Relatively low molecular weight polyisocyanates.

Intermediates: Species possessing free isocyanate groups, formed during use of an isocyanate product by partial reaction of the isocyanate species with a polyol.

CHAPTER 1

1 INTRODUCTION

1.1 Background

Isocyanates have become important occupational hazards in the past couple of decades. Although first described by Wurtz in 1848 (1) it was 136 years later in 1984 that isocyanates received prominence in Bhopal, India. An accidental acute inhalation exposure to methyl isocyanate resulted in the deaths of more than 2,000 people and adverse health effects in more than 170,000 survivors. The probable cause of death in most cases was pulmonary oedema, with many deaths resulting from secondary respiratory infections. Survivors continue to exhibit damage to the lungs and eyes as well as reproductive effects such as stillbirths and spontaneous abortions. The tragedy in Bhopal, India, called worldwide attention to the toxicity of isocyanate compounds (2).

Occupational asthma, one of the diseases caused by isocyanates, has emerged in the past decade as the most important isocyanate-induced occupational respiratory disease, according to disease surveillance programmes in developed countries (3,4).

1.2 Chemical properties

Isocyanates are a group of low molecular weight chemicals that contain highly reactive nitrogen-carbon-oxygen groups attached to aromatic, aliphatic or cycloaliphatic radicals (4). The N-C-O group of the diisocyanates makes the chemical useful in the production of polyurethane foams, elastomers, adhesives, varnishes, coatings and paint hardeners (5).

Isocyanates have a high affinity for compounds containing reactive hydrogen atoms bound to oxygen, nitrogen, or sulphur (6).

$OCN - (CH_2)_6 - NCO$

Figure 1: The structure of the principle monomer of diisocyanate

Isocyanate is produced by reacting with a primary aliphatic or aromatic amine dissolved in a solvent such as xylene, monochlorobenzene or dichlorobenzene with phosgene that is dissolved in the same solvent. Isocyanates contain 2 NCO groups attached to an organic radical and react exothermically with compounds containing active hydrogen atoms (e.g. polyglycols/polyols) to form a prepolymeric mass (polyurethane) (7).

When water (H_2O) is added to the reacting chemical, carbon dioxide (CO_2) is released, causing the fluid mixture to become foam. The presence of excess isocyanate monomer and H_2O result in CO_2 production, but also more volatile isocyanates (7).

$$\mathrm{OCN-R-NCO + HO-R-OH} \rightarrow \left[-\underset{\underset{O}{|}}{C}-\underset{\underset{H}{|}}{N}-\underset{\underset{H}{|}}{R}-\underset{\underset{O}{|}}{N}-C-O-R-O- \right]_n$$

(Diisocyanate) (polyol) ((Poly) urethane)

Figure 2: Isocyanates will React With the Hydroxylic (OH) Group to Form Urethane (Source: Occupational asthma and extrinsic alveolitis due to isocyanates: current status and perspectives. *Br J of Indust Medicine* 1993; 50:213-228) (6)

Isocyanates will react with hydroxylic (OH) groups to form urethane. Isocyanate will also combine with primary and secondary amines, water, urea and urethanes. The elementary molecules of isocyanate are called monomers. These monomers are capable of reacting with themselves to form dimers, trimers and oligomers. This self-prepolymerisation of isocyanates occurs spontaneously and can be accelerated by heating (6).

During the production of polyurethane prepolymers at least 2 (diisocyanates) or more (polyisocyanates) NCO groups in the molecule are required (6).

The structure of the principles monomers of diisocyanates are illustrated in figure 3 and 4.

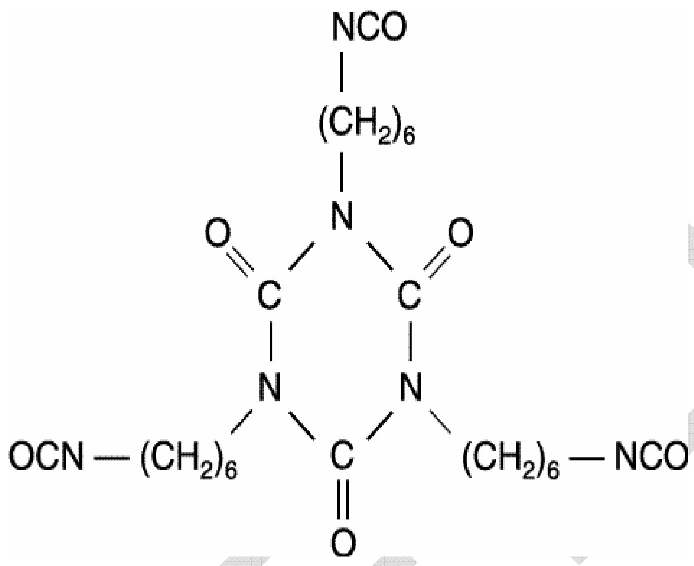

Figure 3: Prepolymers of Isocyanates (see page 12 for definitions)

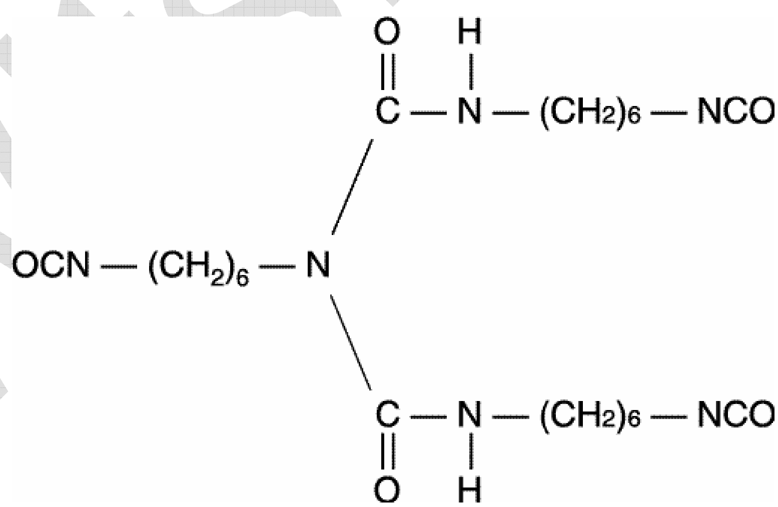

Figure 4: Buiret of HDI (see page 12 for definitions)

1.3 Uses of Isocyanate

Diisocyanates, such as toluene diisocyanate (TDI), 4,4'-methylene bisphenyl diisocyanate (MDI) and hexamethylene diisocyanate (HDI), are widely used for the production of polyurethane foam, as well as increasingly used in the automobile industry for auto body repair, spray paint and manufacture of automotive components, as a sand binder in foundry core making, and for insulation materials in refrigeration and construction (8).

Isocyanates are used in the manufacture of polyurethane foams, polyurethane rubbers and elastomers. They are also found as cross-linking agents in speciality surface coatings, inks, adhesives and binders for foundry cores (9). They have many applications in the manufacturing industry, where they are widely used in surface coatings, polyurethane foams, adhesives, resins, elastomers, binders and sealant (8).

TDI and HDI, the two most toxic forms of diisocyanates, are volatile at room temperature but for isocyanates in general, heating, pressure or lack of ventilation can result in significant workplace exposure (8). During prepolymerisation to polyurethane, various isocyanate contaminants can become airborne (10).

New types of isocyanates - commonly referred to as prepolymer isocyanates - have been introduced to lower the risk of respiratory hazards, due to inhalation of monomer vapours. The prepolymers are less volatile than their parent monomer. Although the products based on prepolymers usually contain only trace amounts of the volatile monomers (less than 1%), the product still contains considerable amounts of reactive isocyanate groups on the non-volatile prepolymers (11).

Prepolymer HDI has a higher molecular weight and lower vapour pressure and reacts slower than the parent monomer HDI and may be included into polyurethane paint to reduce the concentration of the isocyanate monomers in the air (10).

The main use of prepolymer HDI is for the use in vehicle-refinish paint systems (3). HDI is almost exclusively used in the formulation of paints and coatings. This is due to the presence of the aliphatic radical, which provides excellent light and weather resistance in the polyurethane products (3).

1.4 Health Effects

Exposure occurs predominately through inhalation of vapours and aerosols and sometimes through skin contact. Skin exposure from contaminated environmental surfaces can cause respiratory sensitisation, and has been documented in several auto body shops (12). Isocyanate exposure may irritate the skin, mucous membranes, eyes, and respiratory tract, and can be sensitising in susceptible people (8).

The most common adverse health outcome associated with airborne isocyanate exposure is asthma due to sensitisation (11),(13-17). Less common conditions associated with isocyanate exposure are contact dermatitis (both irritant and allergic forms)(18) , urticaria, and hypersensitivity pneumonitis (19),(20).

Occupational asthma has emerged in the past decade as the most important occupational respiratory disease, according to disease surveillance programmes in developed countries (4).

In 1951, Fuchs and Valade found 7 workers with asthma like symptoms; these workers were exposed to TDI. This was the first study to suggest that contact with diisocyanates might lead to the development of hypersensitivity rather than direct toxicity. This observation and a subsequent report from the N-America and Europe showed bronchial respiratory in some workers fulfilled the clinical criteria for hypersensitivity (6).

An estimated 5-20% workers, exposed to isocyanates will develop asthma (14),(21),(22). Studies have shown that monomeric, prepolymeric and polyisocyanate isocyanates species are all capable of producing asthma in exposed workers (14),(23). The dose (concentration of the isocyanate x duration) is a key feature that determines the asthmatic reaction to isocyanates (17). In Europe and North America, approximately 5% of workers in the manufacture of isocyanates develop acute or chronic respiratory symptoms, while 10% display signs of asthma. However in a study performed on 96 African workers manufacturing isocyanate, 50% displayed respiratory symptoms (24).

Meredith *et al* found that in 41% of the cases the occupational asthma symptoms started in the first year after exposure to isocyanate and in 9% of these cases symptoms occurred within three months. There was however no evidence that cases who developed asthma at least one year after first employment had experienced higher concentrations of exposure to isocyanate that the control group. One explanation may be that the aetiology of asthma developed due to short exposure to isocyanate may differ from asthma developed after a longer period of employment (9). A study found that the latency period was shorter for low weight molecular weight chemicals (25).

