가구산업에 사용되는 이소시안화물 폭로에 대한 평가

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Evaluation of Exposure to Isocyanates Used in Furniture Industry

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Abstract : Occupational asthma is commonly known to be induced by isocyanate exposure. Spray painters generally use isocyanates for 2-pack spray painting to coat wooden panel surfaces in the furniture industry in South Australia. Due to a lack of actual exposure data, this study conducted environmental and dermal/ocular monitoring from a company in the furniture industry.
According to this study, there was no significant airborne contamination, due to the use ofhigh volume low pressure (HVLP) spray guns, low concentration of hardener in paint solutions and appropriate respirator like full face-air line respirator. There was no significant HDI detection in the general work area around the spray booths. Owing to the use of disposable nitrile gloves during the spray painting, no significant dermal exposure was found. According to color monitoring, there was a possible dermal exposure from surfaces in the workplace, unless either protective gloves were worn or appropriate working practices like clean-up process and storage in a secure places. No eye contamination was detected from the spray painters. No significant exposure levels from inhalational, dermal, ocular were found. The area of most concern was work practices.

초 록 : 직업성 천식은 시안화물의 폭로에 의해 발생되는 것으로 알려져 있다. 남호주에 있는 가구산업에서는 일반적으로 목재판 위를 피복하기 위해 이중분사도포를 할 때 이소시안화물 도포제가 사용된다. 이 연구는 이와 관련된 분야의 자료부족으로 관련 산업에서의 환경 및 피부와 안구폭로에 대한 모니터링을 위하여 수행되었다.
이 연구결과에 의하면 저압다량(HVLP)의 분사기 사용, 페인트 용액중의 저농도 경화제 및 전면 호흡보호구와 같은 적절한 보호구의 사용시에는 대기로부터 오염물질의 유입은 거의 없었고, 분사실 주변의 일반적인 작업범위에도 HDI가 거의 감지되지 않았다. 페인트분사시의 일회용 장갑착용으로 피부폭로는 발견되지 않았으나, 칼라 모니터링에 의하면 장갑을 착용하지 않거나 청결하게 관리할 수 있는 공정이나 안전한 장소에 보관하지 않으면 작업장으로부터 피부폭로가 있었다. 페인트분사 로부터 눈의 오염은 감지되지 않았고, 호흡기, 피부 및 안구에도 폭로되지 않았으며 유입과 가장 관련성이 있는 것은 작업형태이다.
Key Words : airborne exposure, dermal exposure, furniture industry, isocyanates, ocular exposure, PPE

1. Introduction

Isocyanates are widely used in coating application operations. Occupational asthma is a common respiratory symptom from isocyanate exposure[1-5]. Continuous exposure to isocyanates increased the risk of developing respiratory symptoms for workers in companies using large quantities of isocyanate-based paints[6,7]. From previous studies[2,8,9], it was also discussed that dermal exposure may cause respiratory sensitization. In the case of the furniture industry which uses large quantities of isocyanate (e.g. hexamethylene diisocyanate; HDI) based hardeners, exposure to isocyanates

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occurs from the processes of mixing, spraying and cleaning-up.

While limited, the most common exposure data are based on inhalational exposure measurement[10]. However, there is a lack of dermal exposure data. Even though there is a semiempirical dermal model for spray painters[11], no sampling methodology has been standardized for dermal and ocular monitoring.

The aim of this study is to provide information or exposure routes to workers, investigate the extent of HDI absorption and provide information to minimize these exposures.

2. Study Methods

2.1. Study Subjects

Study subjects (three spray painters, one spray paint mixer and three bystanders in the general area) were recruited from the furniture industry in South Australia. For 2-pack spray painting, very low concentration of hexamethylene diisocyanate(HDI)-based hardener (AKZO NOBEL; Fast, No 895002013, Code 310.700) was used. Outside the spray booth, the spray paint mixer manually stirred the spray paint using a wooden stick in a small container (20 L in vol.).

After the application of a preliminary sealer to wood panels or small pieces of wood, 2-pack spray painting (resin : hardener = 2 : 1, reducer = approx. 10% in total) was carried out with a high-volume low-pressure (HVLP) spray gun (approx. 20-70 psi air pressure) in a downdraft spray booth with a water curtain system. Then, all the sprayed wood panels and small articles of wood were stored in the collecting room (average temperature was around 26℃) to dry out for 12-15 hours. Spray painters wore full-face airline respirators and disposable nitrile gloves (Touch N Tuff™). The spray paint mixer wore a half face respirator, but no eye protection.

For the study subjects, different sampling techniques for inhalational, dermal, surface and ocular monitoring were carried out. Sampling time was based on different spray painters' spray painting task schedule during the monitoring period.

