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Measurement of Airborne Isocyanate during Sanding and Bake Cycle

Results – December 2004 and March 2005

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CONTENTS

EXECUTIVE SUMMARY

Objectives

1. Evaluation of the likely exposure to isocyanate caused by baking and sanding of isocyanate paints.

Main Findings

1. Laboratory work carried out by HSL has detected significant airborne isocyanate during simulated experimental baking of an isocyanate 2-pack paint.

2. Fieldwork carried out in collaboration with an external contractor (sampling/analysis by HSL) has detected no airborne isocyanate during baking of car body parts painted with isocyanate 2-pack paints.

3. Fieldwork carried out in collaboration with an external contractor (sampling/analysis by HSL) has detected no airborne isocyanate during sanding of a recently baked car body part painted with isocyanate 2-pack paint.

4. These results suggest that baking and sanding processes are not a significant source of NCO exposure in the workplace.

Recommendations

1. Further work is recommended in this area. It is suggested that further sampling and analysis during the bake-cycle and during sanding processes in MVR shops is carried out covering a range of circumstances and particularly given the sampling problems encountered with high temperatures and access for sample tubing.

2. Further work on the thermal decomposition of NCO based products is recommended. Particularly the investigation of "lift-off" times for NCO vapour production from NCO based products.

1 INTRODUCTION

Isocyanates (NCO) are highly reactive species widely used in the motor vehicle repair and other 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 workplace exposure limits (WELs) 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).

The hazards associated with spraying of isocyanate paints are well known (HSE, 2004). However hazards associated with other parts of the painting process are less well researched. In the motor vehicle repair industry (MVR) after a car or car-part has been sprayed it is often placed in a booth at elevated temperature to speed curing of the isocyanate. This is known as baking or the bake-cycle. During the bake-cycle the air to the booth is usually re-circulated which could increase airborne isocyanate concentrations inside the booth and associated ductwork. This could lead to NCO exposure if an unprotected worker entered the booth during the bake-cycle or if the booth leaked or was not cleared of residual vapour at the end of the cycle. One aim of the work presented here is to evaluate this risk.

Similarly sanding (flatting) of car-parts painted with NCO containing materials also could be a source of exposure. Sanding is most usually done on primer paints but sometimes a finished car-part may need to be sanded back to the bare metal (i.e. topcoat, colour-cot and primer layers removed) if the spray job has not been successful. Sparer et al (Sparer et al, 2004), Karlsson et al (Karlsson et al, 2000) and Woskie et al (Woskie et al, 2004) have reported NCO emissions in MVR shops from grinding, sanding and welding operations. However, work at HSL (HSL, 2003) found no isocyanate exposure from sanding of a fully cured car door panel.

There are several possible explanations for these anomalous findings. One is that the US investigators have measured background levels of isocyanate-in-air from other sources, e.g. a leaking spray booth. In the US, unlike in the UK, spray booths in MVR body-shops are run at a slight positive pressure and will leak paint aerosol as a result. Another possibility is that isocyanate detected in the non-HSL work is arising from thermal decomposition of the NCO during heat generating activities e.g. welding and grinding. The ability of NCO derived materials e.g. polyurethane foams to generate NCO on heating has been well proven (Sennbro et al, 2004). Very little heat was generated during the sanding operations measured at HSL (HSL, 2003a). A further possibility is that in the non-HSL work the car-parts were not fully cured and NCO was being released in the dust created during sanding, welding and grinding. HSL has already carried out some work on thermal degradation of NCO derived materials (HSL, 2002: HSL, 2003b) and so the work presented here aims to evaluate the second possibility i.e. NCO exposure from partially cured components or immediately after the baking process.

2 EXPERIMENTAL

Laboratory experiments were carried out to mimic baking and sanding of a partially cured isocyanate 2-pack paint. The results of fieldwork carried out at Just Car Clinic, Sheffield in December 2004 and March 2005 are also included in this report.

2.1 LABORATORY EXPERIMENTS

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).

