

**UNITED STATES AIR FORCE
IERA**

**Assessing Worker Exposures During
Polyurethane Paint Application:
Industrial Hygiene Field Guidance for
Bioenvironmental Engineers**

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ASSESSING WORKER EXPOSURES DURING POLYURETHANE PAINT APPLICATION: INDUSTRIAL HYGIENE FIELD GUIDANCE FOR BIOENVIRONMENTAL ENGINEERS

INTRODUCTION

The U.S. Air Force uses polyurethane enamels to coat its weapon systems for both aesthetic and operational purposes, including camouflage and stealth characteristics. Polyurethane enamels contain isocyanates as a reactant. Exposures to isocyanates are of concern because they have been linked to skin, eye, mucous membrane, and respiratory tract irritation, and occupational asthma from sensitization [1-5]. Assessing worker exposures to isocyanates during polyurethane paint application can be challenging because of the reactive nature of the isocyanate functional group and the difficulty in derivatizing collected isocyanate before it reacts with another substance. As a result of these sampling and analysis difficulties, and the poor warning properties of some isocyanates, Air Force policy has, for a number of years, been to mandate the wear of airline respirators during polyurethane spray application [6]. Since this policy was promulgated in the 1980s, sampling and analytical methods have been improved and new isocyanate sampling techniques have been developed.

Using these improved methods, the Industrial Hygiene (IH) Branch of the Institute for Environment, Safety and Occupational Health Risk Analysis (IERA) recently completed an Air Force-wide assessment of worker exposures during polyurethane application. The results indicate overall worker exposures to isocyanates are low during these operations, and at levels that can be adequately controlled by air-purifying respirators with organic vapor cartridges and N95 filters (see Appendix A). As a result of recent changes to the OSHA respirator standard, which abandoned the warning property criteria for air-purifying respirators and replaced it with cartridge change-out schedules, we concluded the Air Force policy automatically requiring airline respirators during the spraying of isocyanate-containing paints was overly restrictive. Based on these findings, the Air Force Medical Operations Agency (AFMOA/SGOE) issued an interim policy change allowing workers to wear air-purifying respirators for protection against isocyanates if air sampling data was available to support this selection [7].

This technical report provides field guidance on assessing exposures to isocyanates during polyurethane painting. It is a compilation of information obtained through field studies at Air Force field units, Air Logistics Centers, and a Navy Air Depot; consultation with military, aerospace industry, and civilian industrial hygienists; collaboration with the National Institute for Occupational Safety and Health on evaluating isocyanate sampling methods; and contacts with personal protective equipment manufacturers.

DESCRIPTION OF POLYURETHANE PAINTS

The primary purpose of coating application is to protect the substrate (such as an aircraft surface) from corrosion or surface deterioration. Secondary considerations include aesthetic enhancement of the surface, ease of maintenance, and stealth characteristics. Modern painting systems may be a mixture of many things but the primary constituents are the pigment and the vehicle [8]. Pigments are finely divided, substantially insoluble, usually opaque materials incorporated into paints to impart color and provide specific properties such as heat reflectance or corrosion inhibition. The vehicle is the liquid portion of the coating including non-volatile and volatile constituents. The vehicle furnishes the desired qualities of adhesion, toughness, flexibility, and resistance to various environments.

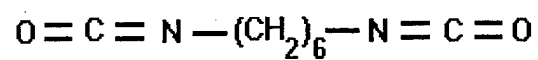
One of the most common organic coating systems used throughout the Air Force is polyurethane enamel. An example of an aircraft polyurethane enamel is MIL-PRF-85285, a high-solids polyurethane topcoat developed to comply with low volatile organic compound (VOC) air quality regulations [8]. The military specification (MIL-SPEC) defines the qualification and engineering parameters of the product. Several manufacturers may supply different products under the same specification, as well as under the same national stock number (NSN). The Deft Corporation and PRC-De Soto (Courtauld's) Aerospace provide the majority of these specification coatings to Air Force Structural Maintenance Shops [9].

Polyurethane coatings used in the Air Force are normally two component paints. The base component contains pigments, solvents, and alcohols. The catalyst component contains a hardener (also called a reactant) and various solvents (also called diluents). The hardener used almost exclusively in the Air Force is 1,6-hexamethylene diisocyanate (HDI). HDI is present in the catalyst component as either the monomer or a prepolymer. Monomers are individual diisocyanate molecules containing two free isocyanate groups (see Figure 1). The polyurethane paints used in the Air Force generally contain only a small fraction of the free HDI monomer, as the catalyst component is comprised almost exclusively of the prepolymer in the unreacted formulation. Prepolymers are species containing free isocyanate groups prepared from the reaction of a polyol with excess monomers. The most common prepolymers are HDI biuret or HDI isocyanurate (see Figure 1). They may be present in various ratios depending on who the manufacturer is or whether the paint is gloss or camouflage. When the base and hardener are mixed, the prepolymers react with the alcohols (diols) to form urethane cross-links and chains as shown in Figure 2 [10-12]. These chains and cross-links result in the tough, abrasion- and corrosion-resistant properties characteristic of polyurethane enamels [10].

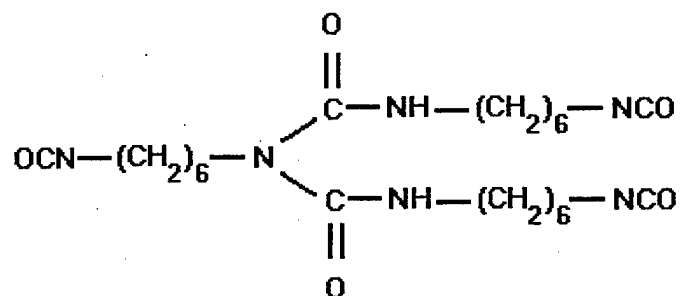
Workers in the Air Force apply polyurethane enamels with either conventional or high volume-low pressure (HVLP) compressed air paint spray guns that produce paint droplets. The droplets contain a mix of both the prepolymer and other partially reacted isocyanates, referred to in sum interchangeably as either polyisocyanates or oligomers, along with other paint components, including the pigments, alcohols, vehicle solvents, and isocyanate monomers. The more volatile free monomer and vehicle solvents exist in the vapor phase as well as in the aerosol.

Figure 1. Chemical Structures of the Monomer and Prepolymers of HDI

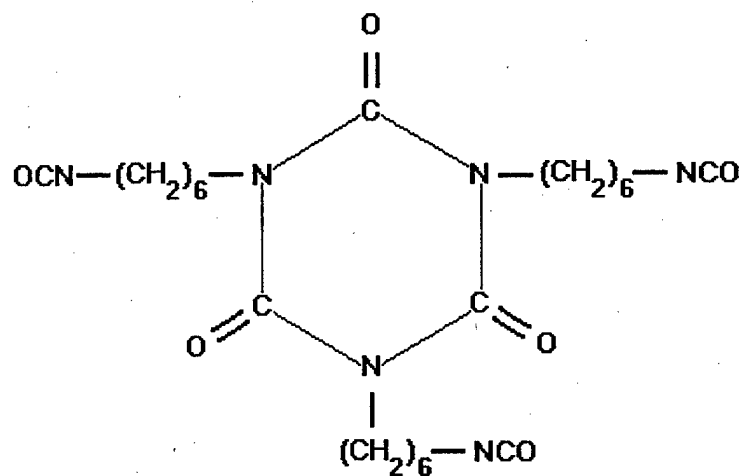
HDI Monomer:



HDI Biuret:



HDI Isocyanurate:



PAINTING PROCESS DESCRIPTION

There are two common methods of applying polyurethane paints in the Air Force: spray finishing and brush application.

Spray Finishing

There are typically four steps in the painting procedure when using two-component polyurethane systems.

Mixing: Adding the catalyst to the base component. Mixing involves thoroughly agitating the base component, usually using a mechanical shaker, and subsequently stirring the catalyst into the base using a wooden paddle (paint may also be mixed by an automatic in-line proportioning system). Components are mixed together according to the manufacturer's instructions. The most common mix ratios are: one part base to one part catalyst, or three parts base to one part catalyst. Manufacturers normally supply the two components in kits, with the correct volume of catalyst for the quantity of base. After mixing, a minimum dwell time (also called an induction time) of thirty minutes is required before spraying so curing can begin. The paint must be applied before its pot life is exceeded (usually two to four hours) or it will be too viscous to spray [8]. Inhalation exposures to the volatile components of the paint, solvents and HDI monomer, are possible during mixing, but will generally be limited because of the brevity of the mixing operation. Dermal exposures could occur to all paint constituents during the mixing process.

Thinning: Adding a solvent to the mixed paint system to decrease the viscosity. Some workers may thin a two-component coating system before spraying using an appropriate thinner to improve spray characteristics and final appearance. Paint viscosity is measured with a Zahn or Ford Cup [8], which is a metal or plastic cup with a small hole in the bottom. Paint is placed in the cup, and the time for the paint to run out of the cup is proportional to the viscosity. Inhalation exposures to thinner solvents and the volatile components of the paint are possible, but again will be limited because of the brevity of the operation. Dermal exposures could occur to all paint constituents during the thinning process.

Application: Spraying of the mixed/thinned coating onto the surface to be painted. Workers may spray coatings using either conventional, high volume-low pressure (HVLP), air-assisted airless, or electrostatic paint guns. The HVLP spray gun is the most widely used spray gun in the Air Force [9]. Workers add paint to a paint cup, a pressure pot, or to a proportioning system. The gun produces droplets of varying sizes that are propelled toward the surface of the weapon system by the force of compressed air. Droplets that fail to impact on the surface form the paint mist or overspray, which can become entrained in the air flow around the aircraft or parts and can be transported back into the worker's breathing zone. Inhalation exposures to components contained in the paint droplets, including HDI oligomers, are possible. In addition, the volatile components of the droplets (HDI monomer and organic solvents) can evaporate from the droplets into the vapor phase, resulting in worker exposures. Dermal exposures to paint constituents can occur if the paint mist contacts the worker.

Curing: Completion of the chemical reaction between the HDI catalyst and the base alcohol component with complete volatilization of the solvents. Curing rate depends upon the temperature and humidity of the painting location. Inhalation exposures to solvents are possible for workers remaining within the painting area. Inhalation exposures to HDI monomer and oligomers are negligible [13,14]. Dermal exposures are not anticipated unless workers touch the curing surface.

Brush Application

The most common polyurethane brush applicator used in the Air Force is the Sempen™. The Sempen resembles a magic marker with a small brush at one end. It contains a total of ten milliliters of a two-component polyurethane paint, with the base and catalyst in separate ampoules.

Mixing: Breaking the ampoules containing base and catalyst contained within the Sempen. After the ampoules are broken, the Sempen is shaken to thoroughly mix the base and catalyst. Worker inhalation and dermal exposures are minimal because the paint components are contained within a plastic tube.

