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HEALTH & SAFETY LABORATORY

Measured Airborne Isocyanate from Mixing and Brush and Roller Application of Isocyanate based 2-pack Paints

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CONTENTS

EXECUTIVE SUMMARY

Objectives

1. Evaluation of the likely exposure caused by mixing and brush and roller application of isocyanate paints.

Main Findings

1. Laboratory work carried out by HSL has detected no airborne isocyanate during mixing and brush and roller application of isocyanates.

2. Field-work carried out in collaboration with an external contractor (sampling done by external contractor/ analysis by HSL) has detected no airborne isocyanate during mixing and brush and roller application of isocyanates.

3. Dermal exposure (dripping on to the gloves) was noticed for the mixing and rollering work and also, to a lesser extent, for the brushing work

Recommendations

1. This work should be taken into consideration when guidance concerning small scale mixing and brush and roller application of 2-pack isocyanate based paints is developed.

1 INTRODUCTION

Isocyanates (NCO) are highly reactive species used in the motor vehicle repair, adhesives, polyurethane and coating industries. They are known respiratory tract and skin sensitizers and are the most common cause of occupational asthma in the UK (HSE, 2004). The Health and Safety Executive (HSE) has set maximum exposure limits, for total isocyanate exposure (i.e. all NCO species), of 70 $\mu g/m^{-3}$ (short term, 15 minute) and 20 $\mu g/m^3$ (8 hour TWA). Isocyanates paints can be applied by spraying or by brush or roller.

The hazards associated with spraying of isocyanate paints are well known (HSE, 2004). This report details work carried out by HSL to determine the potential hazard of mixing and brush and roller application of 2-pack NCO based paints.

The sampling technique used (impinger containing MP reagent in toluene solution with an MP coated filter as back-up) has been shown to effectively sample both droplets/particles (impinger) and vapour (mainly filter) (Hext et al, 2003). Sampling strategies for isocyanate aerosols, including the impinger/filter combination, have been reviewed by Levine et al. (Levine et al., 1995) and Streicher et al. (Streicher et al., 1994).

Any airborne isocyanate present is expected to be primarily in particle (aerosol) form as the oligo-NCO species present in the lacquer have a very low volatility and no heat was being used in the operations described above, so no vapour would be produced. Some examples of vapour pressures for the common diisocyanate species are given in table 1.

Table 1. Vapour Pressures for mono- and oligo- diisocyanates

Diisocyanate	Vapour pressure (mbar)	Temperature (^oC)
HDI	~0.014	25
TDI (2,4 and 2,6 isomers)	~0.02	20
MDI (2,4)	~0.00001	20
MDI (4,4')	~0.00001	20
oligo-HDI formulations	< 0.001 to < 0.0001 depending on formulation	25
oligo-MDI formulations	< 0.0001 to 0.00001 depending on formulation	25
TDI (20/80 mix of monomers)	0.01	20
For the oligo-formulations, values for high % NCO formulations have been quoted, for high solvent (low % NCO formulations) most of the vapour pressure will be from the solvent.		
Values are adapted from; Data sheets (Bayer and Huntsman) "MDI and TDI- Safety, Health and Environment", Pub. John Wiley and Sons, 2003, Eds. Allport DC, Gilbert DS and Outterside SM.		

Particle sizes for oligo-HDI based 2- pack paints (HDI isocyanurate and HDI biuret as major components) are given in Maitre et al. (Maitre et al., 1996). These workers found, for the HDI isocyanurate based paint, > 80% (by weight) of the aerosol had a particle size > 1.5 μm and for the HDI biuret based paint, > 95% (by weight) of the aerosol had a particle size > 1.5 μm.

England et al. also state that the dominant phase in spray painting is aerosol (particulate) (England et al., 2000).

Droplets/particles are sampled mainly by the impinger part of the impinger/filter sampling train. This has been observed at HSL many times, e.g. in spray painting experiments. The isocyanate in spray painting experiments is largely in the droplet/particle form, and these samples usually give a high impinger result with a very low or zero back-up filter result.