A minority of workers equally exposed to isocyanates developed asthma after variable symptoms free latency period (4). The symptoms recur on each exposure even to concentrations at which most subjects do not develop respiratory symptoms (26). Workers often manifest upper and lower respiratory symptoms minutes, hours, and days after exposure to isocyanates. Symptoms typically improve away from work (5). The concentration of diisocyanate to bring on asthma or upper respiratory airway symptoms, but might be lower than the accepted TLV (OHSA) of 20 part per billion (ppb). A diisocyanate-sensitised workers, re-exposures to as low as 1 ppb can reproduce asthmatic symptoms (11).

The prevalence of isocyanate does not correlate closely with the cumulative level of exposure at work. Some evidence shown the development of occupational asthma is associated with acute, often accidental exposures to high concentrations of isocyanates (27), (28).

In South Africa, results from the Surveillance of Work-Related and Occupational Respiratory Diseases in South Africa registry (SORDSA) programme have shown that occupational asthma ranks among the most important occupational respiratory disease after mineral dust related diseases, but that it is likely to be under-diagnosed and under-recognised as an occupational disease (23). In a retrospective study reviewing 609 claims submitted to the Ontario Workers' Compensation Board from 1984 to 1988, it was determined that 39% of all claims was due to occupational asthma. 57% of these occupational asthma cases were caused due to isocyanate exposure (29).

1.5 HDI health effects

HDI causes occupational asthma in various occupational and non-occupational settings (30), (31). During a prospective study which was conducted on 20 workers referred for possible occupational asthma caused by spray paint containing both HDI monomers and HDI, the workers underwent inhalation challenges with monomers and prepolymers of HDI separately (6). Ten subjects had positive inhalation challenges, and 4 subjects out of this group had asthmatic reactions after exposure to prepolymers only. Thus the observation suggested that the prepolymers of isocyanates themselves cause occupational asthma (32).

Four general patterns of respiratory response have been described due to HDI exposure; chemical bronchitis, asthma in sensitised workers, cross-shift decreases in Forced Expiratory Volume expired in 1 second (FEV1), and progressive decline in lung function with continued exposure (33).

1.6 Occupational Exposure Standards for Isocyanates

Currently, in South Africa a control exposure limit for isocyanate has been set at 0.02mg/m^3 in the Regulations for Hazardous Chemical Substances. However, exposure limits for polyisocyanates have not been addressed by the Occupational Health and Safety Act No. 85 of 1993 (34).

The USA's Occupational Safety and Health Administration (OHSA) do not have a permissible exposure limit for HDI as either a monomer or a prepolymer.

The National Institute for Occupational Safety and Health (NIOSH), USA, developed a recommended exposure limit (REL) for HDI monomer of 0.035 mg/m^3 or 0.005 parts per million (ppm), but has not established a recommended exposure limit for the HDI prepolymer. NIOSH has also recommended a ceiling value of 0.14mg/m^3 (0.020 ppm) for HDI monomer (35).

The American Conference of Governmental Industrial Hygienists (ACGIH) has also published Threshold Limit Values (TLV®). TLVs® refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse health effects. However, because of wide variation in individual susceptibility, a small percentage of workers may experience discomfort from some substances at concentrations at or below the TLV. A smaller percentage may be affected more seriously by aggravation of a pre-existing condition or by development of an occupational illness. The TLV for HDI monomer is 0.034 mg/m^3 (0.005ppm). The American Conference of Governmental Industrial Hygienists considers TLVs® to be recommendations to be used as guidelines for good practice (36).

An exposure limit for the HDI prepolymer has not been established by OSHA, NIOSH or ACGIH. Oregon, USA, is the only state OSHA programme that has established an exposure limit, of 0.5 mg/m^3 with a ceiling level of 1mg/m^3 (37). In addition, Bayer Chemicals, a leading producer of HDI, published a corporate recommended ceiling level for monomeric HDI of 0.02 ppm (38).

Table 1: Summary of Some Occupational Exposure Standards for Hexamethylene Diisocyanate (HDI)

Organisation	HDI Monomer	HDI Prepolymer	Ceiling HDI Monomer	Ceiling HDI Prepolymers
OHSA*	-	-	-	-
NIOSH**	0.035mg/m^3	-	0.140mg/m^3	-
ACGIH***	0.034mg/m^3	-	-	-
Oregon, USA		0.5mg/m^3	-	1.0mg/m^3
RSA OEL****	0.02mg/m^3	-	0.07 mg/m^3 STEL	-
Bayer chemical	-	0.5mg/m^3	0.02ppm	-

*

Occupational Safety and Health Administration

** National Institute for Occupational Safety and Health, USA

*** American Conference of Governmental Industrial Hygienists, USA

*** South African Occupational Exposure limit, RSA

1.7 Auto Body Repair Industry and Spray Painting

Successive coats of paint are applied manually by using spray guns in the auto body shops. To shorten the drying time between coats or for coatings, the painted vehicle surface is heated with heat lamps, in special infrared ovens, or in heated spray paint booths. After each coat of primer dries, the surface is sanded to remove any irregularities and to improve the adhesion of the next coat. A sealer is then applied and allowed to dry, followed by the final topcoat. When lacquer is used, the finished surface is usually polished after the final coat has dried, whereas enamel dries to a high gloss and is usually not polished.

Workplace exposures to isocyanates are complex and consist of a mixture of monomers, higher molecular weight prepolymers, and other intermediate products. In the auto body repair shops these compounds are present predominantly as an aerosol. Auto body shop spray painters or workers near spraying operations who are exposed to these compounds have the potential to react adversely to their exposure (39).

Many isocyanate exposed workers are end-users of products, including auto body spray painters, who form a large population at risk. Often a two pack system is used. The pack's ingredients are mixed by stirring into the paint resin the required thinner (for ease of application) (39).

The two-pack mixes of polyurethane paints are widely used in the automotive and other industries because of their excellent gloss, hardness, and adhesion and chemical resistance. 1,6 HDI is used in this 2-component spray paint in the motor vehicle repair industry as a substitute for TDI. Workers who spray paint cars apply a clear coat, which contains polyols and hardeners that are prepolymerized forms of diisocyanates. Generally, these polyisocyanates are trimers of HDI. Most HDI prepolymer based car paints contain a complex mixture of HDI monomers, prepolymers, HDI buiret and free HDI (0.5-1%) (40),(41).

During spray painting in auto body repair shops, workers are exposed to all of the paint components, which are atomized. In addition to polyisocyanates, the aerosols constituents include organic solvents, metals such as lead and chromium (42).

If isocyanate-containing paint is applied by brush, roller or dipping, in a cool, well-ventilated area, there is generally no more hazard than with ordinary paints, as these methods usually do not produce a dangerous concentration of isocyanate vapour. Mixing the two-pack paints is generally a safe operation provided it is done in a well-ventilated place and care is taken in removing the lids and mixing. After curing, polyurethane paints do not release isocyanates and are not harmful under normal conditions of use (43). However, the use of compressed air spray guns will generate paint aerosols (4).

In fieldwork performed by the Health and Safety Executive (HSE, UK) it was shown that the time for isocyanate to clear after spraying operations had stopped was between 5-30 minutes. During the baking process, some isocyanate monomers are driven off (41). Considerable amounts of aerosols are generated during spray painting operations (6).

During a study in Sweden, it was found that monomer exposures were common during thermal decomposition of polyurethane coating (44). Less often exposures occur during thermal decomposition of polyurethane, for example welding of surfaces coated with polyurethane paints (45).

Few studies on isocyanate-induced asthma and sensitisation have been done on spray painters, although this occupational category has one of the highest occupational asthma incidence rates in the UK, according to surveillance data. An estimated average of 1464 new cases per million employed spray painters occurs each year in the UK (46).

In a cross-sectional South African study of Durban based spray painters, in auto body repair shops, exposed to HDI, 25% of the 40 subjects had clinically significant decreases in cross-shift FEV1. Ten percent had shortness of breath with wheezing, 32% had hand dermatitis and 55% had eye irritation (33).

Spray painters using several types of isocyanates in a large aeroplane assembly plant had a prevalence of occupational asthma of 12% (14). Sequin et al., found that 11.8% of spray painters spraying aeroplanes had isocyanate-induced asthma (14).

Based on self-reported symptoms of asthma assessed by questionnaire, 20% of 102 employees in auto body shops in the New Haven area fulfilled the definition of occupational asthma, although none had had a previous diagnosis of asthma (47).

The main risk factors for HDI induced asthma appear to be dose and duration of exposure. Frequent peak exposures of HDI above $0.2 mg/m^3$ were recorded in Swedish spray painters. The number of peak exposures correlated with a progressive decline in lung function, suggesting that it was the over-exposures which contributed to the adverse effects of HDI and not the mean exposures (31).

Atopy does not seem to be a predisposing risk factor, and the role of smoking is contentious. Regular use of air-supplied respirators was protective for occupational asthma in workers who painted full- or part-time (47). Both HDI monomers and prepolymers can induce occupational asthma. HDI causes sensitisation and asthma, but the mechanism is poorly defined (48).

1.8 Control Technology

During the spray painting process, a wide range of control methods and technologies have been developed to control occupational exposures during spray painting. Engineering controls are the most effective controls, particularly high volume low pressure spray guns and downdraft spray paint booths. New paint formulations have been developed to meet regulatory requirements in reducing solvent emissions. Other controls such as personal protective equipment including respiratory protection are also used to reduce employee exposures (49).

1.8.1 Paint Spray Equipment

Spray guns used with compressed air spray the paint mist onto the vehicle surface. The four different types of spray guns are:

- Conventional Air Spray Guns
- High Volume Low Pressure Spray Guns
- Low Volume Low Pressure Spray Guns
- Electrostatic Spray Guns and Powder Coating Systems

The mechanism used in atomization and delivery of the paint will affects the efficiency of the painting process. Transfer efficiency is the ratio of the amount of coating solids deposited onto the surface of the part to the total amount of coating solids that exit the spray gun nozzle.

The waste paint directed outside the main spray pattern and not deposited onto the vehicle surface is referred to as “overspray”. In addition, the “bounce back” is when paint pulled away from the car surface by compressed air currents deflected by the car surface and the spray painter. The bounce back can account for 20% of the 60% of the paint which does not reach the car surface when conventional spray guns are used (49).