Application: Brushing the polyurethane paint onto the surface being coated. The Sempen is designed to paint approximately one square foot [15]. Limited dermal and inhalation exposures to solvents are anticipated because of the brevity of the operation and the brush method of application.

Curing: Completion of the chemical reaction between the HDI catalyst and the base alcohol component with complete volatilization of the solvents. As with spray finishing, curing rate depends on the temperature and humidity of the painting location. Inhalation exposures to isocyanates and solvents are not anticipated. Dermal exposures are not expected unless workers touch the curing surface.

AIR SAMPLING METHODOLOGY

During polyurethane painting operations, workers can be exposed to solvents and HDI monomers that evaporate from the paint, as well as HDI oligomers contained in the paint overspray. To adequately assess exposures to isocyanates, both the free monomer and the oligomeric fractions must be measured. There are five sampling methods you can use to measure isocyanates. The one you choose depends on the procedure you're sampling and to some degree on personal preference. Table 1 compares the different methods. The reader is referred to the NIOSH Manual of Analytical Methods for a more complete discussion of isocyanate sampling methodology [16].

NIOSH 5521

This method was originally developed only for isocyanate monomer, however, since the method was published means have been developed to also analyze for the oligomers [17]. Samples are collected with an impinger containing the derivatizing agent 1-(2-methoxyphenyl)-piperazine in toluene. Collected isocyanate is derivatized to the corresponding urea during sampling, which is subsequently analyzed by the analytical laboratory. You should be aware impinger methods have certain disadvantages. Toluene, the primary content of the impinger fluid, is volatile and must be replenished periodically during sampling if the impinger solution falls below 10 milliliters so loss of analyte does not occur. Spilling may occur with traditional impingers, potentially exposing personnel to the impinger fluid and the analyte. We've found spill-proof impingers are best for use during spray finishing; a picture is shown in Figure 3. Another disadvantage is poor aspiration efficiency for the inhalable portion of the spray aerosol, causing paint to accumulate on the impinger straw inlet and at the tip of the jet, causing material losses and underestimating worker exposure. Impingers are also known to be less efficient at collection of condensation aerosols (<0.2 μm diameter) that may be formed during spray painting operations.

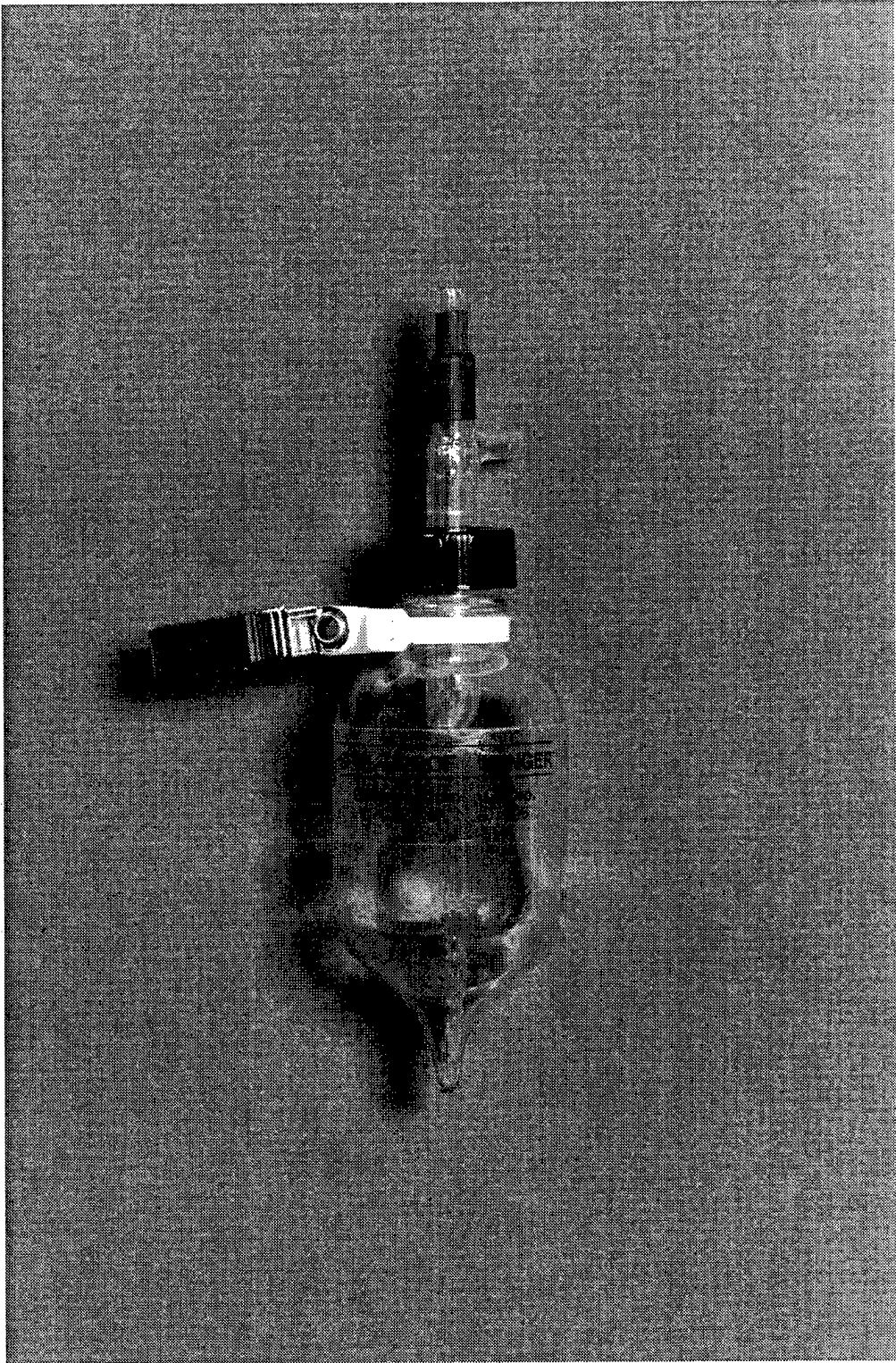
You can formulate the impinger solution at your base by adding 43 milligrams of purified, liquid reagent grade 1-(2-methoxyphenyl)-piperazine (available from Fluka Chemical, 1-800-558-9160) to one liter of High Performance Liquid Chromatography (HPLC) reagent grade toluene (available from Fisher Scientific, 1-800-766-7000) [18]. High purity chemicals are necessary so the impinger solution is not contaminated. Contract analytical laboratories will also mix the impinger solutions at your request for a fee. Sample at a rate of 1.0 L/min. After sampling, transfer the impinger solution to a clean vial. Rinse the impinger and jet with two to three milliliters of HPLC grade toluene and add the rinsate to the sample for analysis. Provide field blanks of the impinger solution to the analytical laboratory. Refrigerate the sample and the blanks as soon as possible after sampling. When requesting an oligomer analysis, a bulk of the catalyst and a copy of the Material Safety Data Sheet is required.

If you use NIOSH 5521, proper cleaning of impingers is required. Impingers and jets should be rinsed with tap water, soaked overnight in tap water and Alconex or another glassware detergent, triple rinsed with tap water, and then triple rinsed with distilled water. The impingers should be dried, preferably in a 300 degree Fahrenheit oven [19]. No water can be present in the impinger during sampling; water will react with isocyanates, destroying subsequent isocyanate samples.

Table 1. Comparison of HDI Sampling Methods

	NIOSH 5521	NIOSH 5522	Iso-Chek	OSHA 42	TAMM (NIOSH 0500)
Monomer	Yes	Yes	Yes	Yes	No
Oligomer	Yes	Yes	Yes	No	Yes
Personal	Yes	No	Yes	Yes	Yes
Sampler	impinger	impinger	PTFE + coated GFF	coated GFF	5- μ m PVC
Reagent	MOPP in toluene	tryptamine in DMSO	MAMA/MOPP	1-2PP	None
Sampling Rate	1 L/min	1-2 L/min	1 L/min	1 L/min	1-2 L/min
Sampling Volume	5-500L	15-360L	15-30L	15L	7-133L
Operation					
Mixing	Yes	Yes	No	Yes	No
Thinning	Yes	Yes	No	Yes	No
Spray application	Yes	Yes	Yes	No	Yes
Curing	Yes	Yes	No	Yes	No
Sempen usage	Yes	Yes	No	Yes	No

Figure 3. Spill-Proof Impinger



NIOSH 5522

This method was developed specifically to measure both the monomer and oligomer. As with NIOSH 5521, it samples with an impinger, but uses the derivatizing agent tryptamine in dimethyl sulfoxide (DMSO) [20]. Although DMSO does not pose an exposure hazard, this solvent carries chemicals readily through the skin. Therefore, skin exposure to solutions of DMSO containing isocyanates should be avoided. NIOSH recommends the method be used only for area monitoring. If you use a spill-proof impinger, however, the chance of skin exposure is very limited, so you can consider using NIOSH 5522 for personal sampling. Since this method uses impingers, it has the same disadvantages as discussed for NIOSH 5521.

Specialized equipment is required to make the impinger solution. Because most Bioenvironmental Engineering offices don't have this equipment, you'll have to obtain the solution from a contract lab. Sample at 1.0 L/min. After sampling, transfer the impinger solution to a clean vial. Rinse the impinger and jet with two to three milliliters of clean impinger fluid and add the rinsate to the sample for analysis. Provide field blanks of the impinger solution to the analytical laboratory for analysis. If requesting oligomer analysis, a bulk of the catalyst and a copy of the Material Safety Data Sheet is required. The impinger requires cleaning after sampling as outlined for NIOSH 5521.