2 EXPERIMENTAL

Laboratory experiments were carried out to simulate mixing and brush and roller application of an isocyanate 2-pack topcoat. The results of some field-work carried out in May 1997 are also included in this report.

2.1 MIXING

The paint used in the laboratory work was a 2-pack 1,6-diisocyanatohexane (HDI) based topcoat (hardener/lacquer). The hardener is predominantly a mixture of oligo-isocyanates (biuret, dimer, isocyanurate and tri-uretidinedione-isocyanurate) with a very small fraction of HDI monomer. This was mixed 2:1 (hardener/lacquer) as suggested by discussions with the supplier (Hallam Factors, Sheffield). Mixing was carried out in the roller tray.

Air samples were taken as described in MDHS 25/3 (HSE, 1999) using an impinger/back-up filter combination. Samplers were placed within 15 cm of the tray, to the left, right and back. A personal sample was also taken. Mixing was carried out using a glass rod for 4 minutes. An air fed visor was worn during mixing and for subsequent operations. The results of this work are given in table 2.

2.2 BRUSH APPLICATION

Brush application was carried out using the same sampling points described for the mixing work. A car door was painted for 5 minutes using a 50 mm brush. Two coats were applied to the car door. The results of this work are given in table 2.

2.3 ROLLER APPLICATION

Roller application was carried out using the same sampling points described for the mixing work. A car door was painted for 2 minutes using a 200 mm roller. Two coats were applied to the car door. The results of this work are given in table 2.

2.4 BIOLOGICAL MONITORING

Urine samples were taken at the end of each operation and analysed using the HSL method (hydrolysis to the amine) (Williams et al, 1999). The results of this work are given in table 3.

2.5 FIELD-WORK – BRUSH AND ROLLER PAINTING OF PETROL STATIONS

In May 1997 HSL analysed samples taken (by an external contractor) during painting of the external metalwork of several petrol stations. The paint used was a two-pack paint comprising of a pigment (base) and an activator/hardener (oligo-HDI based). Samples taken were a mix of personal and static impingers/filters. The results of this work are given in table 4.

3 RESULTS

Table 2. Mixing, Brush and Roller Application Airborne NCO Results

Sample	μg NCO/m^3
Mixing, left	Not detected
Mixing, right	Not detected
Mixing, front of car door	Not detected
Mixing, personal sampler	Not detected
Rollering, left	Not detected
Rollering, right	Not detected
Rollering, front of car door	Not detected
Rollering, personal sampler	Not detected
Brushing, left	Not detected
Brushing, right	Not detected
Brushing, front of car door	Not detected
Brushing, personal sampler	Not detected
Brush application to car door for 5 minutes Roller application to car door for 2 minutes Mixing paint components for 4 minutes Estimated LOD for brushing ~ 4 μg NCO/m^3 Estimated LOD for rollering ~ 8 μg NCO/m^3 Estimated LOD for mixing ~ 5 μg NCO/m^3	

Comments on Table 2

No airborne isocyanates were detected during the brush, roller and mixing operations.

For roller application and mixing operations, a large amount of dripping and dribbling of the paint onto the gloves of the operator was noticed. Dripping/dribbling on to the operator's gloves also occurred for the brush application experiments but to a much lower extent. These observations suggest dermal exposure will be more significant for mixing and roller operations than for brush application.

Table 3. Biological Monitoring for Mixing, Brush and Roller Application

Operation	[NCO] as HDA μmol/mol creatinine
Pre-	Not detected
After mixing	Not detected
After brushing	Not detected
After rollering	Not detected
Post-	Not detected

Comments on Table 3

No hexamethylenediamine (HDA) was detected in these samples suggesting no NCO exposure had occurred during these operations.