1.8.2 Conventional Air Spray Guns

Conventional air spray guns have been the standard spray equipment used to apply coatings in the automotive refinishing industry. Low volume (0.05 to 0.3 cubic meters per meter (cfm)) of air is pressurized and forced through a nozzle; the paint is atomized in the air at the nozzle throat. Conventional spray guns are usually operated with air pressures of 30 to 90 pounds per square inch (psi) at a fluid pressure of 10 to 20 psi.

Air is supplied by an air compressor during spraying operations. The advantage of conventional spray guns is their capability to achieve very fine atomization. The disadvantages of this equipment are the development of excessive spray mist and over spray fog. Conventional spray guns equipment has a transfer efficiency in the range of 20% to 40%, and therefore most of the paint becomes an over spray that may contaminate the air in the worker’s breathing zone (50).

1.8.3 High Volume Low Pressure Spray Guns (HVLP)

These spray guns have a high volume (30 cfm to 200 cfm) and a low pressure (pressure at the gun of between 0.1 and 10.0 psi) and a fluid pressure of 50.0 psi. This lower velocity of the atomizing air stream results in a more controlled spray pattern, less bounce back, and enhanced transfer efficiency. HVLP guns are estimated to have a transfer efficiency of at least 65% (50). Some disadvantages to this equipment include:

- Higher initial cost

- Inability to atomize coatings as finely as can be achieved with conventional spray guns
- slower application speed
- the need for operator training

HVLP technology has become commonplace in auto body shops because of reduced paint usage and the acceptable finish quality provided by the guns on the market.

Testing conducted by the National Institute for Occupational Safety and Health (NIOSH) in an equipment manufacturer's test facility, demonstrated that particulate over spray concentration was reduced by a factor of 2, and that there was a 30% increase in the ratio of paint film thickness to mass of paint applied when a HVLP spray gun was used. These results indicate that using an HVLP spray painting gun can reduce paint usage and over spray production, resulting in noticeably lower worker exposures (50).

1.8.4 Low Volume Low Pressure Spray Guns (LVLP)

LVLP spray guns, like HVLP guns atomize coatings at lower pressure (9.5 to 10 psi) and at a lower velocity than conventional spray guns but use approximately 45 to 60 percent smaller volume of air than HVLP guns. Energy costs for air compression are reported to be less than with HVLP guns (49).

1.8.5 Electrostatic Spray Guns and Powder Coating Systems

Electrostatic spraying systems, which have deposition efficiencies of between 60 and 90 percent, are widely used in automotive assembly plants. Air-powered, electrostatic spray guns function in essentially the same way as electrostatic spray guns. This system is not practical for refinishing systems, for the following reasons:

- prohibitively high cost of electrostatic spray guns,
- large amount of coating contained in the hose connecting electrostatic spray gun to pot, which must be removed when changing colors,
- high curing temperatures required for powder systems (i.e., resulting in damage to other vehicle components), and
- grounding methods required for electrostatic systems in an OEM environment cannot be duplicated for automobile refinishing (49).

1.8.6 Spray painting booths

Three types of spray-painting booths are generally used in the auto body repair industry. These are downdraft booths, semi-down draft booths and cross draft booths. In the downdraft spray painting booth, air enters the booth through a filter extending the full length and width of the ceiling. The air passes down over and around the vehicle and is exhausted from the booth through an opening in the floor that is the full length and width of an average vehicle. In a cross draft spray painting booth, air enters the booth through a filter extending half of the length of the ceiling. The air passes down and across the vehicle and is exhausted from the booth through an opening at the back of the booth that extends the full length and width of the back panel of the booth. For a cross draft spray booth, air enters the booth through a filter extending the length and width of the front panel of the booth. The air passes across the vehicle and is exhausted from the booth through an opening in back of the booth that extends the full length and width of the back panel of the booth. The concept and operation of these booths are illustrated in Figure 5.

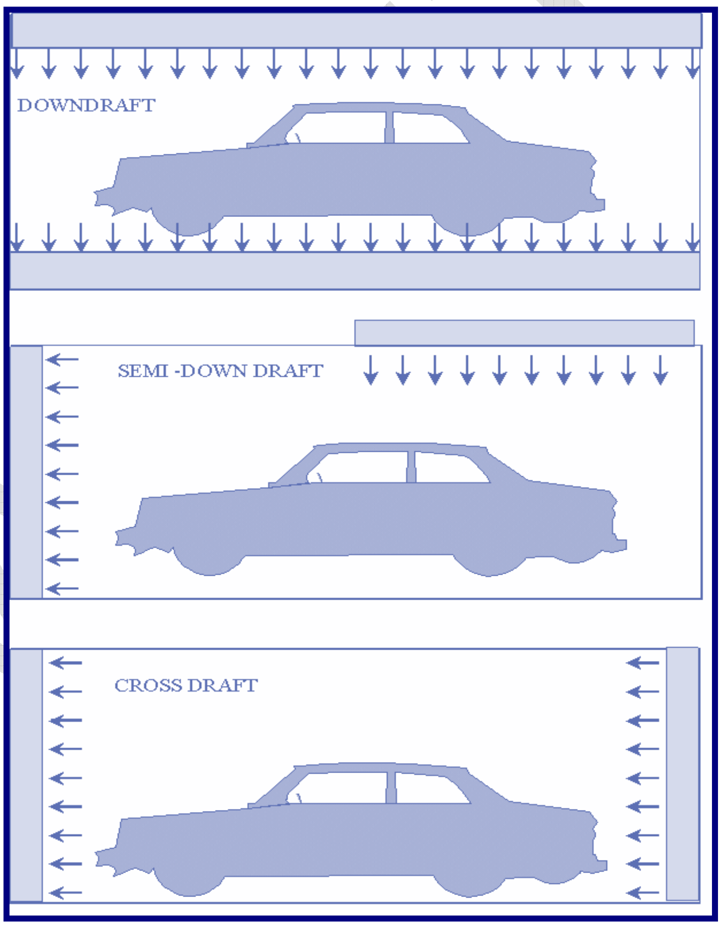

Figure 5: Types of Spray Booths

(Source: Heitbrink WA. NIOSH NTIS Pub. 45226-1998)(51)

Previously reported measurements found that exposures to paint overspray in downdraft booths are lower than in the other two types of booths. In a downdraft booth the paint overspray was dispersed without flowing back into the worker's breathing zone. In a cross-draft booth and in semi-down draft booths, the paint overspray is dispersed into the incoming fresh air, causing the workers exposure to be elevated. As a result, geometric mean particulate overspray concentrations were 1.9 and 2.7 mg/m^3 at two different downdraft booths versus 23 mg/m^3 at a cross draft booth (52).

HVLP spray painting guns are more efficient than conventional spray painting guns. This can cause particulate overspray concentrations to be reduced by a factor of two and spray painting gun efficiency appeared to increase by 30%. As spray painting gun efficiency increases, the painter uses less paint and there is a more than proportionate decrease in worker exposure to particulate overspray (50).

1.9 Motivation for this Study

As previously stated, isocyanates are the most frequently reported causative agent for occupational asthma cases submitted to SORDSA from October 1996 to December 1999 (16.7% of the cases) (53). Studies suggest that asthma caused by isocyanates exposure may be severe and resistant to treatment even after exposure ceases (13), (21), (54). For these reasons, it is important to identify where potentially hazardous exposure to isocyanates is occurring, and to prevent sensitisation and asthma development where possible.

Auto body repair shops, typically small, medium and micro enterprises (SMMEs), are targeted in this study due to the anticipated lack of medical surveillance or occupational hygiene programmes (55). Studies show that isocyanate exposed workers in small factories have a significantly higher prevalence of respiratory symptoms than a control group (56).

The study was initiated to quantify the exposure to HDI in auto body establishments in Gauteng. HDI is a potent respiratory sensitiser and a chemical component in spray paint. The aims of this study were to identify and quantify exposure to HDI and to evaluate control measures, in randomly selected auto body repair shops in Gauteng. The findings of the study would be used to propose recommendations for reducing exposure.

1.10 Research Objectives

1) To conduct exposure assessments to identify and quantify exposure to HDI in selected South African auto body repair shops belonging to Highveld SAMBRA
2) To describe the measures used to control HDI exposure in these auto body repair shops.

CHAPTER 2

2 MATERIALS AND METHODS

2.1 The study setting: Auto body repair shop

Auto body repair work includes frame straightening, panel repair/replacement, body filling and final painting and detailing. Repair is conducted typically in an open shop with body work performed, detail, cleaning and painting in the same building.

Most top coat spraying is conducted in a paint spray booth. The downdraft spray booth has a separate exhaust system. The booth also has the capacity to be heated to accelerate paint drying.

Adjacent to the spray booth is the paint mixing room where the paint components are stored and mixed. The paint mixing room is usually ventilated with a separate supply duct.

When painting, multiple thin layers of the different paints are applied. When base metal is exposed, these areas are first covered with a primer. Once the vehicle is ready for final painting, several base coats are applied, the paint is allowed to sit a short while (10-20 minutes), then the colour paint is applied, again in several thin coats. Lastly, the clear top coat is sprayed on until a uniform gloss is achieved. The vehicle is then allowed to sit overnight or in a heated booth for 1-2 hours to allow the paint to dry.

New, High Volume, Low Pressure (HVLP) spray guns are often used to reduce the amount of paint over-spray. While most painting is usually done in the spray booth, sometimes, due to the number of cars being painted and the limitations on drying times, many of the various primer, base, and colour coats are applied outside the spray booth. Most of the clear coats are applied in the spray booth to insure a dust-free finish coat.

2.2 Selecting auto body repair shops for study

From a list of about 200 spray-painting establishments registered with the South African Motor Body Repairers' Association (SAMBRA), 10 establishments were sampled by means of a table of random numbers. All the spray painters and employees working directly with the paint had HDI exposure levels measured for the duration of the spray painting operation. This included the preparation and clean-up procedures.

Employees working under the same roof as the spray paint booth (for example; panel beaters, sanders, mechanics etc.), up to a total of 12 employees, were also included in the study.

2.3 Occupational hygiene evaluation

2.3.1 Exposure measurements

An evaluation of the workplace airborne HDI concentration was conducted by using an indirect air measurement for HDI.