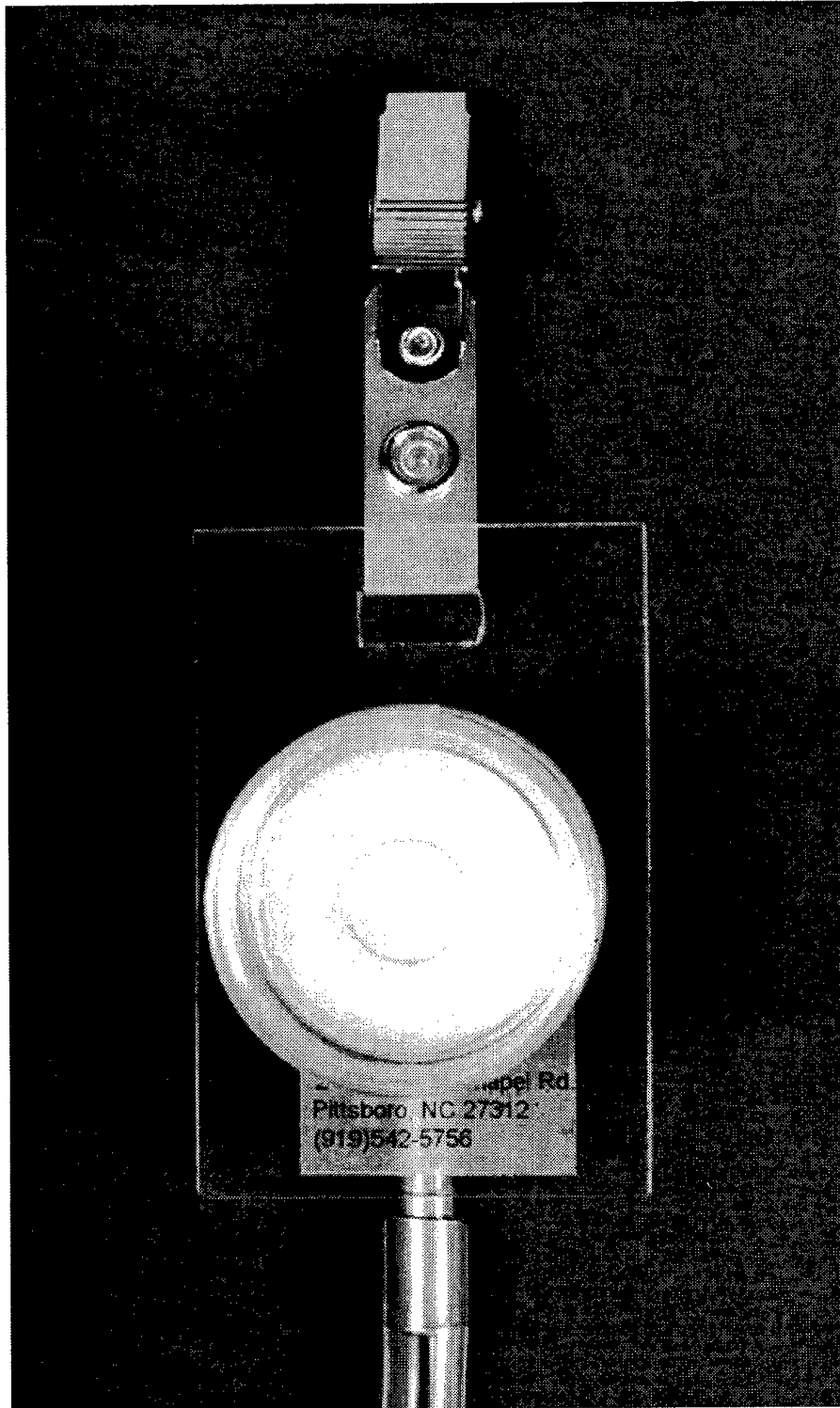
Iso-Chek™

The Iso-Chek™ method samples for both monomer and oligomers. It draws air through a three-stage 37-mm cassette containing two filters. The first filter, a 5- μ m teflon (PTFE) filter, collects the paint aerosol. After sampling, the teflon filter is placed in a 5-ml solution of 1-[2-methoxyphenyl] piperazine in toluene. Monomer and oligomer species react with the derivatizing reagent to form urea derivatives. The second filter, a glass fiber filter impregnated with 9-[N-methylaminomethyl] anthracene (MAMA), captures and derivatizes the HDI monomer in the vapor phase. The piperazine solution and the glass fiber filter are sent to an analytical laboratory for analysis. The lab desorbs the glass fiber filter and analyzes for the monomer fraction. Desorption solution from the teflon filter is analyzed for the oligomer fraction [21].

Because the spray aerosol contains a significant portion of its mass in the inhalable size range, sampling in closed-face mode will result in sampling bias and an underestimation of the exposure. We recommend you modify the cap by drilling a 15-mm hole in it to better collect the inhalable mass fraction [22]. We also recommend you use a special cassette holder designed to keep the face of the cassette parallel to the worker's body. This configuration reduces particulate sampling bias from sampler orientation [23]. A picture of three-piece cassette with the modified cap and cassette holder is shown in Figure 4. Sample at a flow rate of 1.0 L/min with a maximum sampling time of 30 minutes. If you sample longer than 30 minutes, isocyanates collected on the teflon filter will begin to cure before you have a chance to derivatize them. If the spraying operation lasts longer than 30 minutes, you'll have to use several Iso-Chek samplers to sample the entire operation. IERA/ Occupational Chemistry Branch has the capability to analyze Iso-Chek samples.

The Iso-Chek samplers, derivatizing agent, and cassette holders can be obtained through Omega Specialty Instrument Company (1-800-346-8253). Current cost (June 1999) is \$170 for ten samplers with derivatizing agent. Cassette holders are \$42.50 for five. Because of the cost, we don't recommend Iso-Chek use for monomer-only sampling.

Figure 4. Three-Piece Cassette With Modified Cap and Holder



OSHA 42

This method uses a glass fiber filter treated with derivatizing agent 1-(2-pyridyl)piperazine [24]. The derivatizing agent reacts with isocyanate monomers in the vapor phase. In addition, derivatizing agent may react with a fraction of the oligomers in the paint mist droplets that contact the filter. Because of the physical arrangement of the individual filter fibers, not all the free isocyanate in the droplet will contact the derivatizing reagent impregnated on the filter. Therefore, some of the unreacted isocyanate will not be derivatized, leading to an underestimation of the isocyanate exposure [25]. Therefore, OSHA 42 is not recommended for oligomer sampling but is more suited to measuring monomer concentrations, as found during mixing, thinning, and curing processes. OSHA 42 is similar to OSHA 47, the main difference being the amount of derivatizing agent applied to the filter.

Filters are placed in three-piece 37-mm cassettes, available from the IERA/Occupational Chemistry Branch. Filters require refrigeration prior to sampling. Sample at 1.0 L/min in open-face mode. After sampling is complete, cap the cassette and send it to IERA for analysis.

Total Aerosol Mass Method

The total aerosol mass method (TAMM) uses collected aerosol mass to estimate the oligomer concentration. Total aerosol mass samples are collected with three-piece 37-mm sampling cassettes. Sampling media is 5- μ m polyvinyl chloride filters. The filters are weighed before and after the painting procedure per NIOSH Method 0500 to determine the total mass of solids collected. Oligomer concentrations are estimated from the weight percentage of prepolymer and paint solids in the paint using the following formula:

$$C_{\text{oligomer}} = \frac{\text{mass solids collected}}{\text{sampling volume}} \times \frac{\text{mass prepolymer in paint}}{\text{mass solids in paint}} \quad (1)$$

where:

$$\frac{\text{mass prepolymer in paint}}{\text{mass solids in paint}} = \frac{(\text{Volume}_{\text{catalyst}})(\text{SG}_{\text{catalyst}})(\% \text{Prepolymer}_{\text{catalyst}})}{(\text{Volume}_{\text{catalyst}})(\text{SG}_{\text{catalyst}})(\% \text{Prepolymer}_{\text{catalyst}}) + (\text{Volume}_{\text{base}})(\text{SG}_{\text{base}})(\% \text{Solids}_{\text{base}})} \quad (2)$$

and SG is the specific gravity of the specific components. The total aerosol mass method assumes that all prepolymers present in the paint and collected on the filter are unreacted. Because the paint begins to cure immediately upon mixing, resulting in a mix of reacted and unreacted isocyanate groups, this assumption causes an overestimation of the oligomer concentration. The TAMM therefore represents a theoretical upper limit on oligomer exposures.

As discussed before with the Iso-Chek sampler, drill a hole in the cap of the cassette top to improve collection of the inhalable mass fraction, and use a cassette holder designed to keep the cassette face parallel to the worker's body [22,23]. Sampling painting operations in closed-face mode with the cassette directed downward will seriously underestimate worker exposures. The cassette holder and modified cap are shown in Figure 4. The cassette holders can be obtained from Omega Specialty (1-800-346-8253). Sample at 2.0 L/min. Analyze the filters per NIOSH Method 0500, which requires pre- and post-weighing filters with a 0.001 mg sensitivity scale [26]. If you don't have a scale with this sensitivity, use match-weighted filters and submit for analysis.

Solvents

Paint formulations contain a variety of solvents. Based on the constituents in the paints used at your base, use the appropriate NIOSH sampling method [27]. The methods are listed in the NIOSH Manual of Analytical Methods; most are available on the NIOSH web site at <http://www.cdc.gov/niosh/nmam/nmampub.html>. Note that some solvents have short-term exposure limits (STEL) and therefore require short-term sampling.

Recommended Sampling Methodology

Table 2 summarizes our recommended sampling methods for specific painting procedures. These recommendations are based on our experience sampling numerous painting operations throughout the Air Force and our collaboration with NIOSH. They reflect what we believe are the best methods for Bioenvironmental Engineers to evaluate these operations.

Table 2. Recommended Isocyanate Sampling Methodology

Operation	Substance	Sampling Method	Sampling Media	Sample Flow Rate (lpm)
Mixing	HDI monomer	OSHA 42	Impregnated glass fiber filter	1.0
	Solvents	NIOSH Method ^a	Variable	0.2
Thinning	HDI monomer	OSHA 42	Impregnated glass fiber filter	1.0
	Solvents	NIOSH Method ^a	Variable	0.2
Spray application	HDI monomer/oligomer	Iso-Chek ^b	Iso-Chek sampler with 15-mm hole drilled in cap, cassette holder	1.0
	HDI oligomer (estimate)	TAMM	5-µm PVC filter, 37-mm cassette with 15-mm hole drilled in cap, cassette holder	2.0
	Solvents	NIOSH Method ^a	Variable	0.2
		OSHA 42	Impregnated glass fiber filter	1.0
Curing	Solvents	NIOSH Method ^a	Variable	0.2
	HDI monomer	OSHA 42	Impregnated glass fiber filter	1.0
Sempen usage	HDI monomer	OSHA 42	Impregnated glass fiber filter	1.0
	Solvents	NIOSH Method ^a	Variable	0.2

^aSpecific method depends on solvents contained in the paint formulation

^bIso-Chek samplers should not be used for more than a thirty minute sampling time

ISOCYANATE ANALYTICAL CHEMISTRY

HDI Monomer

HDI monomer samples are analyzed by reversed-phase high performance liquid chromatography (HPLC). HPLC involves the high-pressure flow of a liquid mobile phase through a metal tube (column) containing a stationary phase, with electronic detection of mixture components occurring on the effluent end [28]. Two detectors in series analyze for the monomer, an ultraviolet (UV) detector (242 nanometers) and an electrochemical (EC) detector (+0.8 V vs. Ag/AgCl). The more sensitive EC detector is used for quantification. The resulting signal is displayed as peaks on a strip-chart recorder. The retention time in the column identifies the substance while the peak height is proportional to the quantity of substance present. For HDI monomer, the amount of the urea derivative resulting from derivatization of the isocyanate is measured and related to the number of isocyanate groups present. Since HDI monomer is a pure compound with a known, consistent molecular weight, the number of isocyanate groups is related to the mass of monomer present. The analytical results are reported as "milligrams HDI monomer."