The mixed paint (0.9g) was painted onto a metal disc and then placed in a petri dish on a hot plate. Over the petri dish was placed an inverted glass funnel, covering the petri dish but not preventing the flow of air through the funnel. To the glass funnel was attached a sampling pump and Swinnex head containing a 1-(2-methoxyphenyl)piperazine (MP) impregnated glass fibre (GF/A) filter as described in MDHS25/3 (HSE,1999). The painted disc was heated at ~85^{o}C for 40 minutes to simulate the baking process. This is baking for slightly longer and at a slightly higher temperature than that used in the MVR body-shop visited during the field work (30 minutes at 80^{o}C, see section 2.2) and so should considered as a "worst-case" experiment. During the baking period the air above the disc was sampled at 2L/min. After the simulated baking process the painted disc was wiped with an MP coated swab to see if any NCO could be detected on the surface. The results of this work are given in table 1, section 3.

A second experiment using the set-up described above was carried out. In this experiment 4.6g of mixed paint was used and this was heated to ~75^{o}C for 35 minutes. The results of this work are reported in table 1, section 3.

Analysis was carried out as described in MDHS 25/3.

2.2 FIELDWORK – SAMPLES TAKEN DURING BAKE CYCLE AND SANDING OPERATIONS IN A MVR BODY-SHOP

In December 2004 and March 2005 HSL carried out sampling and analysis of samples generated during baking and sanding of car-parts at a MVR body-shop. The paints used were two-pack paints comprising of a pigment (base) and an activator/hardener (oligo-HDI based). Samples taken were static and personal impingers/filter combinations, bulk paints and swabs of dust and baked surfaces.

Sampling and analysis was carried out using a modified version of MDHS 25/3 as described in HSL report OMS/2003/12 (HSL, 2003c). The chief modification was the use of butyl benzoate as the solvent for the MP solution. This was because toluene, which is the usual solvent for MDHS 25/3, would evaporate if left in the baking booth at 80^{o}C. Removal of the butyl benzoate was carried out using silica gel solid phase extraction (HSL, 2003c). Confirmation of the composition of the bulk isocyanates was carried out by LC/MS/MS (HSL, 2003d). The results of this work are given in table 2, section 3.

The December 2004 visit looked solely at baking operations, with five separate bake cycles being sampled. The biggest problem faced with the sampling was the high temperature and potential effects on the pump, typically sampling pumps are only given an upper operating range of around 40- 50^{o}C. So a suitable length of tubing was run from inside the booth (near the air inlet) and out through a small gap in the doors, sample pump and impinger/filter were located outside in the main workshop thereby avoiding the extreme temperature. There was a slight concern in doing this that the sample tubing may become restricted on closing/sealing the doors, although flow rates were measured with the doors closed and no problems observed.

The March 2005 visit sought to address this concern (possible reduction of flow rate on closing of the doors) thus it was decided that pumps would be placed inside the booth itself. Each pump/impinger was attached to a clamp and stand between 50-75 cm off the floor. A minimum of three samples was taken per bake cycle, positions being altered each cycle due to different cars and/or car parts being cured. The elevated temperature did cause problems with the sampling pumps, with a high proportion of pump failures being observed, however, at least one of the pumps was still working at the end of each of the four bake cycles sampled.

Additionally one sanding (flatting) operation was sampled. A car wing was sprayed with a commonly used 2-pack NCO-containing lacquer and cured as normal in the booth. Sanding was carried out within 20 minutes of the car-part being removed from the bake booth. This is not normal industry practice but this experiment was intended to provide a “worst case” scenario for potential NCO exposure and so the wing was sanded until all the freshly applied paint had been completely removed. In practice it is extremely unlikely that all the paint applied would be removed. Usual industry practice is to leave the baked part for several hours to "finish" prior to sanding. The flatting was carried out with the extraction system on the sander switched off, the operator using air fed RPE for increased protection. These results are given in table 2.

3 RESULTS

The results of the experimental and fieldwork described above are given below.