The standard recommended method according to NIOSH method 5525 was used to measure HDI concentrations. These samples were collected by drawing a known volume of air though a quartz fibre filter with a diameter of 37mm. The filters were impregnated with 1.1μg of 1-(9-anthacenylmethyl)-piperazine (MAP) and placed into a three-piece cassette. The samples were wrapped end-to-end with a seal band.

Calibration was performed with a primary calibrator (Gilibrator) on each sampling pump with a representative sampler in line before the survey. The flow rate was set at 2L/min. The filter cassette was attached to a sampling pump and the inlet cover of the cassette removed. Personal breathing zone samples of the employee were taken. Immediately after sampling, the filter was placed in a wide-mouth jar with a PTFE-lined screw cap containing 5mL of 1 x 10^{-4} M MAP in MeCN. Samples were stored in a refrigerator and the samples were ship with ice packs.

Bulk sample of at least 3mL was obtained in each workshop. These bulk samples are necessary for oligomer analysis. This was shipped and stored in a separate container from the air samples.

Three-field control filters per sample set and three field reagent blanks were obtained. Two field controls and 2 field reagent blanks for every 10 samples were analysed. The field controls and field reagent blanks were used to identify non-isocyanine peaks. Field controls and reagent control samplers were handled exactly the same as samples except in filter controls no air was drawn through them and no filters were placed into the reagent controls.

After sampling filters were taken out of the filter cassette and place in the jar with 5.0mL of extracting solution instead and recap and swirl to wet all surfaces of the filter. All samples filter cassettes were pre-labelled with an indelible marker on a label. Samples were collected from the 10 workshop over 10 days of sampling.

2.3.2 Control measures

During a walkthrough inspection of each repair shop, a checklist was completed to document the type of isocyanate control measures in use and the nature of personal protective equipment (PPE) provided to workers (See Appendix 1).

2.4 Laboratory analysis of exposure measurements

2.4.1 Liquid chromatography measurements for isocyanate

HDI was measured by the laboratory of the National Institute of Occupational Health (NIOH). The NIOSH 5525 method for Isocyanate analysis was used to measures both monomeric isomers and polyisocyanates. This method uses both UV and Fluorescence High Performance Liquid Chromatography (HPLC) detectors. Filters were prepared in the laboratory by impregnating the filter with 1-(9-anthracenylmethyl) piperazine (MAP). 1-(9-anthracenylmethyl) piperazine (MAP) gives better sensitivity and selectivity (0.4 ppb). This method uses the pH gradient, thus this helps minimise interference.

2.4.2 Sample preparation

Upon receiving the filter samples in the reagent, acetylate with 5µl of acetic anhydride and these reacted overnight in the refrigerator, or at least for 2 hours at room temperature before proceeding.

Attach the outlet of a 0.45-µm PTFE Luer-lock syringe filter to the solid phase extraction (SPE) vacuum manifold with disposable liner. Place an empty polypropylene syringe barrel in the inlet of the syringe filter. Add the entire extraction solution into the syringe barrel.

Force the sample through the PTFE filter using either positive or negative pressure and collect in a pre-weighted 20ml vial glass vial with a PTFE-lined cap.

The volume was reduced by evaporation to exactly 1,0ml and the exact volume determined by using the sample weight and the density of acetonitrite (0.786g/ml).

2.5 Calibration and Quality Control

Calibration was performed daily with six working standards in the range of interest and interspaced standards among samples. Recommended standard concentration in terms of moles Isocyanate group per litre (N) are $1x10^{-5}$ N, $3x10^{-6}$ N, $1x10^{-6}$ N, $3x10^{-7}$ N, $1x10^{-7}$ N and $3x\ 10^{-8}$ N.

Preparation calibration curves (response vs. normality of standard solution) for both UV and florescence detectors were performed. Two field controls and 2 field reagent blanks for every 10 samples were analysed. The field controls and field reagent blanks were used to identify non-isocyanine peaks. Bulk products used at the worksite that are representative of the controls being collected in the sample were analysed.

Three quality control blind spikes and three analyst spikes were analysed to ensure the calibration graph was in control.

2.6 Liquid Chromatography method used

2.6.1 Equipment

A High Performance Liquid Chromatography System (HPLC) consisting of Spectra Systems SCM 1000 liquid chromatograph equipment with AS 3000 auto-sampler, (ultraviolet) UV 6000 diode array and Fluorescence (FL) detectors with ChromQuest Software (all premier Technologies/SMM Instruments) was used.

2.6.2 HPLC conditions

(1) Column : 150 X 4.6 mm Inertsil C_8, 5 μm, titanium frits in a constant temperature column oven set at 30 °C.

(57) Mobile phase : 65% acetonitrile / 35% triethylammonium phosphate /formate, 10mM in both, pH 6.0 to 1.6, 1.5 mL/ml.

Post column addition of 65% acetonitrile / 35% 4.4 N phosphoric acid, 0.7 mL/ml.

(7) Gradient program : 0 – 4 min 100% mobile phase A (65% acetonitrile /35%, pH 6 buffer)

4 – 17 min Linear gradient form 100% phase A to 100% mobile phase B (65% acetonitrile /35%, pH 1.6 buffer)

17 – 30 min Hold 100% phase B

30 – 36 min Re-equilibrate at 100% mobile phase A

(3) Sample injection : 30μL

(58) Detector **:** UV (253 nm) followed by fluorescence (ex : 368 nm, em : 409nm, xenon lamp or ex : 254 nm, em: 409 nm, deuterium lamp).

2.7 Ethical Considerations

Management or owners of the sampled workplaces were fully informed of the aims of the study and the procedures that were to be carried out. The participation of the workplaces was voluntary. Once verbal consent from the workplaces was obtained, voluntary informed written consent from subjects was obtained. Once again the research objectives and procedures were explained in the subject‘s preferred language. Confidentiality and anonymity was guaranteed. Ethical approval was obtained from the Wits Human Ethics Committee (M02-04-28) and the NIOH Research Committee (see appendix 4 – Ethics clearance certificate).

2.8 Data Handling

Data were analysed with Microsoft Excel and STATA. The HDI concentrations are presented in tables and figures using the median, range and interquartile range.

The sample mean is usually calculated for estimating the central tendency of normal distributed data, and the sample median for skewed data (typically with the range and interquartile range)

Therefore, since exposure data are usually skewed, with some unusually high values, the median is likely to be a better descriptor of central tendency than the mean. This was true for the HDI measurements in this report, so the median was used as a measure of central tendency and the dispersion of the data is shown by the range and interquartile range.

In presenting Box Plots, outliers were defined as values above or below the 90th and 10th percentile respectively.

2.9 Response rate

All 10 shops invited to participate in the study agreed (i.e. 100% response rate). All workers who were invited to wear personal samplers agreed to do so (i.e. 100% response rate).

CHAPTER 3

3 RESULTS

The aims of this study were to identify and quantify exposure to HDI, and second, to describe the control measures currently used in these auto body repair shops.

In this chapter the HDI concentrations in 10 auto body repair shops are presented for HDI monomer, prepolymer and total HDI. This is followed by exposure classified by job/task and then a description of the control measures in place.

Ten establishments were studied, and a total of 113 personal measurements were taken in 10 auto body repair workshops for HDI monomer. One sample had to be discarded due to a faulty pump, thus 112 samples were available for presentation.

3.1 HDI Monomer Concentrations

Table 2: Personal Airborne HDI Monomer Concentrations in 10 Auto body Repair Shops

HDI Monomer concentration mg/m^3					
Workshop	**N**	**median**	**25% Percentile**	**75% Percentile**	**IQR (75%-25%)**
1	10	0.002	0.0012	0.0026	0.0014
2	12	0.002	0.0010	0.0025	0.0015
3	12	0.034	0.0305	0.0625	0.0320
4	10	0.039	0.0260	0.0465	0.0205
5	12	0.088	0.0800	0.0995	0.0195
6	12	0.053	0.0471	0.0622	0.0152
7	11	0.053	0.0420	0.0755	0.0335
8	12	0.074	0.0410	0.1885	0.1475
9	10	0.011	0.0100	0.0140	0.0040
10	11	0.112	0.1020	0.1760	0.0740
Total	112	0.043	0.011	0.087	0.076

*IQR = Interquartile range (75% percentile – 25% percentile=IQR)

During the study a total of 112 personal samples were taken in 10 auto body repair workshops for HDI monomer exposure. The median in these 10 workshops ranged from 0.002 to 0.112 mg/m^3. The Occupational Exposure

Limit in the Regulations for Hazardous Chemical Substances, RSA, has a set limit of 0.02mg/m^3 for HDI monomers.

In, seven of the 10 workshops, median HDI concentrations exceeded the HDI OEL of 0.02mg/m^3 and concentrations ranged from 0.002 - 0.112mg/m^3. These HDI monomer concentrations exceeded the OEL by 1.67 – 5.80 times. In seven workshops most of the samples exceeded the OEL of 0.02mg/m^3.