HDI Oligomers

Oligomers are measured by a photodiode array (PDA) detector. Oligomer concentrations are determined by comparing the PDA UV spectra of the HPLC peaks with an established PDA UV reference spectrum for the derivatized monomer. HDI oligomer values are reported as "HDI oligomer as monomer." This value indicates how much mass there would be if the oligomers had the same equivalent weight as the monomer. But oligomers don't have the same equivalent weight as the monomer. The equivalent weight of HDI monomer is 84; the equivalent weight of HDI biuret is 191 while the equivalent weight of HDI isocyanurate is 195. This means that an oligomer sample containing the same number of isocyanate groups as a monomer sample will weigh about 2.3 times as much. To properly interpret HDI oligomer results so they may be compared to an occupational exposure limit, the analytical results must be multiplied by 2.3 to account for the differences in the equivalent weights of HDI monomer and oligomer [29]:

$$C_{\text{oligomer}} (\text{actual}) = C_{\text{oligomer}} (\text{as monomer}) \times \frac{\text{equivalent weight of oligomer}}{\text{equivalent weight of monomer}} \quad (3)$$

If a different type of HDI prepolymer is in the paint formulation besides HDI biuret or isocyanurate, you'll have to find out the equivalent weight of the prepolymer in use. TAMM estimates oligomer concentrations directly from the prepolymer mass, so multiplication by the ratio of equivalent weights is unnecessary if you use that method.

DATA EVALUATION

Process Timelines

Sample each painting task separately. Sample as many workers involved in the task as possible. Make sure to record a timeline during each procedure, specifically the time the workers actually perform the procedure (task length). The task length is not necessarily the time the sampling pumps were turned on and off, since workers tend to take breaks or do other work during the procedures.

Calculating Exposures

Using the mass of analytes reported from the sampling method you used, calculate both the task exposure and the 8-hr time-weighted average (TWA) exposure. The task exposure is the average concentration over the length of the task, and is useful for determining effectiveness of engineering controls and respiratory protection. For example, engineering controls that keep task exposures below the 8-hr TWA exposure limit will protect the worker even if an operation is performed for an entire eight-hour work day. Use the following equations to calculate exposures (Note: some labs report task exposures directly):

$$\text{Task Exposure} = \frac{(\text{mg contaminant})(10^3 \text{ L/m}^3)}{(\text{sampling rate [L/min]})(\text{task length [min]})} \quad (4)$$

$$8\text{-hr TWA} = (\text{Task Exposure}) \times \frac{(\text{task length [min]})}{(480 \text{ min})} \quad (5)$$

Comparison to Exposure Standards

The ACGIH TLVs, NIOSH RELs, and OSHA PELs for most of the substances you'll encounter during polyurethane painting operations are shown in Table 3 [30-32]. There is no ACGIH TLV for HDI polyisocyanates. The State of Oregon has set an exposure limit of 0.5 mg/m³ as an 8-hr TWA for HDI polyisocyanates with a ceiling limit of 1 mg/m³ [33]. OSHA has not set regulatory limits for either HDI monomer or HDI-based polyisocyanates. Note: If you encounter a chemical that does not have an established exposure limit, that does not preclude air sampling. Air sampling is needed to document exposures in case an exposure standard is adopted in the future and to determine the effectiveness of engineering controls.

Table 3. Exposure Limits for Common Substances Encountered During Painting Operations (mg/m³)

Substance	ACGIH TLV		NIOSH REL			OSHA PEL		
	15-min STEL	8-hr TWA	Ceiling	15-min STEL	8-hr TWA	Ceiling	10-min STEL	8-hr TWA
HDI monomer	--	0.034	0.14	--	0.035	--	--	--
HDI oligomer	--	-- ^a	-- ^b	--	-- ^a	-- ^b	--	-- ^a
n-Butyl acetate	950	713	--	950	710	--	--	710
Ethyl acetate	--	1440	--	--	1400	--	--	1400
Methyl n-amyl ketone	--	233	--	--	465	--	--	465
Methyl ethyl ketone	885	590	--	885	590	--	--	590
Methyl isobutyl ketone	307	205	--	300	205	--	--	410
Toluene	--	188	--	560	375	300	500	200
Xylenes	651	434	--	655	435	--	--	435

^bState of Oregon has an 8-hr TWA of 0.5 mg/m³

^aState of Oregon has a ceiling limit of 1.0 mg/m³

VENTILATION DURING AIRCRAFT PAINTING

Facilities With Limited Ventilation

Many painting facilities in the Air Force were not designed for painting although they are used as such, e.g., aircraft hangars. It is important to realize that the primary purpose of ventilating painting operations is to prevent the build-up of potentially explosive vapors and aerosols (controlling exposures is a secondary consideration). Hangars that were not designed as painting facilities must be evaluated and approved by Fire, Safety, and Bioenvironmental Engineering as required by T.O. 42A-1-1 [34]. To assist you in evaluating whether an explosion hazard exists during aircraft painting, an example calculation is in Appendix B.

Air Flow Configuration

Our evaluations indicate crossdraft ventilation designs provide better capture of the paint overspray during full-aircraft painting compared to downdraft configurations. The aircraft blocks laminar air flow in a downdraft booth, resulting in negative pressure gradients underneath the aircraft where the workers spend considerable time during corrosion procedures. These negative pressure gradients can cause the contaminants to reverse-flow into the worker's breathing zone, increasing the exposure [35]. This reverse-flow can also impact the quality of the coating appearance, causing repaints and additional exposures. In a crossdraft configuration the aircraft has a smaller signature to the air flow and negative pressure gradients will not be produced in the areas the worker is spraying, resulting in lower overall worker exposures.

Air Flow Measurement

To properly evaluate painting facilities, take air velocity readings at the cross section of the booth without the aircraft inside. An average air velocity of 100 feet per minute is recommended [36]. Smoke testing with the ventilation system on and the aircraft in-dock can indicate whether contaminants in the painting facility are being effectively removed or recirculated. Perform smoke tests at the entrances and exits to the painting facility to determine whether the painting area is under positive or negative pressure. Painting areas should always be under negative pressure to limit potential explosive hazards [37].

Adjacent Areas

Painting operations are sometimes conducted in hangar areas adjacent to office work areas. In these instances, complaints are often heard from individuals working in these areas. One way to avoid complaints and protect those not involved in the painting task is to accomplish the painting task after normal duty hours. If painting must be performed during normal duty hours, determine air flows into and out of the administrative areas. Administrative areas adjacent to the painting area should have a positive pressure relative to the painting area. Consider taking air samples in the administrative areas to determine the concentrations of solvents present.

RESPIRATORY PROTECTION

Our minimum recommended respiratory protection requirements for polyurethane painting are shown in Table 4.

Background

Previous polyurethane paint formulations contained large percentages of monomeric isocyanates. When these formulations were prevalent years ago, the odor thresholds of some of these isocyanates were above the existing exposure limits. In the original OSHA respirator standard issued in 1971, odor detection was the primary method of determining when to change air-purifying organic vapor cartridges. Airline respirators were recommended for substances, including some isocyanates, having odor thresholds above the exposure limit. There have been substantial changes in polyurethane paint formulations in the last ten years. Most modern polyurethane enamels the Air Force uses today contain less than one percent HDI monomer. In addition, the recently updated OSHA respirator standard no longer includes odor threshold as a criteria for replacing cartridges [38]. As a result, there is no longer a valid reason to wear airline respirators during spray finishing operations.

HDI Monomer

Laboratory and field studies indicate that monomeric isocyanates in the vapor phase are effectively controlled by organic vapor cartridges [11,39]. Therefore, an organic vapor cartridge respirator will provide sufficient protection against HDI monomer up to a level equal to the assigned protection factor (APF) of the respirator times the exposure limit. A powered air-purifying respirator (PAPR) with a hood (APF = 25) can be used up to a maximum 8-hr TWA of 0.85 mg/m³; a full-face air-purifying respirator (APF = 50) will provide adequate protection up to 1.7 mg/m³ [40]. The exposures you'll find at your base will, in all likelihood, be well below these levels. As a result, organic vapor cartridge respirators provide sufficient protection against the HDI monomer.

HDI Oligomers

HDI oligomers are non-volatile and are present exclusively in the paint mist. Therefore, to protect against the oligomer, it is necessary to collect the paint mist. The mass median aerodynamic diameter (MMAD) of paint mists generated during spray painting operations have been found to range from 15 to 20 micrometers (µm) [23]. N95 filters provide adequate capture of aerosols with a MMAD greater than 2-µm [30]. Because the MMAD of the paint mist is greater than 2-µm, the paint mist, and therefore the HDI oligomers, will be effectively captured by an N95 filter. A recent study confirmed N95 filters effectively remove isocyanate aerosols [41]. Based on the Oregon exposure standard, a hooded PAPR will protect against oligomers up to an 8-hr TWA of 12.5 mg/m³, well above any levels you'll likely find at your base.

Solvents

Although our sampling results indicate an organic vapor cartridge is not strictly needed for protection against the HDI monomer, it is still prudent to wear one during spray painting operations. HDI

Table 4: Minimum Recommended Controls and PPE for Polyurethane Painting Operations^a

Operation	Engineering Controls	Personal Protective Equipment						
		Respiratory	Hand	Ear	Eye	Body	Foot	
Mixing	General dilution ventilation	None	Disposable nitrile gloves	None ^b	Safety goggles or faceshield	Cotton or Tyvek coveralls	Safety toe boots	
Thinning	General dilution ventilation	None	Disposable nitrile gloves	None ^b	Safety goggles or faceshield	Cotton or Tyvek coveralls	Safety toe boots	
Spray application	Paint spray booth/facility	Half-face air-purifying w/ OV/N95 filters ^c	Disposable nitrile gloves	None ^b	Safety goggles ^d	Cotton or Tyvek coveralls	Safety toe boots	
Curing	General dilution ventilation	None	None	None ^b	None	None	Safety toe boots	
Sempen usage	General dilution ventilation	None	Disposable nitrile gloves	None ^b	None	None	Safety toe boots	

^aLocal Bioenvironmental Engineer may recommend more restrictive controls or PPE based on exposure monitoring

^bHearing protection may be required in locations where hazardous noise is produced from other sources

^cA powered air-purifying respirator with hood may be the best choice for spray paint application

^dNot required if a full-facepiece or hooded respirator is worn

oligomers are non-volatile and will therefore remain on the N95 filter until the isocyanate fully reacts. The solvents in the paint aerosol, however, are volatile. These solvents will evaporate from the filter as a result of air being drawn across it, either by the worker's breathing or, in the case of a PAPR, a blower, possibly leading to a significant exposure. Therefore, an organic vapor cartridge is desirable whenever spray painting. An air-purifying respirator with organic vapor cartridges and N95 filters will provide adequate protection in most situations. The potential for eye contact with the paint mist makes a full-face or hooded air-purifying respirator a better choice over a half-face respirator, unless some sort of eye protection can be worn without affecting the facepiece seal.