3.1 LABORATORY EXPERIMENTS

Table 1. Laboratory Work

Sample	μg NCO/ sample	μg NCO/m^3	Air volume (l)
Experiment 1 filter	109.4	1,368	80
Experiment 1 swab	38.3	---	---
Experiment 2 filter	78.9	1,271	70
Experiment 2 swab	88.1	---	---

<u>Comments on Table 1</u>

High concentrations of NCO were detected in the air during the simulated baking process.

It should be noted that this represents a "worst case" scenario as the volume of the glass funnel used as the sampling head is very small compared to the volume of the average baking booth i.e. volume of glass funnel ($\pi/3$ x $0.035m^2$ x 0.04m) ~ 5.1 x 10^{-5} m^3, volume of HSL baking booth (5.3m x 4.2m x 2.95m) ~ 66 m^3 i.e. about a million fold lower. However, these results do demonstrate that there is a possibility of NCO being released during the bake cycle. This could be important if the booth had a long clearance time after baking or if baking temperatures were poorly controlled and significantly exceeded the 80^oC set point.

Commonly quoted limits of detection for isocyanates by MDHS 25/3 as used at HSL are 0.2 μg/m^3 for a 100 l sample. A million-fold dilution of the airborne NCO levels found in table 1 would give values of ~ 0.001 μg NCO/m^3 (~1,000 μg NCO/m^3/~1,000,000 = ~0.001) i.e. well below the detection limit for MDHS 25/3 as currently used at HSL. This could lead to these emissions not being detected.

One question that arises from this work is the precision of the temperature control on the hot plate used. Most hot plates are controlled by a bi-metallic thermostat or similar device. This type of control means that the temperature is on average at the set point but oscillates above and below it. This could lead to pulses of NCO being released as the hot-plate goes above the set temperature. More work, preferably with a precise hot plate or oven is recommended. A study of the "lift off" times for NCO formulations is recommended. Some preliminary work on hot-melt glues will be reported in the Complex Substances call-off project report (in preparation). This work suggests that, for the three types of hot-melt glues examined (HDI, TDI and MDI based), temperatures in excess of 100^oC are required for significant NCO vapour to be released from these materials.

The swab samples also gave positive NCO results. This suggests that the paint was not fully cured after the simulated bake cycle. It was noted that the painted disc was "sticky" to the touch.

These experimental baking results suggest that the baking process has the capacity to cause some airborne NCO exposure albeit very low.

3.2 FIELDWORK – SAMPLES TAKEN DURING BAKE CYCLE AND SANDING OPERATIONS IN A MVR BODY-SHOP

Table 2. Fieldwork - Baking and Sanding of Baked Car-Parts

Laboratory sample No.	Sample Type	[NCO] µg/ sample	[NCO] $\mu g/m^3$	Air Volume (l)	Comments
VISIT 1, 21/12/04					
01914-05	impinger/filter	N.D.	N.D.	7.8	Bake cycle 1, sample 1, bake cycle is ~ 30 minutes at 80°C.
01915-05	impinger/filter	N.D.	N.D.	14.5	Bake cycle 1, sample 2
01916-05	bulk	N.D.	N.D.	-	Lacquer for Bake cycle 1
01917-05	bulk	NCO detected mainly oligo-HDI		-	Hardener for Bake cycle 1
01918-05	impinger/filter	N.D.	N.D.	18	Bake cycle 2, sample 1
01919-05	bulk	NCO detected mainly oligo-HDI		-	Paint for Bake cycle 2 (black)
01920-05	impinger/filter	N.D.	N.D.	8.5	Bake cycle 3, sample 1- same paint as Bake cycle 1
01921-05	impinger/filter	N.D.	N.D.	14.5	Bake cycle 3, sample 2
01922-05	impinger/filter	N.D.	N.D.	7.5	Bake cycle 4, sample 1 - same paint as Bake cycle 1
01923-05	impinger/filter	N.D.	N.D.	15	Bake cycle 4, sample 2
01924-05	bulk	NCO detected Mainly oligo-HDI		-	Paint for Bake cycle 4, (2K lacquer as applied)
01925-05	impinger/filter	N.D.	N.D.	18	Bake cycle 5, sample 1- same paint as Bake cycle 1
VISIT 2, 18/03/05					
01926-05	impinger/filter	-	-	FAIL	Bake 1, sample 1 -Pump failure
01927-05	impinger/filter	N.D.	N.D.	54	Bake 1, sample 2
01928-05	impinger/filter	-	-	FAIL	Bake 1, sample 3 -Pump failure
01929-05	impinger/filter	N.D.	N.D.	84	Bake 2, sample 4
01930-05	impinger/filter	-	-	FAIL	Bake 2, sample 5 – Pump failure
01931-05	impinger/filter	-	-	FAIL	Bake 2, sample 6 -Pump failure
01932-05	impinger/filter	ND	ND	8	Sample 7, flatting, personal - carried out with 30 minutes of bake cycle
01933-05	impinger/filter	ND	ND	26	Sample 8, flatting - static