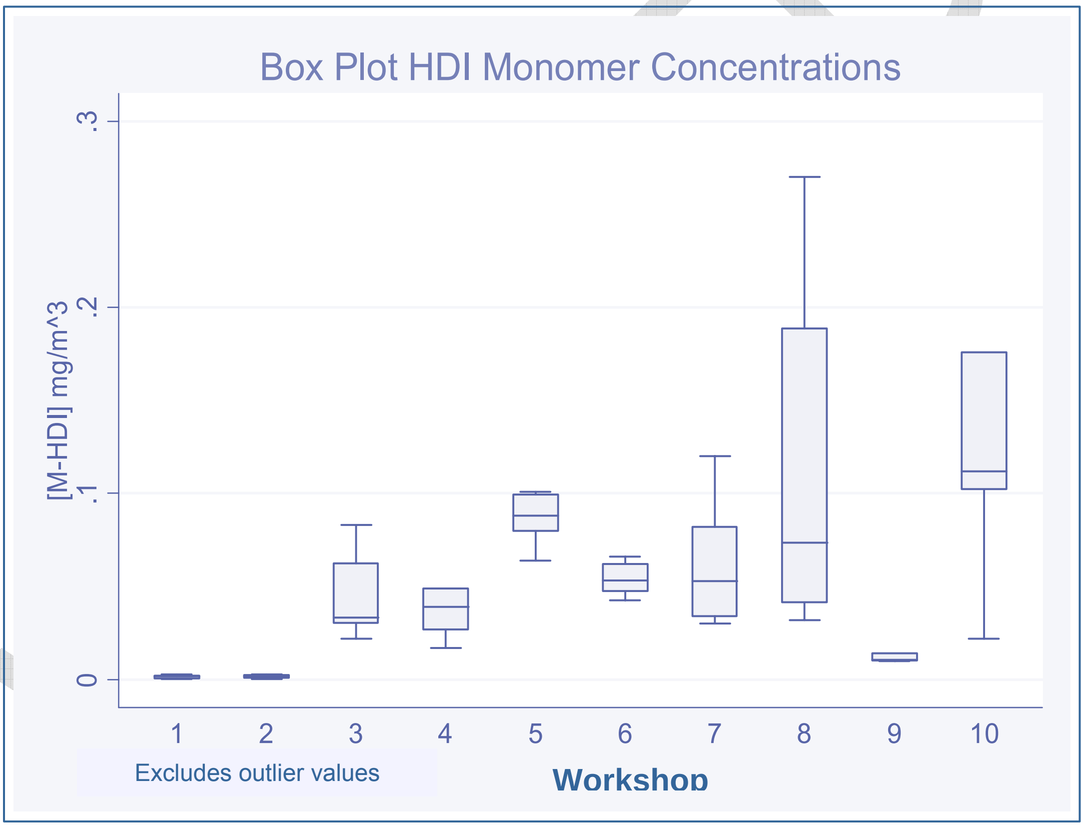

Figure 6: Box Plot of Personal HDI Monomer Concentrations in Each Workshop

Figure 6 shows box plots of the HDI monomer measurements from each workshop. The bottom and top horizontal lines of each box denote the inter-quartile range (i.e., the 25th and 75th percentiles) and the solid horizontal line across the centre indicates the sample median. The whiskers on the boxes in Figure 6 extend to the 10th and 90th percentiles of the distributions.

Workshop 8 has the greatest spread of data, thus the largest variability of HDI monomer concentrations. Workshop 10 had two outlier samples with a HDI monomer concentration of 0.789 and 1.5 mg/m^3 (not shown in fig 6). Most of the workshops had a skewed distribution of data.

3.2 HDI Prepolymer Concentrations

Table 3: Personal Airborne HDI Prepolymer Concentrations in 10 Auto Body Repair Shops

HDI Prepolymer concentration mg/m^3					
Workshop	N	median	25% Percentile	75% Percentile	IQR (75%-25%)
1	10	0.015	0.006	0.019	0.013
2	12	0.018	0.010	0.024	0.013
3	12	0.077	0.066	0.140	0.074
4	10	0.156	0.105	0.252	0.147
5	12	0.278	0.214	0.392	0.179
6	12	0.275	0.239	0.317	0.078
7	11	0.205	0.104	0.242	0.138
8	12	0.172	0.106	0.251	0.145
9	10	0.171	0.139	0.195	0.056
10	11	0.274	0.222	0.408	0.186
Total	112	0.171	0.066	0.255	0.189

During the study a total of 112 personal samples were taken in 10 auto body repair workshops for HDI prepolymer exposure. The median in these 10 workshops ranged from 0.015 to 0.278 mg/m^3. Miles Laboratories recommends in their MSDS for Glasurit HDI-based paints that a limit of 0.5mg/m^3 be followed for prepolymeric isocyanates.

All the workshops' median values were below the HDI exposure limit of 0.5mg/m^3

The maximum measured HDI concentrations ranged from 0.024 to 2.004 mg/m^3. Thus from the highest concentrations measured in each workshop, 2 out of 10 of these concentrations exceeded the recommended limit of 0.5mg/m^3.

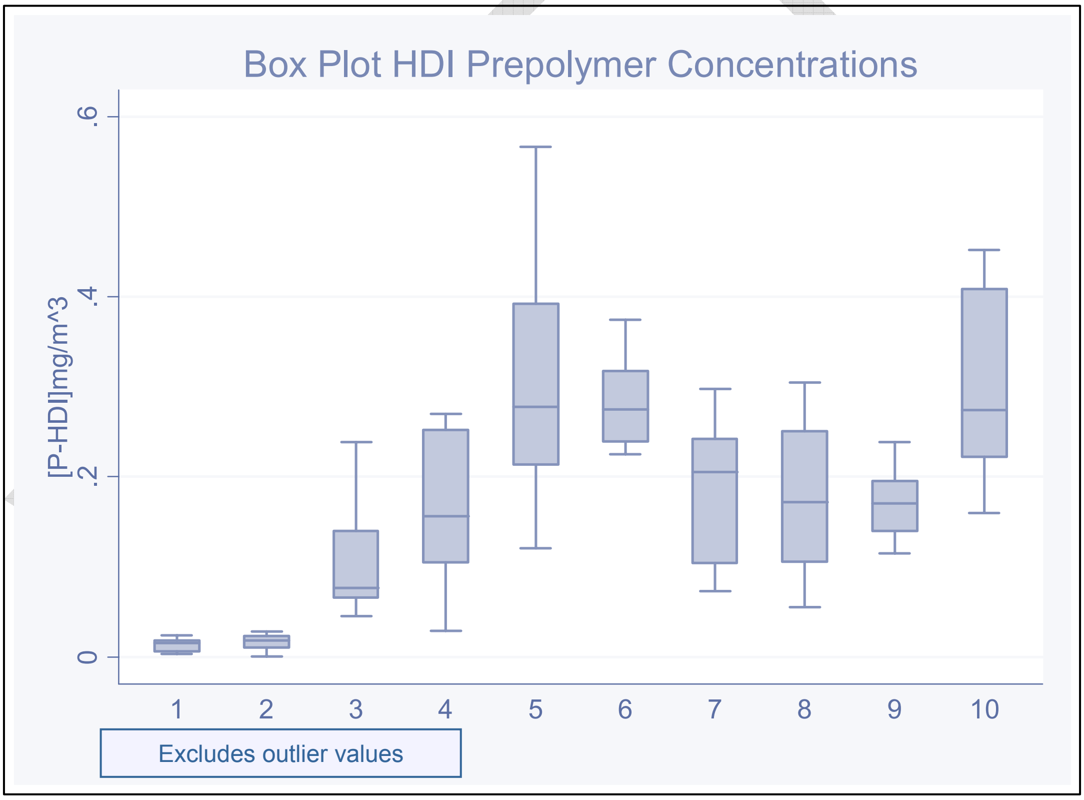

Figure 7: Box Plot of HDI Prepolymer Concentrations in Each Workshop

Figure 7 shows box plots of the HDI Monomer measurements from each workshop. The bottom and top horizontal lines of each box denote the 25th and

75th percentiles respectively and the solid horizontal line across the centre indicates the sample median. The whiskers on the boxes in Figure 7 extend to the 10th and 90th percentiles of the distributions.

Workshop 5 has the greatest spread of data, thus the largest variability of HDI monomer concentrations. Workshop 10 had one outlier: a sample with a HDI polymer concentration of 2.004 mg/m^3. Most of the workshops had a skewed distribution of data.

3.3 Total HDI Concentrations

Table 4: Airborne HDI Total Concentrations Exposure in 10 Auto Body Repair Shops

HDI Total concentration mg/m^3					
Workshop	N	median	25% Percentile	75% Percentile	IQR (75%-25%)
1	10	0.017	0.007	0.021	0.014
2	12	0.020	0.011	0.026	0.015
3	12	0.109	0.097	0.202	0.106
4	10	0.194	0.132	0.319	0.187
5	12	0.365	0.255	0.491	0.236
6	12	0.331	0.285	0.382	0.097
7	11	0.258	0.138	0.324	0.186
8	12	0.245	0.148	0.440	0.293
9	10	0.182	0.149	0.209	0.060
10	11	0.385	0.322	0.575	0.253
Total	112	0.212	0.093	0.356	0.264

During the study a total of 112 samples were taken in 10 Auto body repair workshops for HDI Total exposure. The median in these 10 workshops ranged from 0.017 to 0.385 mg/m^3.

The maximum measured HDI concentrations ranged from 0.027 to 2.7 mg/m^3.

Table 5: Percentage of HDI Concentrations Exceeding Exposure Limits

	% HDI measurements > reference concentrations	
	HDI monomers (RSA OEL= 0.02mg/m^3)	**HDI prepolymers (guideline limit = 0.5mg/m^3)**
Samples (n=112)	**81.5**	**3.4**
Workshops (n=10)	**90**	**30**

81.5 % of all HDI monomer measurements exceeded the South African OEL of 0.02mg.m^3, but only 3.4% of the prepolymer HDI samples were higher than a guideline limit. Ninety percent of establishments had at least one HDI airborne monomer concentration above the OEL and 30% for prepolymer HDI concentrations.