Powered Air-Purifying Respirator (PAPR)

A good solution to many of the respiratory protection needs of Structural Maintenance workers is the PAPR with hood [42]. PAPRs consist of a cartridge, blower, and battery pack that mount on the worker's belt. Air is provided to the worker through a breathing tube fitted to either a tight-fitting facepiece or a loose-fitting respiratory inlet covering. The loose-fitting hood completely covers the head and neck and may cover portions of the shoulders (see Figure 5). The loose-fitting hooded PAPR offers several benefits compared to a tight-fitting facepiece. Hoods don't require either fit-testing or positive/negative seal (fit) checks before use, reducing workload for BEEs and training time for workers. Hoods provide a wider field of view and better peripheral vision. They allow civilians to wear beards and glasses, increasing their acceptance. Air flow into the hood provides cooling and makes it more comfortable to wear than a tight-fitting facepiece in hot environments. There are no valves, straps, or rubber facepieces to inspect and wear out. Most hoods are disposable, reducing the time needed to clean the respirator.

Cartridge Change-Out Schedule

The new OSHA Respirator Standard, as mentioned above, no longer designates odor breakthrough as the primary criteria for cartridge change-out. Air-purifying respirators now require either an end-of-service-life indicator (ESLI) or formal change-out schedule based on chemical concentrations in the workplace and the adsorptive properties of the cartridge. As there is currently no ESLI for isocyanates (although they are under development), you must implement a formal change-out schedule. Modeling of cartridge breakthrough is not a new concept and is discussed extensively in the literature [43-45]. Some respirator manufacturers have applied these models and developed breakthrough guidance for their specific cartridges, while others are developing guidance in response to the OSHA Standard. For example, the 3M Corporation has developed a database and software program entitled "3M Respirator Service Life Software," available free at the 3M web site (www.mmm.com/occsafety) [46].

Figure 5. Powered Air-Purifying Respirator



OTHER PERSONAL PROTECTIVE EQUIPMENT

Our minimum recommended PPE requirements for polyurethane painting are shown in Table 4.

Coveralls

Workers should always wear either cotton or Tyvek® coveralls when mixing, thinning, and applying paint to reduce the potential for skin contact with the paint. Disposable coveralls such as Tyvek® ensure contaminated protective equipment will not be reused. Workers, however, generally prefer to use cotton coveralls because they are cooler to wear.

Gloves

Workers should always wear gloves when mixing, thinning, and applying paint. Disposable nitrile gloves provide adequate protection against paint overspray containing solvents and HDI [47,48]. Disposable nitrile gloves provide workers better manual dexterity than leather, cloth, or reusable rubber gloves. Note: If the workers use a gun cleaning compound to clean their spray guns, the solvents typically in gun cleaners require a different glove than disposable nitrile. Contact the manufacturer for the most appropriate glove to wear with the specific gun cleaner in use.

Head and Foot

If workers do not wear coveralls with hoods, a paint sock should be worn during paint application to keep paint aerosol from contacting skin on the head and neck. Safety toe boots should always be worn in industrial work areas [49].

WORKPLACE PRACTICES

Spray Gun Air Cap Pressures

Workers should maintain spray gun air cap pressures and compressed air input pressures at levels recommended by the manufacturer. The transfer efficiency of a spray gun (the fraction of the spray droplets that impact on the part being painted) is influenced by the input air pressure and the resulting air cap pressure. High input air pressures results in high air cap pressures, producing an overall smaller droplet size distribution of the spray [23]. All other factors being equal, a smaller droplet size distribution will result in lower transfer efficiencies and increased exposures. Proper air cap pressures limit overspray generation. The recommended pressure at the air cap for HVLP guns (the most common in the Air Force) is 10 pounds per square inch absolute (psia). Spray gun manufacturers make air cap connectors that allow the workers to measure the pressure at the air cap. Structural Maintenance should maintain and use air cap connectors for each type of spray gun used in the shop.

Worker Movement

Workers' exposures during painting greatly depend on their technique. Whenever possible, only one worker should paint in a facility at a time. If this is not possible, workers should position themselves while painting to avoid spraying directly at each other. When painting in a crossdraft facility workers should avoid spraying in an upwind direction and spray with their back or sides to the air flow. Spraying with back or sides to the air flow will help to reduce exposures to paint overspray [23,50].

Hygiene

To control the movement of chemicals out of the work area, workers should remove dirty coveralls before exiting the work area. Workers should not eat or drink in areas where paint is being mixed, thinned, or applied. Workers should wash their hands and face after applying paint and before consuming food or drink. Another good practice is to shower at the end of the work day.

REFERENCES

1. R. Von Burg: "Toxicology Update: Hexamethylene Diisocyanate." *Journal of Applied Toxicology*, 13:435-439 (1993).
2. O. Vandenplas, A. Cartier, J. Lesage: "Prepolymers of Hexamethylene Diisocyanate As a Cause of Occupational Asthma." *Journal of Allergy and Clinical Immunology*, 91(4):850-861 (1993).
3. J.S. Ferguson, M. Schaper, Y. Alarie: "Pulmonary Effects of a Polyisocyanate Aerosol: Hexamethylene Diisocyanate Trimer (HDI₃) or Desmodur-N (DES-N)." *Toxicology and Applied Pharmacology*, 89:332-346 (1987).
4. P. Séguin, A. Allard, A. Cartier, J. Malo: "Prevalence of Occupational Asthma in Spray Painter Exposed to Several Types of Isocyanates, Including Polymethylene Polyphenylisocyanate." *Journal of Occupational Medicine*, 29(4): 340-344 (1987).
5. J. Nielson, C. Sangö, G. Winroth: "Systemic Reactions Associated with Polyisocyanate Exposure." *Scandinavian Journal of Work and Environmental Health*, 11:51-54 (1985)
6. Air Force Occupational Safety and Health Standard 48-1, *Respiratory Protection Program* (25 February 1994).
7. AFMOA/SGOE Letter: *Interim Guidance, Respiratory Protection Requirements During Spray Painting with Isocyanate-Containing Paints* (24 June 1999).
8. T.O. 1-1-8, *Application and Removal of Organic Coatings, Aerospace and Non-Aerospace Equipment*, 1 September 89; with change 17 dated 18 July 1997.
9. Personal Correspondence, Chief Owen Jett and Mr John Lindsey, Air Force Corrosion Prevention and Control Office (April 1999).
10. A. Maitre, A. Deplay: "Comparison Between Solid Sampler and Impinger for Evaluation of Occupational Exposure to 1,6-Hexamethylene Diisocyanate Polyisocyanates During Spray Painting." *American Industrial Hygiene Association Journal*, 57:153-160 (1996).
11. C. Rosenberg, T. Tuomi: "Airborne Isocyanates in Polyurethane Spray Painting: Determination and Respirator Efficiency." *American Industrial Hygiene Association Journal*, 45(2):117-121 (1984).
12. T. Solomons: *Organic Chemistry*, 5th ed. John Wiley and Sons, Inc., New York, NY (1992).
13. Det 1 HSC/OEMI Consultative Letter: *Isocyanate Exposures and Respiratory Protection Requirements During Fuel Cell Polyurethane Coating Operations, Hill AFB, UT*. AL-OE-BR-CL-1998-0048 (20 March 98).
14. Armstrong Laboratory: *Hill Air Force Base Isocyanate Study Field Notes*. Hill AFB, UT (July 1997).
15. Personal Correspondence, Technical Division, Courtauld's Aerospace (April 1999).

16. R.P. Streicher, C.M. Reh, R. Key-Schwartz: "Determination of Airborne Isocyanate Exposure" in *NIOSH Manual of Analytical Methods*, 4th ed. DHHS (NIOSH) Publication No. 94-113. NIOSH, Cincinnati, OH (1994).
17. R. Key-Schwartz: "Analytical Problems Encountered with NIOSH Method 5521 for Total Isocyanates." *American Industrial Hygiene Association Journal*, 56:474-479 (1995).
18. National Institute for Occupational Safety and Health: "Isocyanates, Monomeric: Method 5521" in *NIOSH Manual of Analytical Methods*, 4th ed. DHHS (NIOSH) Publication No. 94-113. NIOSH, Cincinnati, OH (1994).
19. Personal Correspondence, Dr Rosa Key-Schwartz, National Institute for Occupational Safety and Health (February 1997).
20. National Institute for Occupational Safety and Health: "Isocyanates: Method 5522" in *NIOSH Manual of Analytical Methods*, 4th ed. DHHS (NIOSH) Publication No. 94-113. NIOSH, Cincinnati, OH (1994).
21. J. Lesage, N. Goyer, F. Desjardins: "Workers' Exposure to Isocyanates." *American Industrial Hygiene Association Journal*, 53(2):146-153 (1992).
22. J. Vincent, D. Mark: "Entry Characteristics of Practical Workplace Aerosol Samplers in Relation to the ISO Recommendations." *Annals of Occupational Hygiene*, 34(3):249-262 (1990).
23. G. Carlton, M. Flynn: "Influence of Spray Painting Parameters on Breathing Zone Particle Size Distributions." *Applied Occupational and Environmental Hygiene*, 12(11):744-750 (1997).
24. Occupational Safety and Health Administration: "Diisocyanates: Method 42" in *OSHA Analytical Methods Manual*, 2nd ed. OSHA, Salt Lake City, UT (1990).
25. National Institute for Occupational Safety and Health: "Determination of Airborne Isocyanate Exposure" in *NIOSH Manual of Analytical Methods*, 4th ed. DHHS (NIOSH) Publication No. 94-113. NIOSH, Cincinnati, OH (1994).
26. National Institute for Occupational Safety and Health: "Particulates Not Otherwise Regulated, Total: Method 0500" in *NIOSH Manual of Analytical Methods*, 4th ed. DHHS (NIOSH) Publication No. 94-113. NIOSH, Cincinnati, OH (1994).
27. National Institute for Occupational Safety and Health: *NIOSH Manual of Analytical Methods*, 4th ed. DHHS (NIOSH) Publication No. 94-113. NIOSH, Cincinnati, OH (1994).
28. J. Kenkel: *Analytical Chemistry for Technicians*, 2nd ed. Lewis Publishers, Ann Arbor, MI (1994).
29. Personal Correspondence, Dr. Robert Streicher, National Institute for Occupational Safety and Health (January 1999).
30. Air Force Occupational Safety and Health Standard 48-8, *Controlling Exposures to Hazardous Materials* (1 September 1997).