2.2. Environmental Measurement

Air monitoring

Based on the HSE MDHS, UK 25/3 method[12], quantitative inhalational exposure monitoring was carried out. Type A/E glass fibre filters (25mm, PALL Life Sciences) were impregnated with 1-(2 methoxyphenyl) piperazine[1-2MP] (Aldrich). An air sampler (3 piece cassette) was attached within the worker's breathing zone operating at a flow rate of 1 L/minute. The general area was also measured to determine potential exposure of other employees or bystanders.

Dermal and surface monitoring

Quantitative dermal monitoring was conducted by using Ghost™ Wipe pads (Environmental Express, USA)[13] after pure isopropyl alcohol (IPA) was sprayed on the skin. Permea-Tec™ (Aliphatic Iso. Omega Speciality Instrument Company, USA)[14] and Colorimetric Swype Indicators (GMD SYSTEMS Inc. Replacement Detection Tape Cassette; Aliphatic Isocyanates, approx. 1cm^2)[10,13] were used to qualitatively observe the presence of isocyanates from wipes of the skin, surfaces and PPEs. IPA was sprayed on the surfaces before wiping.

Ocular monitoring

As there was no standardized sampling method for ocular monitoring, a commercial product (Allergan "Refresh" having over 2% recovery rate of isocyanates in 4 minutes) was used for semi-quantitative ocular monitoring conducted immediately as soon as the spray painters had finished the spray painting. This was done by using a medical cotton tip wiping the corner of each eye.

2.3. Analysis

In order to avoid contamination by hands, disposable nitrile gloves were worn and tweezers were used for the sampling. All samples were reacted with 1-2MP in 10mL of derivative solution (500μg 1-2 MP in 1mL of acetonitrile) after sample collection. The reacted samples were stored in a cool container and safely transferred to the laboratory. Acetic anhydride (200 μL) was added after 24 hours, and left

for 30 minutes. The solution was evaporated under pure nitrogen gas. After that, 10mL of the dissolving solution (acetonitrile) was poured into each vial. For eye samples, 5mL was used.

The Health and Safety Executive method (HSE, MDHS, 25/3, UK) was used for isocyanate analysis. Retention times of monomeric and polymeric HDI were 3.08 minutes and 7.8 minutes respectively. Limits of detection were approximately 0.03μgNCO (EC) and 0.08μgNCO (UV) in the 10mL acetonitrile solution. If there is no detection of isocyanates from samples using the two detectors in HPLC, the results will be interpreted as limit of detection. The paper tape was slightly more sensitive (0.02μgNCO), based on dilution of standard HDI solutions.

There are no exposure criteria for dermal, surface and ocular exposure, except for airborne exposure (0.02mg/m^3 -8 hours TWA, 0.07mg/m^3 -15min STEL).

3. Results

3.1. Air monitoring

Personal airborne monitoring for both the spray painters and the spray paint mixer was carried out. Table 1 represents the monitoring results indicating insignificant exposure.

Table 1. HDI airborne exposure levels inside the spray booth

Personal I.D.	Total isocyanate (gNCO)	Sampling time (min)	Total air Volume (L)	Isocyanate conc. (gNCO/m^3)
F1	< 0.03	18	20	< 2.00
F2	< 0.03	200	200	< 1.00
F3	< 0.03	156	156	< 1.00
F3	< 0.03	390	390	< 1.00

< 0.03gNCO; limit of detection,
F1 & F2: Touch-up spray painter working inside the booth, F3: Spray paint mixer working in mixing area.

Table 2. HDI airborne exposure levels in general area

Site I.D.	Total isocyanate (gNCO)	Sampling time (min)	Total air Volume (L)	Isocyanate conc. (gNCO/m^3)
A1	< 0.03	440	440	< 1.00
A2	< 0.03	445	445	< 1.00
A3	< 0.03	445	445	< 1.00

< 0.03gNCO; limit of detection,
A1: Sampling at collecting room beside the spray booth, A2 & A3: Sampling outside the spray booth.

Table 3. HDI dermal exposure levels of the spray painters and the spray paint mixer

Personal I.D.	Sampling time (min)	Total isocyanate (gNCO)							
		N	FH	LBH	RBH	LP	RP	LW	RW
F1	4	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
F2	525	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
F3	240	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03

< 0.03gNCO; limit of detection,
F1 & F2: Touch-up spray painter working inside the booth, F3: Spray paint mixer working in mixing area.
N; Neck, LBH: Left back hand, RBH: Right back hand, LP: Left palm, RP: Right palm, FH: Forehead, LW: Left wrist, RW: Right wrist

Table 2 represents airborne exposure levels of fixed positions in general area. Monitoring locations were both beside the spray booth (the mixing area) and in the middle of the work area, located over 10m away from the spray booth. No measurable HDI was detected.