3.4 Occupational Categories

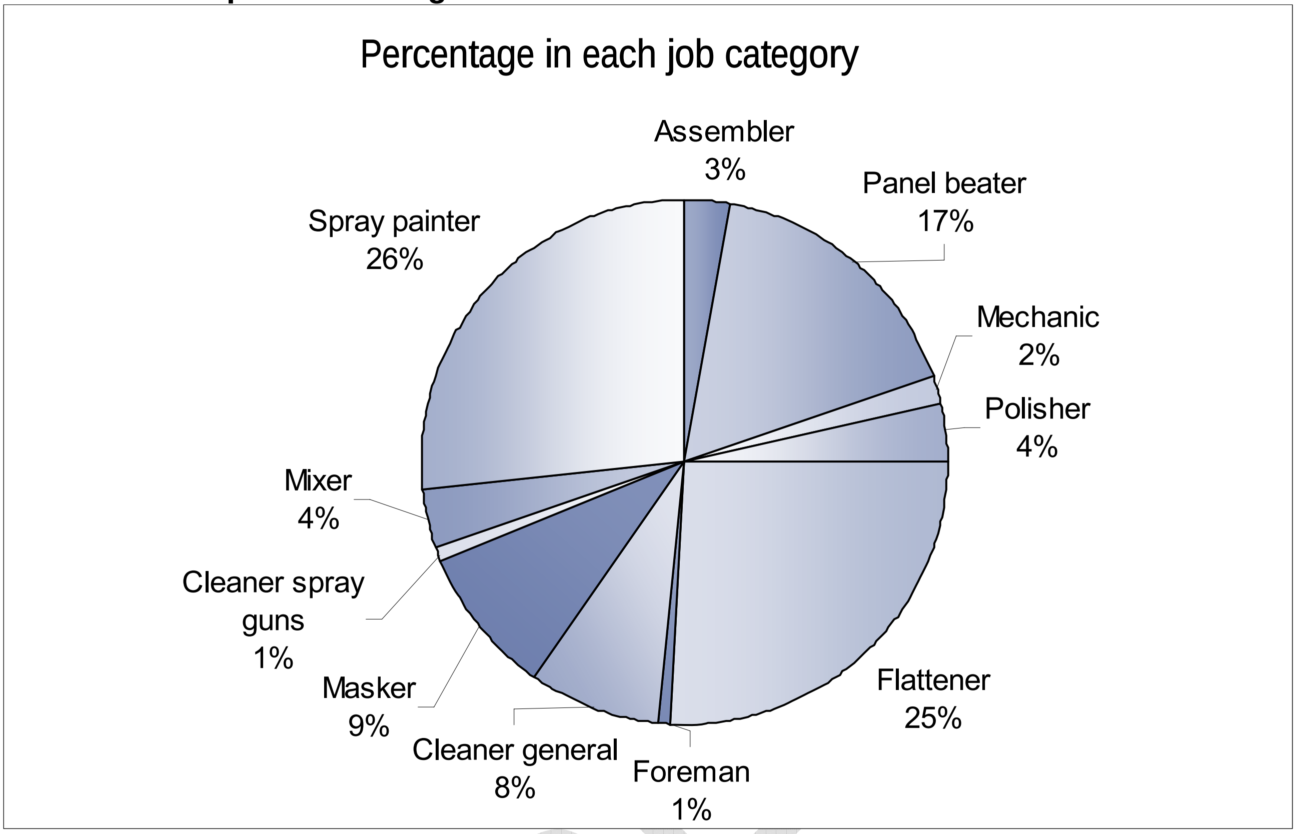

Figure 8: The Percentages of Workers in Each Occupational Category

All the 112 workers' occupations were placed into one of 11 occupation categories. These categories ranged from those directly in contact with the HDI-based paint to workers in the vicinity of spray painting operations. The spray painters consisted of 26% and flatteners (dent body fillers) 25% of the total study sample. The third biggest occupational group was panel beaters, which included all panel beaters and assistant panel beaters

Table 6: Airborne Monomeric HDI Concentrations by Occupational Categories

Occupation	N	HDI median concentration mg/m^3		
		Monomer	Prepolymer	Total
Assembler	3	0.001	0.006	0.007
Cleaner general	9	0.055	0.149	0.226
Cleaner spray guns	1	0.27	0.298	0.567
Flattener	29	0.07	0.194	0.272
Foreman	1	0.069	0.23	0.299
Mechanic	2	0.031	0.074	0.105
Mixer	4	0.095	0.27	0.365
Masker	10	0.046	0.22	0.266
Panel beater	19	0.066	0.204	0.3
Polisher	4	0.016	0.214	0.23
Spray painter	30	0.058	0.223	0.289
Total	**112**	**0.071**	**0.189**	**0.266**

81% (9/11) of these occupational categories' median values exceeded the HDI monomeric OEL of $0.02 mg/m^3$ and these exceeding concentrations ranges from 0.031 to 0.27 mg/m^3.

The occupational category with the highest number of workers exposed was the flatteners (dent body fillers). There were 25 workers out of a group of 29 who were over exposed. The next most exposed group was the spray painters, with 25 out of 30 workers over exposed to monomeric HDI in the workshops. During the study, 86.6% (97 out of 112) of all workers were over exposed to HDI monomers during spray painting operations.

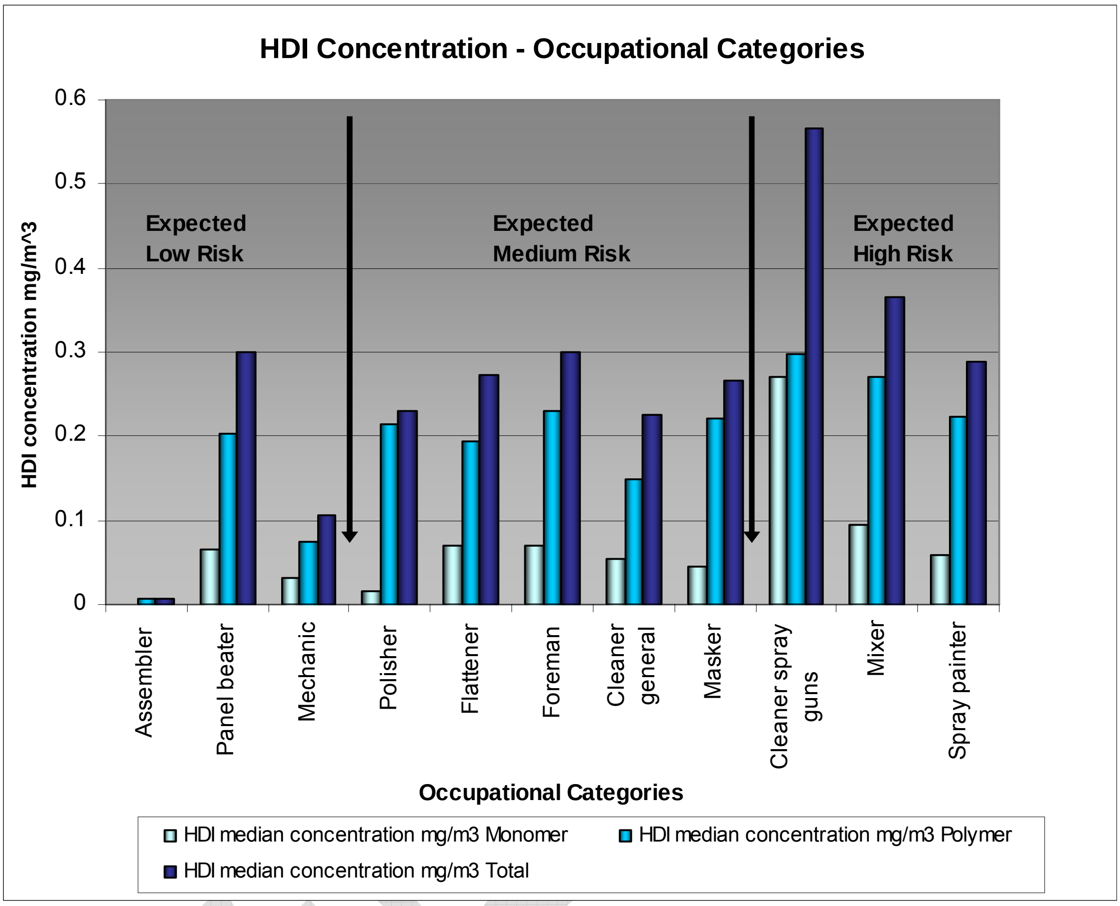

Figure 9: The HDI Concentrations in the Different Job Categories.

The 112 workers were divided into 11 occupational categories. These categories were divided into 3 exposure risk groups based on likelihood of direct contact with HDI. **Low:** Employees who are not in direct contact with paint containing HDI. However they might be exposed to some fugitive paint exposure. **Medium**: Everybody not categorised in low or high groups. **High:** Employees who are directly in contact/exposed to paint containing HDI.

As can be seen from Figure 9, there was not a clear demarcation in exposure between these three groups (expected low, expected medium, expected high).

3.5 Description of the control measures

Table 7: The Usage of Personal Protective Equipment (PPE), Spraying Equipment And Paint in the Workshops

				PPE				
Workshop	**Paint name**	**S/Booth***	**S/gun****	**Eye**	**Respirator**	**Hearing**	**Coverall**	**Gloves**
1	Metacryl	D/draft***	HVLP	0	0	0	0	0
2	Standox	D/draft	HVLP	0	0	0	1	0
3	Spies Hecker	D/draft	HVLP	0	1	0	1	0
4	PPG Delter	D/draft	HVLP	0	1	0	1	0
5	Glasurit	D/draft	HVLP	0	1	0	1	0
6	Spies Hecker	D/draft	HVLP	1	1	0	1	1
7	Spies Hecker	D/draft	HVLP	0	1	0	0	0
8	Standox	D/draft	HVLP	0	1	0	1	0
9	Spies Hecker	D/draft	HVLP	0	0	0	0	0
10	Spies Hecker	D/draft	HVLP	0	1	0	1	0
TOTAL % PPE				**10**	**70**	**0**	**70**	**10**

***S/Booth – Spray Booth**
****S/Gun – Spray Gun**
*****D/draft – Downdraft**
1 = usage of PPE
0 = no PPE used

To obtain information on PPE usage, a checklist was completed for each workshop. Only 10 % of the workplaces used eye and hand protection during the spray painting process. 70% of the workshops supplied respirators and coveralls. No hearing protection was supplied in the 10 workshops.

The respirators ranged from particulate paper masks to air-line supplied respirators. The hand protection used was latex gloves in the one auto body repair shop. All the coveralls were disposable chemical suits. All the workshops used a downdraft spray booth and a HVLP spray gun.

CHAPTER 4

4 DISCUSSION

The aim of this study was to quantify HDI exposure and describe the control measures in small automotive repair shops in Gauteng. The project had some limitations.

The first was that for economic and methodical reasons, the sample time for HDI measurement was about four hours, and not eight. However, the sample period was taken during at least one full spray painting activity.

The sample size is 112 workers. However, the number of workers in the each job category is small. This small number might lead to non-representative data for some job categories.

Due to inherent variability in the process from day-to-day and the differences in work practises, one must view the HDI exposure results with caution. Newly developed analytical method was used to analyse HDI monomers and prepolymers, but the measurements were done by an experienced laboratory will good quality control procedures.