31. American Conference of Governmental Industrial Hygienists: *1999 TLVs and BEIs: Threshold Limit Values for Chemical Substances and Physical Agents, Biological Exposure Indices*. ACGIH, Cincinnati, OH (1998).
32. Occupational Safety and Health Administration: 29 CFR 1910.1000, *Air Contaminants*.
33. Oregon State Occupational Safety and Health Administration: *Oregon Administrative Rule (OAR) 437-002-0382* (22 April 1997).
34. T.O. 42A-1-1, *Safety, Fire Precaution and Health Promotion Aspects of Painting and Paint Removal*, 26 December 1985; with change 4 dated 15 April 1992.
35. T. Kim, M.R. Flynn: "Modeling a Worker's Exposure from a Hand-Held Source in a Uniform Freestream." *American Industrial Hygiene Association Journal*, 52(11):456-463 (1991).
36. American Conference of Governmental Industrial Hygienists: *Industrial Ventilation, A Manual of Recommended Practice*, 23rd ed. ACGIH, Cincinnati, OH (1995).
37. National Fire Protection Association: *NFPA 33 Standard for Spray Application Using Flammable or Combustible Materials*. NFPA, Quincy, MA (1995).
38. Occupational Safety and Health Administration: 29 CFR 1910.134, *Respiratory Protection* (8 April 1998).
39. J. Vasta: "Respirator Cartridge Evaluation for Isocyanate Containing Imron[®] and Centari[®] Enamels." *American Industrial Hygiene Journal*, 46(1):39-44 (1985).
40. National Institute for Occupational Safety and Health: NIOSH Respirator Decision Logic. DHHS (NIOSH) Publication No. 87-108. NIOSH, Cincinnati, OH (1987).
41. M.W. Spence, T.D. Landy, D.W. Huff: "Evaluation of the Effectiveness of Air-Purifying Respirator Cartridges in Removing MDI Aerosols from Air" in *Polyurethanes World Congress 1997 Proceedings*. Society of Plastics Industry, Washington, DC (1997).
42. American National Standards Institute: *American National Standard for Respiratory Protection, ANSI A88.2-1992*. ANSI, New York, NY (1992).
43. T. Hall, P. Breyse: "Effects of Adsorbed Water Vapor on the Adsorption Rate Constant and the Kinetic Adsorption Capacity of the Wheeler Kinetic Model." *American Industrial Hygiene Journal*, 49(9):461-465 (1988).
44. E. Moyer: "Organic Vapor (OV) Respirator Cartridge Testing—Potential Jonas Model Applicability." *American Industrial Hygiene Journal*, 48(9):791-797 (1987).
45. H. Cohen, R. Garrison: "Development of a Field Method for Evaluating the Service Life of Organic Vapor Cartridges: Results of Laboratory Testing Using Carbon Tetrachloride." *American Industrial Hygiene Journal*, 50(9):486-495 (1989).

46. 3M Corporation: *3M Respirator Service Life Software*, 3M Corporation, St. Paul, MN (1998).
47. Personal Correspondence, North Products Technical Service (5 May 1997).
48. Personal Correspondence, Best Manufacturing Technical Service (5 May 1997).
49. S. Mansdorf: *Complete Manual of Industrial Safety*. Prentice Hall, Englewood, NJ (1993).
50. G. Carlton, M. Flynn: "A Model to Estimate Worker Exposure to Spray Paint Mists." *Applied Occupational and Environmental Hygiene*, 12(11):744-750 (1997).
51. Det 1 HSC/OEMI Consultative Letter: *1,6-Hexamethylene Diisocyanate Exposures During Polyurethane Spray Painting Operations*. AL-OE-BR-CL-1998-0105 (28 Aug 98).
52. AL/OEM Consultative Letter: *Isocyanate Exposures and Respiratory Protection Requirements During Sempen Usage*. AL/OE-CL-1997-0199 (29 Oct 1997).
53. P. Hewett, G.H. Ganser: "Simple Procedures for Calculating Confidence Intervals Around the Sample Mean and Exceedance Fraction Derived from Lognormally Distributed Data." *Applied Occupational and Environmental Hygiene*, 12(2):132-142 (1997).
54. P. Reist: "Explosive Aerosols" in *Aerosol Science and Technology*, 2nd ed. McGraw-Hill Inc., New York, NY (1993).
55. Personal Correspondence, Dr David Leith, Aerosol Technology Committee (October 1996).

APPENDIX A – FIELD SURVEY RESULTS

Survey Locations

Field studies were completed at Kelly, Tinker, Robins, Hill, Cannon, Holloman, Langley, and Nellis AFBs. The results are discussed extensively in the individual consultative letters and AL-OE-BR-CL-1998-0105, *1,6-Hexamethylene Diisocyanate Exposures During Polyurethane Spray Painting Operations* and AL/OE-CL-1997-0199, *Isocyanate Exposures and Respiratory Protection Requirements During Sempen Usage* [51,52].

Polyurethane Spray Painting

Isocyanates: Samples were collected during polyurethane spray painting of aircraft and aircraft parts using NIOSH 5521, the Iso-Chek sampler, and TAMM. Tables A-1 and A-2 summarize personal exposures to HDI monomer and oligomer, calculated as a task exposure (average concentration over the length of the task) and as an 8-hr TWA. The data was approximately lognormally distributed; means and 95% confidence intervals were determined from Land's procedure for calculating exact confidence intervals around the mean of lognormally distributed data [53]. Figures A-1 and A-2 present the monomer results graphically, while Figures A-3 and A-4 illustrate the oligomer results (sample numbers are rank-ordered by oligomer task exposures to improve graph readability). Dashed lines indicate the Oregon ceiling and 8-hr TWA exposure limits. All personal task exposures to HDI monomer are below the NIOSH ceiling limit of 140 $\mu\text{g}/\text{m}^3$; all 8-hr TWAs are below the ACGIH TLV-TWA of 34 $\mu\text{g}/\text{m}^3$.

Table A-1. Personal Exposures to HDI Monomer ($\mu\text{g}/\text{m}^3$)

Exposure	Sampling Method	Range	Mean	95% Confidence Limits
8-hr TWA	NIOSH 5521	0.31 – 3.51	0.67	(0.59, 0.79)
	Iso-Chek	0.03 – 2.84	0.90	(0.66, 1.44)
Task	NIOSH 5521	3.05 – 53.1	15.5	(13.5, 18.5)
	Iso-Chek	1.00 – 102	17.5	(12.9, 27.3)

Table A-2. Personal Exposures to HDI Oligomer (mg/m^3)

Exposure	Sampling Method	Range	Mean	95% Confidence Limits
8-hr TWA	NIOSH 5521	<0.01 – 0.17	0.01	(0.01, 0.03)
	Iso-Chek	<0.01 – 0.36	0.11	(0.07, 0.23)
	TAMM	<0.01 – 0.58	0.18	(0.14, 0.24)
Task	NIOSH 5521	<0.01 – 3.36	0.33	(0.21, 0.77)
	Iso-Chek	<0.01 – 5.77	2.27	(1.52, 4.43)
	TAMM	0.22 – 17.3	3.75	(3.01, 5.06)

Exposures to HDI oligomers were more elevated. Mean task exposures indicated by either the Iso-Chek or TAMM are above the Oregon ceiling limit of 1 mg/m³. When examined on an 8-hr TWA basis, however, exposures are much lower, with only one sample exceeding the Oregon standard of 0.5 mg/m³.

Solvents: Table A-3 summarizes solvent exposures found at two of the facilities. Both task and 8-hr TWA exposures are far below the AF occupational exposure limits for the chemicals sampled.

Table A-3. Personal Exposures to Solvents (mg/m³)

Chemical	Task Exposure		8-hr TWA Exposure		Air Force OEL-TWA
	Range	Mean	Range	Mean	
Butyl acetate	1.99 – 3.63	2.71	0.25 – 0.68	0.42	713
Ethyl benzene	0.18 – 2.38	1.07	0.02 – 0.70	0.30	434
Isopropyl alcohol	0.26 – 0.29	0.28	0.03 – 0.05	0.04	983
Methyl ethyl ketone	0.09 – 0.38	0.22	0.01 – 0.08	0.04	590
Methyl isobutyl ketone	0.20 – 3.79	1.18	0.02 – 0.47	0.16	205
Toluene	0.18 – 42.6	13.5	0.03 – 12.5	3.91	188
Xylenes	0.09 – 6.91	3.25	0.01 – 2.02	0.94	434

Sempen Usage

Task exposures found during Sempen usage are shown in Table A-4. Because these procedures were of relatively short duration, task exposures provide a more useful indication of the adequacy of respiratory protection than the 8-hr TWA. All measured exposures are far below the applicable standards.

Table A-4. Personal Exposures to Sempen Components (mg/m³)

Chemical	Task Exposure		8-hr TWA Exposure		Air Force OEL-TWA
	Range	Mean	Range	Mean	
HDI Monomer	0.006 – 0.047	0.030	0.002 – 0.002	0.002	0.034
Methyl Propyl Ketone	0.010 – 0.017	0.014	0.001 – 0.004	0.002	705
Methyl Amyl Ketone	0.03 – 4.00	1.57	0.01 – 0.28	0.17	233
Toluene	0.017	--	0.007	--	188