Table 4. Field-Work, Brush and Roller Painting of Petrol Stations
Airborne NCO monitoring Results

Sample Number	Comments	Air Volume (l)	[NCO] μg NCO/m^3
01067/97	Painters – mixing and brush and roller application of 2-pack paint – 23/04/97	250.7	Not detected
01068/97		30.45	Not detected
01069/97		163.8	Not detected
01070/97		24.08	Not detected
01071/97		32.4	Not detected
01072/97	Samples taken ~7m downwind of painting 23/04/97	53.5	Not detected
01073/97		522.5	Not detected
01074/97		547.4	Not detected
01075/97	Blank 1	---	Not detected
01076/97	Blank 2	---	Not detected
01077/097	Painters – mixing and brush and roller application of 2-pack paint – 07/05/97	32.18	Not detected
01078/97		216.24	Not detected
01079/97		221.69	Not detected
01080/97		30.6	Not detected
01081/97	Samples taken ~ 10m downwind of painting 07/05/97	455.63	Not detected
01082/97		440.1	Not detected
01083/97	Blank 1	---	Not detected
01084/97	Blank 2	---	Not detected
01085/97	Activator/hardener bulk	---	Mixture of oligo-HDI detected
01086/97	Base bulk	---	Not detected
Worksheet # OH/217/97			
Estimated LOD ~0.01 μg NCO/m^3 for a 100 l sample			

Comments on Table 4

No airborne isocyanates were detected during brush and roller application of a 2-pack HDI based paint used to paint the exterior metalwork of petrol stations. Isocyanates (oligo-HDI0 were detected in the bulk activator/hardener.

4 CONCLUSIONS

The laboratory tests found no airborne isocyanate during small scale mixing and brush and roller application. The static samples were carried out close to the operations under test and so represent a "worst-case" series of results. The personal samplers were worn as normal and so should give a good simulation of worker exposure. These results suggest that airborne isocyanate is not a significant hazard during these operations

This conclusion was confirmed by the field-work which also found no airborne isocyanate during the mixing, brushing and rollering operations carried out.

The potential for dermal exposure, especially during rollering and mixing should be considered as dripping and splashing onto the protective gloves was noticed especially during mixing and rollering operations. The biological monitoring results associated with this work found no evidence of isocyanate exposure suggesting that the personal protective equipment (PPE) worn during these operations was adequate to prevent exposure.

5 REFERENCES

England E, Key-Schwartz R, Lesage J, Carlton G, Streicher R and Song R (2000)
Comparison of sampling methods for monomer and polyisocyanates of 1,6 hexamethylene diisocyanate during spray finishing operations
Applied Occupational and Environmental Hygiene, 15(6), p 472-478.

Health and Safety Executive (2004)
hse.gov.uk/asthma/substacesinfo
HSE website.

Health and Safety Executive (1999)
Organic isocyanates in air
Methods for the determination of hazardous substances
Method 25/3.

Hext PM, Booth K, Dharmarajan V, Karoly WJ, Parekh PP and Spence M (2003)
A comparison of sampling efficiencies of a range of atmosphere samplers when collecting polymeric diphenylmethane diisocyanate (MDI) aerosols
Applied Occupational and Environmental Hygiene, 18(5), p346-357.

Levine SP, Hillig KJD, Dharmarajan V, Spence MW and Baker MD (1995)
Critical review of methods of sampling, analysis and monitoring for TDI and MDI
Am Ind Hyg Assoc J, 56, p581-589.

Maitre A, Leplay A, Perdix A, Ohl G, Boinay P, Romazini S and Aubrun JC (1996)
Comparison between solid sampler and impinger for evaluation of occupational exposure to 1,6 hexamethylene diisocyanate polyisocyanates during spray painting
Am Ind Hyg Assoc J, 57, p153-156.

Streicher RP, Kennedy ER and Lorberau CD
Strategies for the simultaneous collection of vapours and aerosols witj emphasis on isocyanate sampling
Analyst, 119, p89-97.

Williams NR, Jones K and Cocker J (1999)
Biological monitoring to assess exposure from use of isocyanates in motor vehicle repair
Occup Environ Med, **56**, p598-601.