The existing airborne Occupational Exposure Limit (OEL) in South Africa for aliphatic diisocyanates is 0.02mg/m^3; however, there is no existing OEL for prepolymers. The Bayer Corporation has established a Manufacturer's

Guideline Limit, of 0.5mg/m^3 for prepolymer HDI (59). This limit was also later adopted by the Oregon State OSHA as an 8-hour Permissible exposure limit.

4.2 Quantification of exposure to HDI

4.2.1 HDI Monomer

Eight-one percent of the samples exceeded the OEL for monomeric HDI with a range between 0.002 to 0.112 mg/m^3 as illustrated in Table 2 and 7. Monomeric HDI vaporizes quite easily, leading to inhalation and dermal exposures of workers who come in contact with the air containing the HDI vapors. Monomeric HDI, like other diisocyanates, can produce both a local irritation to the nasal and respiratory tract and an asthma-like condition in sensitized people at air vapor concentrations range, from approximately 0.0014to 0.14mg/m^3 (60).

Ambient air concentrations of monomeric HDI in 3 automobile spray paint shops and one trade school for spray painters in Finland were found to range from 0.006 to 0.12 mg/m^3. The monomeric concentrations as shown in Table 2, (0.002 to 0.116 mg/m^3) fall into this range found in Finland (23).

Hulse (1984) conducted a combined workplace and laboratory study to evaluate the exposure potential of HDI in vapour and aerosol states from HDI polyurethane spray paint aerosols. Sampling in 2 workplaces selected to represent worst-case exposures typical of spray painting in light aircraft maintenance facilities resulted in total personal and area HDI concentrations ranging from 0.013 to 0.043 mg/m^3 and 0.039-0.063 mg/m^3, respectively (61).

In a study of U.S. workers involved in the mixing or application of HDI-BT spray paints, mean ambient air concentrations of HDI ranged from <0.00008 to 0.038 mg/m^3 (62).

Substantially higher ambient air concentrations of HDI were found at 4 different spray-painting operations at a U.S. Air Force base in Biloxi, Mississippi, ranging from 0.012 to 0.059 mg/m^3; HDI-BT levels were not monitored (63).

During this study higher exposure HDI concentrations were measured (0.14 mg/m^3). This could be due to work practices, such as spray painting outside the spray booths.

In South Africa, Randolph et al, 1997 found TDI concentration levels ranging from below detection to 23.54mg/m^3 (33).

4.2.2 HDI Prepolymer

HDI buiret and trimer (both prepolymer forms) can induce respiratory and immunological reactions. However, these prepolymeric forms have a very low vapour pressure, and are unlikely to vaporise at the paint shop ambient temperature. Exposure to these prepolymeric forms is via inhalation and dermal routes and secondary by oral exposure. This occurs mainly during the spray painting process, when the paint/hardener combination is ejected from the spray nozzle.

Isocyanate prepolymers may induce asthma at the same or greater frequency as diisocyanate monomers (11); therefore, characterization of both monomeric HDI and prepolymeric HDI exposures is important to adequately assess the overall potential for health risk.

Ambient air concentrations of HDI-buiret in 3 automobile spray paint shops and one trade school for spray painters in Finland were found to range from 0.280 - 3.6 mg/m^3, with the concentration of HDI-BT 40 times that of HDI on average (23). The prepolymer ranges in this report (Table 3: 0.017 - 0.304 mg/m^3) were much lower. Reasons could be that the paint might have been stored for longer periods before use, thus *in situ* breakdown of the prepolymers to monomers might have occurred.

In a study of U.S. workers involved in the mixing or application of HDI-BT spray paints, mean ambient air concentrations of HDI-BT ranged from 0.053 to 0.075 mg/m^3, respectively (62). The prepolymer ranges found in this study (Table 3: 0.017 - 0.304 mg/m^3) had a wider range of exposure. This could be due to *in situ* breakdown and higher exposure during the auto body repair process.

In Sweden a study involving reconstruction of exposures of automobile painters in using HDI-BT spray paints, the mean exposure concentration of HDI-BT ranged from 0.010-0.385 mg/m^3 (39). During this study the range of polymer HDI exposure is similar than in this study.

4.2.3 Occupational Categories

The workers mixing the paint were the group that was the highest exposed (Fig 7). The median monomeric HDI concentration was 0.09mg/m^3, 4.5 times higher than the OEL of 0.02mg/m^3. These workers mainly will mix the paint and assist the spray painters with major spraying tasks, thus high exposure to HDI is expected.

However the second highest exposure group was the flatteners. This group repairs the dented area and sands it down. The median exposure for monomeric HDI was 0.07mg/m^3. It was noted that spraying task might take place outside the spray booth in smaller paint tasks, by the spray painters or even the flatteners. This is of concern due to the fact that this group is not educated or informed regarding the hazard of HDI exposure and is not supplied with the correct PPE.

The third highest exposure group was the panel beaters and their median exposure to monomeric HDI was 0.066mg/m^3. This could be due to cross contamination from spray tasks being performed outside the spray booth or due to heating of paint. Heating of polyurethane-containing materials above 150-200 ˚C may give rise to the original monomeric diisocyanates, but also other isocyanates such as the low molecular aliphatic monoisocyanates isocyanic acid (ICA), methyl isocyanate (MIC), ethyl isocyanate (EIC), propyl isocyanate (PIC) and buthyl isocyanate(BIC) (26).

The spray painters were only the fourth highest exposure group (0.058mg/m^3). This group will mostly be educated in the hazards of HDI exposure, wearing PPE and performing spray painting tasks inside spray booths.

4.3 Describing of Control Measures

Respirators are the primary protection from airborne exposures for painters while spraying. 70% of the workshops reported providing a respirator for their painters. All shops the painter wore some kind of respirator at least for clear coating (Table 7).

Spray booths are the primary means of engineering control for airborne isocyanate exposure in this industry (Table. 7). All the workshops had a downdraft spray booth and HVLP spray guns. However this is not tested for efficiency and only maintenance such as filter replacements are performed. This might give the workers a false sense of security.

In this study as seen in Table 7, only HVLP spray guns and downdraft spray booths had been in operation. This might have explained the lower exposure to polymer HDI. Testing conducted by the National Institute for Occupational Safety and Health (NIOSH) in an equipment manufacturer's test facility, demonstrated that particulate over spray concentration was reduced by a factor of 2, and that there was a 30% increase in the ratio of paint film thickness to mass of paint applied when a HVLP spray gun was used. These results indicate that using an HVLP spray painting gun can reduce paint usage and over spray production, resulting in noticeably lower worker exposures (24).

CHAPTER 5

5 CONCLUSION AND RECOMMENDATION

In conclusion, the exposure to monomeric isocyanates during the usage of HDI-containing paint in auto body shops in this study were high with 81% samples exceeding the OEL of 0.02 mg NCO/m^3, despite the widespread use of spray booths as a primary means of exposure control. High concentrations of HDI were common and even indirectly exposed workers were at risk of excessive exposure to HDI. Inadequate exposure control methods were widespread.

5.1 Guideline to Control HDI Exposure

The National Occupational Health and Safety Commission's guideline for spray painting, and measures to control isocyanates exposures (1999), suggested this hierarchy of control to the automotive industry:

1) Elimination of hazards;
2) Substitution with safer alternatives;
3) Engineering controls;
4) Administrative controls; and
5) Use of PPE (64,64)

Complete elimination of the HDI should be the first consideration. Consideration should be given to substitution (the second measure) in the hierarchy if it is not practicable to eliminate HDI. The isolation of the spray painting process should only be considered if the substitution of HDI is not practicable. Engineering controls; which include spray booths, and spray guns, must then be considered, followed by administrative controls; and PPE is a last resort and should be used only if higher level control measures are not practicable or are inadequate.

During a study by Heitbrink (1998), a control strategy for protecting auto body repair workers from polyisocyanate exposure was developed. A combination of a downdraft spray painting booth and an air purifying respirator can be an effective means of controlling worker polyisocyanate exposures. When auto body painting is done in cross-draft or semi-downdraft spray painting booths, the workers should use respirators with an assigned protection factor of 25 or greater (51).

These recommendations were based upon empirical field studies. These recommendations assumed that the companies using the exposure matrix (Table 8) have a respiratory protection program, a hazard communication program, and a program to ensure adequate flow rates in the spray painting booths. In addition, there is a need for the painting companies and the auto body repair industry to continuously collaborate in an effort to keep these recommendations current (51).

Table 8: Control Matrix for Painting in Auto body Repair Shops

Condition	Type of booth	Gun	Respirator
Painting car in booth	Downdraft with an average air flow around car of 80 fpm and no point with an air flow less than 60 fpm.	HVLP	Air Purified Filter (APF)$\geq$ 10 (e.g. Half face piece air purifying or better)
Painting car parts of painting car in booth	Semi downdraft; cross draft	HVLP, conventional	APF$\geq$ 25 (e.g. Supplied air continuous flow, powered air purifying, etc.)
Painting car parts that are not attached to car	Downdraft, paint overspray directed at front or back of booth.	HVLP	APF$\geq$ 10 (e.g. Half face piece air purifying or better)

(Source: Heitbrink WA. A control matrix for spray painting at auto body repair shops. US DHHS, PHS, CDC, NIOSH NTIS Pub. No 45226-1998) (51)

The conditions for using the matrix are listed in Table 9. These conditions address the paint application rate, the polyisocyanate content of the sprayed paint, and the spray painting booth. When the painting conditions are outside of the conditions defined in this table, exposure measurements are needed to select an appropriate respirator.

Table 9: Physical Dimensions to Ensure Adequacy of Matrix.

	Dimension	Specification
1	Paint application rate	Under 150 g/min of paint with a solids content of 50%
2	Polyisocyanate content of applied paint solids	Under 33%
3	Number of painters	One painter
4	Minimum distance between painted surface and workers chin	2 feet
5	Booth flow rate	10,000 - 14,000 cfm
6	Booth size	Approximately 12' × 25' × 8' ft high
7	Cornice for illuminating parts	No more than 1 foot on each side of the booth
8	Criteria for air velocity around a car in a downdraft booth. (INRS):	The air velocity around the perimeter of a car is to be measured at 10 points. Three points are on the side of each car and two are next to the front and rear of the car.