Figure A-1. Distribution of HDI Monomer Task Exposures

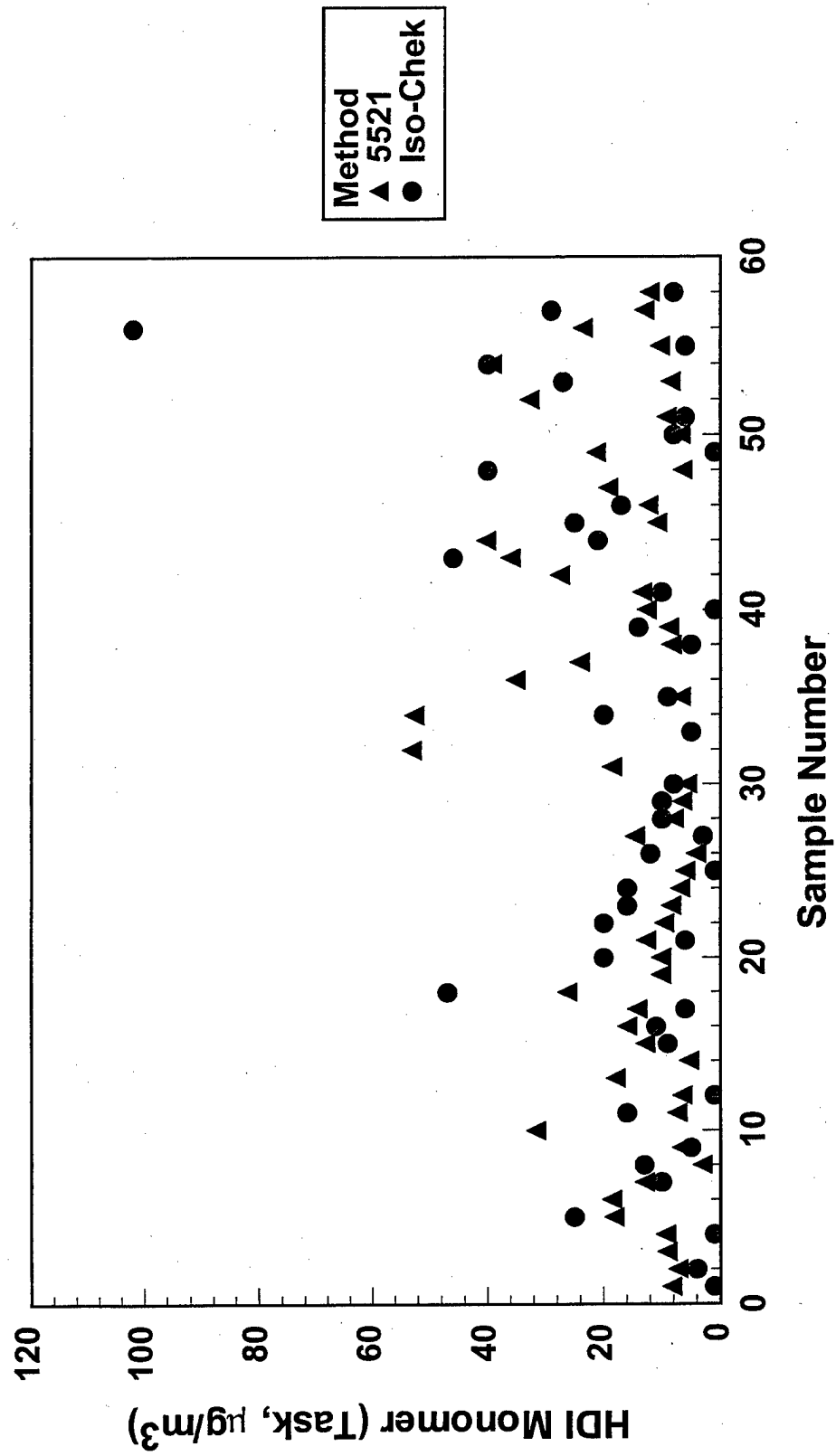


Figure A-2. Distribution of HDI Monomer 8-hr TWA Exposures

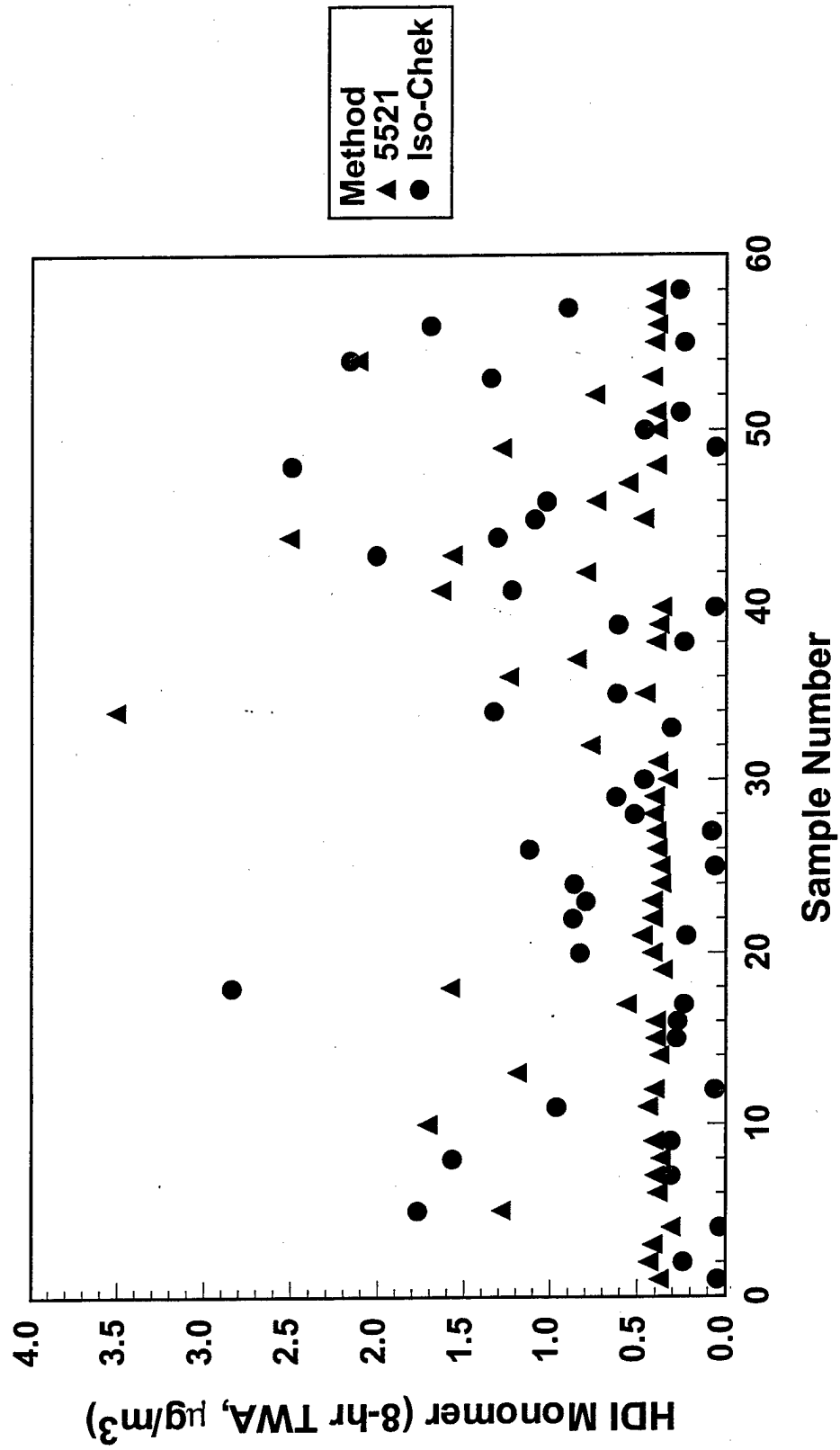


Figure A-3. Distribution of HDI Oligomer Task Exposures

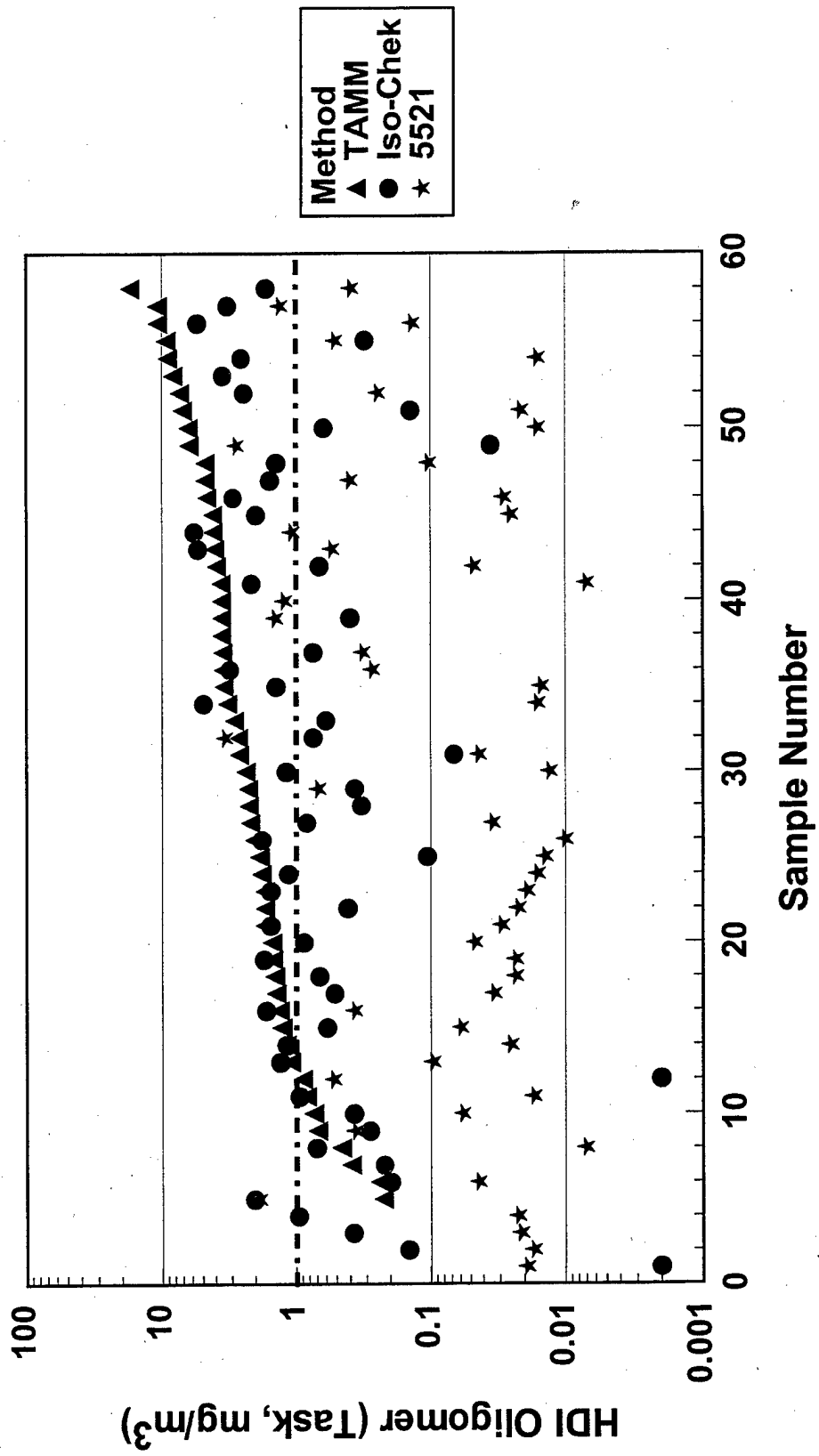
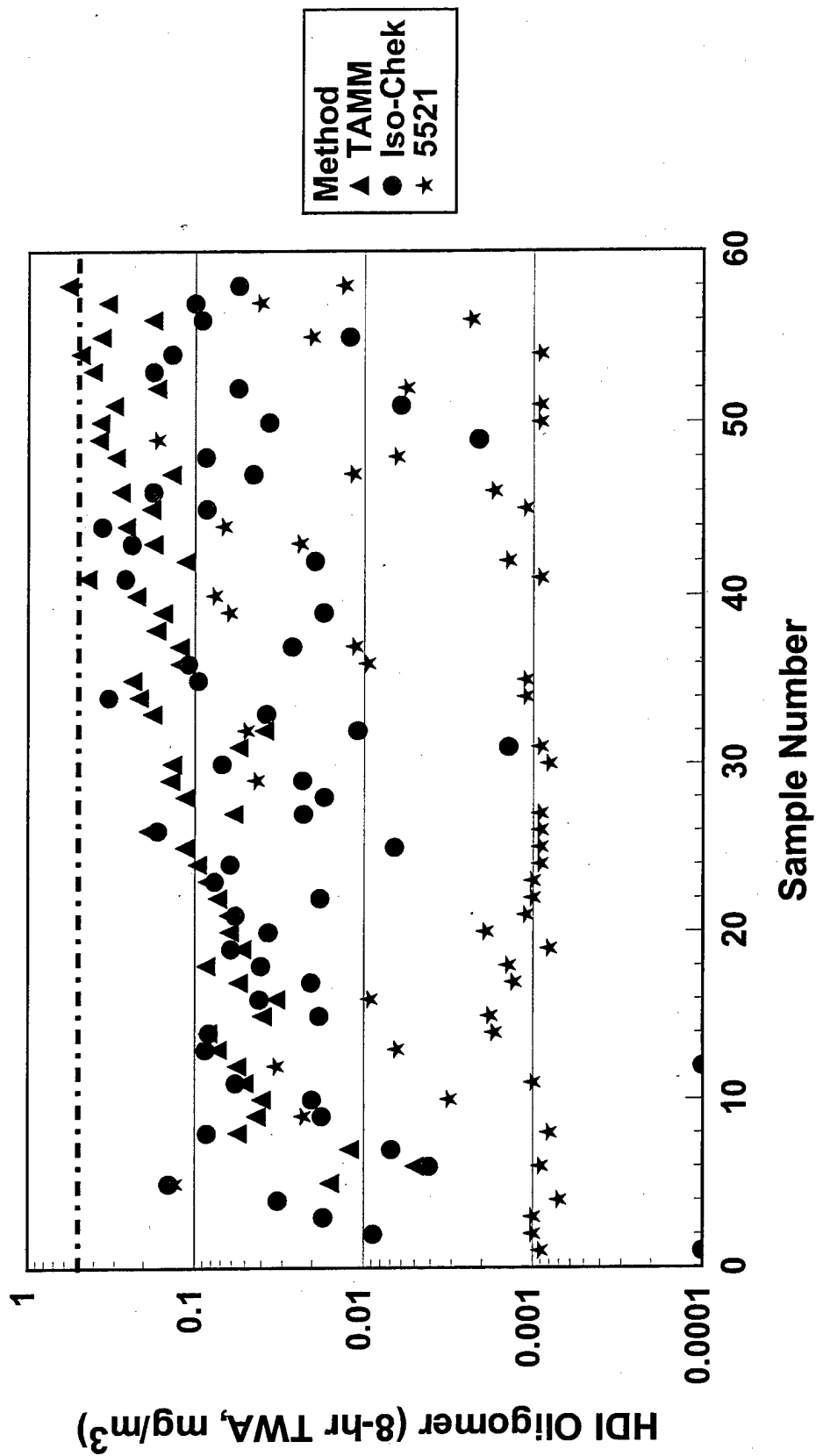