Laboratory sample No.	Sample Type	[NCO] µg/ sample	[NCO] µg/m^3	Air Volume (l)	Comments
01934-05	impinger/filter	ND	ND	26	Sample 9, flatting - static
01935-05	impinger/filter	ND	ND	26	Sample 10, flatting - static
01936-05	swab	ND	ND	-	Swab of dust from flatted panel
01937-05	impinger/filter	-	-	FAIL	Bake 3, sample 11 -Pump failure
01938-05	impinger/filter	ND	ND	78	Bake 3, sample 12
01939-05	impinger/filter	-	-	FAIL	Bake 3, sample 13 -Pump failure
01940-05	impinger/filter	-	-	FAIL	Bake 4, sample 14 -Pump failure
01941-05	impinger/filter	ND	ND	86	Bake 4, sample 15
01942-05	impinger/filter	ND	ND	73	Bake 4, sample 16
01943-05	impinger/filter	ND	ND	82	Bake 4, sample 17
01944-05	bulk	NCO detected Mainly oligo-HDI		-	Paint as applied, used for cycles 1,2 and 4
01945-05	bulk	NCO detected Mainly oligo-HDI		-	Paint as applied, used for cycle 3 (red paint)

Comments on Table 2

Some samples were lost because of pump failure, however for all 9 bake cycles sampled (14 samples in total) no NCO was detected. No isocyanate was detected during the sanding process (1 personal, 3 static and 1 swab sample).

More work is recommended, especially for the sanding process, but these results suggest that baking and sanding of NCO based paints is not a significant exposure hazard in the workplace.

4 CONCLUSIONS

The fieldwork found no airborne isocyanate during baking and sanding operations carried out at an MVR body-shop (baking). Difficulties were encountered in the sampling with issues regarding the high temperatures in the booth being compounded by access limitations for the sample tubing.

The laboratory tests found measurable levels of airborne isocyanate during simulated baking operations although whether such levels would be measurable in a spray-bake booth is unlikely i.e. exposures would be low compared to the isocyanate WELs.

There are several explanations for the seeming differences between these two sets of results (fieldwork and laboratory work). As stated in section 3.1 this could be because of large variations in the temperature of the hot plate used for the laboratory experiments. This would lead to pulses of NCO being emitted and so give larger than expected airborne NCO results. Another possibility is that because of the large dilution factor (glass funnel vs baking booth) the amounts of isocyanate detected in the laboratory work would be below the limit of detection in a baking booth (see section 3.1).

The work presented here suggests that the primary mechanism leading to NCO release from sanding and baking processes is thermal decomposition rather than uncured NCO being released in the dust produced by sanding. Even so, dust levels from uncontrolled sanding could be significant and dust exposure, from sanding, should be effectively controlled.

In conclusion, although laboratory experiments have shown that NCO can be liberated during simulated baking experiments, workplace measurements of NCO suggest that the potential for NCO exposure from baking and sanding processes is low. Further work is suggested to confirm these initial findings.

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