		These measurements are taken 0.5 meters (m) from the side of the car and 0.9 m above the booths floor. The mean value of these points is to be greater than 0.4 m/sec and no point is to have a velocity less than 0.3 m/sec. These measurements are based upon integrated 60 second samples.
9	Criteria for cross draft and semi-downdraft spray painting booth flow rate	100 cfm/ft^2 of cross sectional area. When width times height is greater than 150 ft^2, the criteria is 50 ft/ft^2.
10	HDI monomer content of paint	HDI monomer content of the sprayed liquid shall be less than 0.2% of the polyisocyanate. If the monomer content is greater than 0.2%, the shop must either show the workers exposure to HDI monomer remains below the NIOSH REL or have the workers use supplied air respirators in the spray painting booth.

(Source: Heitbrink WA. A control matrix for spray painting at auto body repair shops. US DHHS, PHS, CDC, NIOSH NTIS Pub. No 45226-1998)(51)

The paint companies and the auto body repair industry need to form a partnership to maintain and update the information basis for this matrix, because spray painting conditions will change and technology will advance. Undoubtedly, these changes will affect the painters' exposure.

Because it is impractical and expensive to collect air sampling data under all possible conditions, exposure modelling for workers performing spray painting is needed. Assuming spray painting gun efficiencies are known and paint application rates are either known or are measurable, computational fluid dynamics can be used to model and predict the worker's exposure to paint overspray (51).

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APPENDIX 1: Checklist – evaluation of control measures

Occupational Hygiene Survey Checklist: Isocyanate spray-painters	
Paint manufacturer's name	
Type of Isocyanates in paint	
Type of spray booth Cross-draft Spray Booth	
Downdraft Spray Booth	
Semi-Downdraft Spray Booth	
Type of spray gun Conventional Air Spray Gun	
High Volume Low Pressure Spray Gun	
Low Volume Low Pressure Spray Gun	
Electrostatic Spray Gun	
Type of PPE used **Eyes:** ____ ____ **Respirator:** ____ ____ **Hearing Protectors:** ____ ____	

APPENDIX 2: Results

Occupation Category	Workshop	HDI monomer mg/m^3	HDI prepolymer mg/m^3	Total HDI mg/m^3
Assembler	1	0.0006	0.0058	0.0064
Assembler	1	0.0007	0.0059	0.0066
Panel beater	1	0.0016	0.0139	0.0155
Panel beater	1	0.0016	0.0133	0.0149
Flattener	1	0.0019	0.0169	0.0188
Flattener	1	0.0004	0.0034	0.0037
Flattener	1	0.0027	0.0239	0.0266
Polisher	1	0.0021	0.0185	0.0206
Flattener/ Primer spray-paint	1	0.0019	0.017	0.0189
Spray painter	1	0.0025	0.0216	0.0242
Ass. Panel beater	2	0.0022	0.0214	0.0236
Ass. Panel beater	2	0.0005	0.0065	0.007
Panel beater	2	0.0002	0.0039	0.0041
Panel beater	2	0.0053	0.0494	0.05
Cleaner	2	0.0026	0.0239	0.0265
Flattener	2	0.0005	0.0004	0.0009
Flattener	2	0.0019	0.0185	0.0204
Flattener	2	0.0024	0.0233	0.0257
Flattener	2	0.0029	0.0284	0.0313
Spray painter	2	0.0018	0.018	0.0198
Spray painter	2	0.0016	0.0152	0.0167

Spray painter	2	0.0015	0.0141	0.0155
Ass. Mechanic	3	0.034	0.079	0.113
Assembler	3	0.033	0.066	0.099
Cleaner	3	0.083	0.143	0.225
Cleaner	3	0.042	0.137	0.179
Cleaner	3	0.299	0.455	0.755
Flattener	3	0.143	0.239	0.382
Flattener	3	0.031	0.051	0.082
Flattener	3	0.032	0.074	0.105
Masking	3	0.022	0.045	0.067
Paint mixer	3	0.029	0.066	0.094
Primer mixer	3	0.034	0.08	0.114
Spray painter	3	0.03	0.07	0.10
panel beater	4	0.027	0.105	0.132
Mechanic	4	0.025	0.066	0.091
panel beater	4	0.038	0.161	0.199
panel beater	4	0.049	0.27	0.319
panel beater	4	0.039	0.138	0.177
Flattener	4	0.101	0.255	0.356
Flattener	4	0.039	0.151	0.189
Flattener	4	0.017	0.029	0.046
Paint shop s/paint	4	0.044	0.233	0.276
Paint shop s/paint	4	0.157	0.252	0.408
Ass. Panel beater	5	0.088	0.238	0.326
Panel beater	5	0.101	0.402	0.502
Panel beater	5	0.089	0.285	0.374

Panel beater	5	0.085	0.271	0.356
Panel beater	5	0.079	0.163	0.163
Flattener	5	0.088	0.302	0.39
Flattener	5	0.064	0.121	0.121
Masking	5	0.074	0.189	0.189
Spray painter	5	0.135	0.456	0.591
Spray painter	5	0.277	0.566	0.843
Spray painter	5	0.098	0.382	0.48
Spray painter	5	0.081	0.24	0.321
Panel beater	6	0.0614	0.3	0.3614
Panel beater	6	0.066	0.3187	0.3847
Panel beater	6	0.0424	0.2311	0.2735
Flattener	6	0.0506	0.2543	0.3049
Flattener	6	0.0614	0.2961	0.3575
Flattener	6	0.0437	0.2282	0.2718
Flattener	6	0.0649	0.3196	0.3845
Masking]	6	0.063	0.3158	0.3788
Masking]	6	0.045	0.2253	0.2703
Polisher	6	0.0541	0.3747	0.4578
Spray painter /mixing	6	0.0491	0.2465	0.2956
Spray painter /mixing	6	0.0522	0.2519	0.3042
Panel beater	7	0.031	0.086	0.117
cleaner	7	0.053	0.205	0.258
cleaner	7	0.082	0.242	0.324
cleaner	7	0.034	0.104	0.138

Flattener	7	0.097	0.256	0.353
Foreman	7	0.069	0.23	0.298
Spray painter	7	0.12	0.298	0.418
Spray painter	7	0.05	0.164	0.214
Ass. Spray painter	7	0.03	0.073	0.102
Chem. Preparation	7	0.064	0.205	0.268
Spray painter	7	0.053	0.177	0.23
Cleaning s/guns	8	0.27	0.298	0.567
Flatter	8	0.07	0.149	0.218
Flatter	8	0.041	0.099	0.141
Flatter	8	0.077	0.194	0.271
Flatter	8	0.13	0.223	0.353
Flatter	8	0.032	0.055	0.088
Masking	8	0.047	0.132	0.179
Masking	8	0.231	0.255	0.486
Flatter/Primer Spray painter	8	0.033	0.057	0.09
Primer Spray painter	8	0.041	0.113	0.154
Spray painter	8	0.146	0.247	0.394
Spray painter	8	0.268	0.305	0.573
Masking	9	0.022	0.239	0.261
Cleaning	9	0.01	0.149	0.16
Cleaning	9	0.01	0.115	0.125
Flattener	9	0.011	0.179	0.19
Masking	9	0.01	0.139	0.149
Polisher	9	0.011	0.191	0.202

Polisher	9	0.021	0.238	0.259
Spray painter	9	0.01	0.162	0.173
Spray painter	9	0.01	0.115	0.125
Spray painter	9	0.014	0.195	0.209
Preparation	10	0.126	0.245	0.3493
Flatting	10	0.176	0.4522	0.6279
Flatting	10	0.09	0.2833	0.4062
Flatting	10	0.112	0.2019	0.2915
Masking	10	0.789	0.2221	0.3222
Masking	10	0.022	0.4084	0.5748
Mixing	10	0.141	0.274	0.3847
Paint shop paint	10	1.5	2.0036	3.5033
Primer	10	0.11	0.3542	0.5009
Primer	10	0.102	0.2713	0.3789
Spray painter	10	0.105	0.1598	0.2388

APPENDIX 3: Synonyms

1,6-Hexamethylene diisocyanate

Hexane, 1,6-diisocyanato-

Hexamethylene diisocyanate

1,6-hexamethylene diisocyanate

Diisocyanate d'hexamethylene [French]

HDI

Hexamethylendiisokyanat [Czech]

Hexamethylene diisocyanate

Hexamethylenediisocyanate

Hexametilendilsocianato [Spanish]

HEXANE 1,6-DIISOCYANATE

HMDI

ISOCYANIC ACID, DIESTER with 1,6-HEXANEDIOL

Isocyanic acid, hexamethylene ester

METYLENO-BIS-FENYLOIZOCYJANIAN [Polish]

Szesciometylenodwuizocyjanian [Polish]

1,6-DIISOCYANATOHEXANE

1,6-HEXANEDIOL DIISOCYANATE

1,6-HEXYLENE DIISOCYANATE

APPENDIX 4: Ethics Clearance Certificate

UNIVERSITY OF THE WITWATERSRAND, JOHANNESBURG

Division of the Deputy Registrar (Research)

COMMITTEE FOR RESEARCH ON HUMAN SUBJECTS (MEDICAL)
Ref: R14/49 Spies/Rees

CLEARANCE CERTIFICATE PROTOCOL NUMBER M02-04-28

PROJECT	Assessment of The Exposure Associated Health Effects To Hexamethylene Diisocyanate (HDI) In Automotive Spray Painting Processes In Small Medium & Micro Enterprises
INVESTIGATORS	Ms/Prof A/D Spies/Rees
DEPARTMENT	NCOH, Wits Medical School
DATE CONSIDERED	02-04-05

DECISION OF THE COMMITTEE *

Approved unconditionally

DATE 02-04-08 CHAIRMAN ....(Professor P E Cleaton-Jones)

* Guidelines for written "informed consent" attached where applicable.

c c Supervisor: Prof D Rees
Dept of NCOH, Wits Medical School

Werke2\lain0015\HumEth97.wdb\M 02-04-28

DECLARATION OF INVESTIGATOR(S)

To be completed in duplicate and **ONE COPY** returned to the Secretary at Room 10001, 10th Floor, Senate House, University.

I/we fully understand the conditions under which I am/we are authorized to carry out the abovementioned research and I/we guarantee to ensure compliance with these conditions. Should any departure to be

PLEASE QUOTE THE PROTOCOL NUMBER IN ALL ENQUIRIES