Figure A-4. Distribution of HDI Oligomer 8-hr TWA Exposures



APPENDIX B – PAINTING FACILITY EVALUATIONS

Background

Spray painting operations need to be adequately ventilated to prevent the build-up of flammable or combustible vapors and mists. An explosion could result from a high concentration of either the spray paint aerosol or the solvent that evaporates from the aerosol. It is recommended to keep the aerosol and vapor concentrations below 20% of the lower explosive limit (LEL) as a safety factor to ensure explosive concentrations are never reached during spraying operations [37].

The ventilation rate required to prevent the build-up of an explosive atmosphere depends on the materials involved, their generation rate, and the effectiveness of the ventilation system in capturing the contaminants. The following calculation, based on a paint application rate of 2 gal/hr in a facility with a ventilation rate of 35,000 cfm, is an example of how to determine safe paint application rates. It is important to realize that this calculation is applicable ONLY to facilities that have effective ventilation in the spray paint area. An example of a facility with ineffective ventilation is one where the supply and exhaust locations are in the ceiling and short-circuiting occurs, resulting in limited ventilation in the spray area.

Aerosol Concentrations

At a maximum use rate of 2 gal/hr, assuming a task transfer efficiency of 50% for HVLP painting [23] gives a volumetric overspray generation rate of 1 gal/hr. The density of the paint currently being used to overcoat aircraft (found from a Material Safety Data Sheet for a common coating system) is 1.19 g/cm³. The aerosol mass generation rate of aerosol is:

$$G_a = (\dot{V}_o)(\rho) \quad (B-1)$$

where: G_a = aerosol generation rate (g/hr)

\dot{V}_o = volumetric overspray generation rate (gal/hr)

ρ = paint density (g/cm³)

Therefore,

$$\begin{aligned} G_a &= \frac{1 \text{ gal}}{\text{hr}} \times \frac{1.19 \text{ g}}{\text{cm}^3} \times \frac{3785 \text{ cm}^3}{\text{gal}} \\ &= 4504 \text{ g/hr} \end{aligned}$$

The aerosol concentration at steady-state (assuming there is efficient ventilation in the facility), is [36]:

$$C_a = \frac{(G_a)(K)}{(Q)} \quad (B-2)$$

where: C_a = aerosol concentration (g/m^3)

Q = facility ventilation rate (cfm)

K = ventilation mixing factor

The K factor accounts for imperfect mixing or distribution of the contaminant within the ventilated space. K is usually chosen as 10 because make-up air is generally poorly distributed in painting facilities [36]. The air flow in the above equation is the air currently being exhausted from the spray paint area. Therefore,

$$\begin{aligned} C_a &= \frac{(4504 \text{ g/hr})(35.31 \text{ ft}^3/\text{m}^3)(10)}{(35,000 \text{ ft}^3/\text{min})(60 \text{ min/hr})} \\ &= 0.76 \text{ g}/\text{m}^3 \end{aligned}$$

Reference [54] sets an LEL of $20 \text{ g}/\text{m}^3$ for most non-volatile aerosols. There is very limited information on the LELs of volatile aerosols. In the absence of this data, we believe it is prudent to reduce the LEL by at least a factor of three, as a volatile aerosol would presumably have a lower LEL than a non-volatile aerosol. This results in an LEL of $6.7 \text{ g}/\text{m}^3$. The maximum calculated aerosol concentration in the facility from the example is about 11% of this level, indicating explosive concentrations of aerosols during spray painting operations would probably not be generated.

Vapor Concentrations

In addition to the generation of aerosols, volatile components in the paint mist can evaporate, which also can present an explosion hazard. A high-solids polyurethane paint currently being used in the Air Force consists of 34.73% volatiles and has a lower explosion limit of 0.76% (7600 parts per million, [ppm]). The concentration of vapor generated in the facility assuming complete evaporation of the volatile components is [36]:

$$C_v = \frac{(\text{CONSTANT})(G_v)(K)(\text{SG})}{(Q)(\text{MW})} \quad (B-3)$$

where: C_v = vapor concentration (ppm)

CONSTANT = volume 1 gal of liquid will occupy at STP when vaporized
(3.22×10^9 ft³/gal)

G_v = vapor generation rate (gal/hr)

K = mixing factor

SG = specific gravity of liquid solvent

Q = ventilation rate (cfm)

MW = molecular weight of solvent

Normally, when a mixture of explosive gases are present in an area, the entire mixture is regarded as consisting of the component requiring the highest amount of dilution air per unit liquid volume (i.e., the component with highest vapor pressure of the solvents in the paint system used). The characteristics of toluene are selected for this analysis (SG = 0.87; MW = 92.1); see Table B-1 for properties of other solvents commonly present in paints. Therefore, assuming complete evaporation of the paint volatiles at an application rate of 2 gal/hr,

$$C_v = \frac{(3.22 \times 10^9 \text{ ft}^3/\text{gal})(2 \text{ gal/hr})(0.3473)(10)(0.87)}{(35,000 \text{ ft}^3/\text{min})(92.1)(60 \text{ min/hr})}$$
$$= 100 \text{ ppm}$$

This represents 1.3% of the LEL for the paint, below the recommended 20% maximum concentration level.

Mixture of Aerosols and Vapors

Because in reality there will be a mixture of both paint aerosols and vapors during spraying operations, it is recommended to maintain both aerosols and vapors below 20% of their respective LELs and avoid any additive effects. The best way to ensure an explosion does not occur is to keep the sum of the aerosol and vapor cumulative fractions below 1.0 [55]:

$$\sum \frac{C}{20\% \text{ LEL}} \leq 1.0 \quad (\text{B-4})$$

In our example,

$$\frac{C_a}{20\% \text{ LEL (aerosol)}} + \frac{C_v}{20\% \text{ LEL (vapor)}} = \frac{0.75 \text{ g/m}^3}{1.3 \text{ g/m}^3} + \frac{100 \text{ ppm}}{1520 \text{ ppm}} = 0.65$$

This analysis indicates that at the current use rate of 2 gal/hr, an explosive mixture of aerosols and vapors should not be produced in the facility. Irrespective of what the aerosol and vapor concentrations are inside the paint facility, it is important to realize there is always the POTENTIAL for development of explosive mixtures even if ventilation is available. Therefore, whenever you are spraying a flammable material into an area, ensure there are no ignition sources present in the facility that could initiate an explosion.

Table B-1. Solvent Properties

Solvent Compound	Synonyms	Vapor Pressure (mmHg)	Specific Gravity	Molecular Weight	Lower Explosive Limit (%)
n-Butyl acetate	Butyl acetate	10	0.88	116.2	1.7
n-Butanol	Butyl ethanoate	6	0.81	74.1	1.4
	Butyl alcohol				
2-Butoxy ethanol	1-Butanol	0.8	0.90	118.2	1.1
	Butyl cellosolve				
Ethyl acetate	Ethylene glycol monobutyl ether	73	0.90	88.1	2.0
	Acetic ester				
	Ethyl ethanoate				
Methyl n-amyyl ketone	2-Heptanone	3	0.81	114.2	1.1
	Amyl methyl ketone				
Methyl ethyl ketone	MEK	78	0.81	72.1	1.4
	2-Butanone				
	Methyl acetone				
Methyl isobutyl ketone	MIBK	16	0.80	100.2	1.2
	Hexone				
	4-Methyl 2-pentanone				
Toluene	Toluol	21	0.87	92.1	1.1
	Methyl benzene				
Xylene	Xylol	9	0.86	106.2	1.1
	Dimethyl benzene				