3.2. Dermal and surface monitoring

Dermal monitoring results for both the spray painters and the spray paint mixer are illustrated in Table 3. No measurable HDI was detected on the skin, even though some of their body regions (e.g. neck, forehead and wrists) were not fully protected as there were incorrect work practices including inappropriate PPE use.

Table 4 represents the monitoring results of surface samples. Door handles of the spray booth did not show any detectable contamination of HDI, and no measurable HDI was detected on the spray gun.

Table 5 represents the monitoring results of HDI permeation through the disposable nitrile gloves (Touch N Tuff^{TM}).

Table 4. HDI exposure levels of surface samples at both spray and mixing areas

Personal I.D.	Total isocyanate (gNCO)		
	SG	IDHSB	ODHSB
F1	< 0.03	< 0.03	< 0.03
F3	< 0.03	-	-

< 0.03gNCO; limit of detection,
F1: Touch-up spray painter working inside the booth, F3: Spray paint mixer working in mixing area.
SG: Spray gun, IDHSB: Inside door handle at spray booth, ODHSB: Outside door handle at spray booth

Table 5. Hand monitoring of the spray painters and the spray paint mixer wearing protective gloves (Touch N Tuff™)

Personal I.D.	Sampling time (minute)	Color reaction (P:positive, N:negative)			
		Left palm	Right palm	Left index	Right index
F1	7	N	N	N	N
F1	240	N	N	N	N
F2	180	N	N	N	P a
F3	95	N	N	N	N
F3	200	N	N	P b	P b
F4	220	N	N	P c	P d

F1 & F2 : Touch-up spray painter working inside the booth, F3: Spray paint mixer working in mixing area, F4: Spray painter and paint mixer. a: A hole was observed, b: Touched the fingers with thinner and acetone, c: Damaged glove surface by repeated work, d: A hole and damaged glove surface were observed.

The Permea-Tec™ Pads were attached on both palms and index fingers to measure HDI permeation through the gloves during working hours. There was no measurable HDI penetration through the gloves at up to 240 minutes (F1). However, when the gloves either had a small hole(s) or were torn after the sprayed wood panels were moved to either to the spray booth or the collecting room, positive results were detected from samples F2 and F4. Sample F3 had a positive result caused by frequent contact with a hardener container and solvents (e.g. thinners and acetone) used to clean up the spray gun and prepare the spray paint.

3.3. PPE monitoring

PPE monitoring of the spray painters was conducted with the half face respirator. No detectable HDI was found inside of the respirator, which was wiped after 4 minutes and 240 minutes.

3.4. Ocular monitoring

Ocular monitoring was conducted for both one spray painter and the spray paint mixer after finishing spray painting. Table 6 represents the results of the ocular monitoring. No measurable HDI was detected. Note that the spray paint mixer did not have any eye protection and that there was a low HDI concentration in the spray paint.

4. Conclusion

The results of inhalational, dermal and ocular monitoring of exposure to hexamethylene diisocyanate(HDI) were obtained from a company in the furniture industry in South Australia. In particular, this study has attempted to measure potential eye exposure to isocynates, which has not been previously conducted.

It appears that inhalational, dermal and ocular exposures are not likely to be considered as significant exposure routes to the spray painters and bystanders (e.g. $< 0.03\mu gNCO$ for inhalational, dermal and surface samples and $< 0.015\mu gNCO$ for ocular samples), due to appropriate PPE use, high volume low pressure (HVLP) spray guns and low concentration of HDI (around 0.1mgNCO/g liquid hardener)-based spray paints.

Both using a HVLP spray gun and providing a good ventilation system may control airborne concentrations of isocyanate inside the spray booth.

During the working processes like mixing and spraying, disposable nitrile gloves appeared to provide good hand protection. However, if there is continuous or repeated glove usage causing physical damage (Table 5), significant dermal exposure to iscyanates may occur through the gloves[15,16]. Furthermore, if there is a lack of care with taking off the gloves, skin contamination can also occur.

From the observation of the gloves, the parts of the gloves of the index and middle fingers were swollen. In the mixing area, spills of solvents and hardeners were observed. The mixing process should be carried out in a well ventilated space to protect bystanders from HDI exposure[17,18].

While there was no positive result of ocular exposure, appropriate eye protection like safety goggles would still be recommended for mixing of the paints, as well as the spraying process.

In general, in order to avoid cross contamination from surfaces and minimize exposure levels to HDI in the workplace, good work practices and appropriate PPE use is recommended. A regular educational program is also recommended.

From personal observation, the sprayers' lower arms, wrists, forehead, neck and chest were likely to be contaminated, due to inappropriate work practices. Therefore, these regions of the body should also be

measured as potential routes of dermal exposure. Also, ocular sampling methodology should be further developed.

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