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ISOCYANATE MONITORING USING N-P-NITROBENZYL-N-PROPYLAMINE GLASS--ETC(U)
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USAF OEHL REPORT
82-022-EH163HAE



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ISOCYANATE MONITORING USING N-P-NITROBENZYL-N-PROPYLAMINE
GLASS FIBER SAMPLING TUBE
AUGUST 1982

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USAF Occupational and Environmental Health Laboratory
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Isocyanate Monitoring Using N-p-nitrobenzyl-N-propylamine

Glass Fiber Sampling Tube

August 1982

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I. INTRODUCTION

Isocyanates are widely used in the Air Force as components in coatings, varnishes, foams, and adhesives. The basic chemical structure of an isocyanate is:



where R represents some aromatic or aliphatic group. The primary aromatic isocyanates used in the Air Force are toluene diisocyanate (TDI), used to form flexible foams, and diphenyl methane diisocyanate (MDI), which forms rigid foams. Hexamethylene diisocyanate (HDI), an aliphatic isocyanate, is a component in polyurethane paints. Exposure to isocyanates can cause allergic sensitization in susceptible individuals, aggravation of existing respiratory problems, a decrease in respiratory capacity, and irritation of the skin and mucous membranes of the eyes and respiratory tract.

Colorimetric procedures for detecting aromatic isocyanates have existed since they were first widely used in the early 1950s. However, analytical procedures for detecting aliphatic isocyanates have not been available until relatively recently. In 1980, in Volume 6 of its Manual of Analytical Methods, NIOSH published a chromatographic method which can detect both aromatic and aliphatic isocyanates. In December 1981, the USAF Occupational and Environmental Health Laboratory (USAF OEHL) initiated trial use of the method at base level. The primary task of the USAF OEHL Industrial Hygiene Branch was to provide a field evaluation of the method for HDI-sampling during aircraft spray painting operations. A secondary objective was to field test the method for TDI/MDI sampling during foam operations. The following report details the procedures and results of the field evaluation.

II. BACKGROUND

The isocyanate method tested by the USAF OEHL is a variation of NIOSH Method No. P&CAM 326, which is based upon the chromatographic method of Vogt, Ko, and Ryan (9). In this method, N-p-nitrobenzyl-N-propylamine, otherwise known as nitro reagent, is coated on fibrous glass wool which is then placed inside a shortened section of Pasteur pipette. When air is drawn through this sampling tube, the isocyanate reacts with the nitro reagent to form the urea derivative of the isocyanate. The urea derivative of the isocyanate is then eluted from the glass fiber in the laboratory and detected using High Performance Liquid Chromatography (HPLC).

In two previous aircraft spray paint surveys for HDI, the USAF OEHL used an earlier NIOSH method, No. 240, in which the same chemical reaction occurs in a toluene/nitro solution in an impinger (2,6). Prior to these surveys, the USAF OEHL also performed two HDI surveys using the DuPont method (1,3). The DuPont method is a colorimetric procedure using a midjet impinger containing a dimethyl sulfoxide-hydrochloric acid absorbing solution. Neither of these impinger methods is satisfactory for routine sampling at the base level.

However, sampling for TDI and MDI has been possible at base level using the Bendix Air Analysis Kit and the MDA 7005 tape monitor. The Bendix sampling method is a semiquantitative variation of the Marcali method. This colorimetric method, which is specific for aromatic isocyanates, also requires

impingers and is subject to negative interference by tertiary amines. The MDA 7005 tape monitor detects and measures the change in optical density which occurs when TDI or MDI react with a chemically impregnated paper strip. NIOSH recommends the tape monitor as a valuable method for continuous monitoring of aromatic isocyanates, particularly TDI (7).

The glass fiber method tested by the USAF OEHL would be suitable after validation for routine, base-level monitoring of both aromatic and aliphatic isocyanates, and would eliminate the need for impingers and costly monitoring equipment. Analysis by HPLC allows detection of TDI, MDI, and HDI monomers, and HDI biuret trimer. NIOSH classifies this method as a Class D method, which is one generally accepted by industrial hygiene analysts, although not completely evaluated by anyone. NIOSH has tested Method P&CAM 326 in the laboratory for TDI vapor using nitro-coated glass fiber sampling tubes and for MDI aerosol using nitro-coated 13 mm glass fiber filters (8).

III. SAMPLING PROCEDURES

A. Aircraft Spray Painting

Sampling for HDI included three separate surveys performed at Hangar 48, an aircraft spray paint hangar at Randolph AFB, during complete and touch-up painting of T-37 and T-38 aircraft. The ventilation in the hangar was push-pull with two units delivering 80,000 cfm and three fans exhausting 71,000 cfm. The paint used was Deft Polyurethane Coating, NSN 8010-00-181-8281, MIL-C-83286B (Appendix 1). Paint was applied using a DeVilbiss, Size 30 (4-hole) air spray gun and pressure cup for touch-up painting, and a DeVilbiss, Size 78 (10-hole) air spray gun and pressure pot for complete painting.

For both complete and touch-up painting, application of the first coat required 30-45 minutes. Then after a 15-30 minute drying period, the second coat was applied. Unless otherwise indicated, sampling pumps operated continuously from the beginning of the application of the first coat through the application of the second coat. Other sampling conditions varied during each of the three surveys and are specified in Table I and in Section IV.

B. Foam-in-Place Operation

The USAF OEHL conducted one survey for MDI concentrations at a foam-in-place operation at Bldg 310, Kelly AFB. Local exhaust ventilation resulted in an air velocity of 150-165 fpm across the face of the application area. A Guzmur Model 630 unit mixed Universal Polymers Maxpak 454 components A and B to form the foam, which was applied to the packing boxes through a sprayless nozzle. Component A consisted of MDI monomer, higher polymers, Freon 11, and a trace amount of methylene chloride. Component B consisted of a high molecular weight polyalcohol, a tertiary amine catalyst, and Freon 11.

TABLE I. ISOCYANATE SURVEY CONDITIONS

Survey	Location	Isocyanate Sampled	Operation	Temperature °F	Humidity %
I	Hangar 48 Randolph AFB	HDI	Complete Painting T-37	84	40
II	Hangar 48 Randolph AFB	HDI	Complete Painting T-38	68	75
III	Hangar 48 Randolph AFB	HDI	Touch-up Painting T-38	69	76
IV	Bldg 310 Kelly AFB	MDI	Foam-in-Place Packing	68	72

C. General Protocol

The USAF OEHL developed the following general guidelines for field evaluation of the nitro-coated glass fiber method for HDI sampling during spray paint operations and for TDI and MDI sampling during foam operations.

1. Determine the limits of the method.
2. Screen for interferences.
3. Verify the stability of the reagents and the products of the reaction.
4. Estimate the sampling precision.
5. Estimate the accuracy of the method.

IV. DISCUSSION AND RESULTS

A. HDI Sampling During Aircraft Spray Painting

1. Limits

The sampling tube containing the nitro-coated glass fiber is used in the same way as the familiar charcoal tube, except a higher flow rate of 2.0 Lpm is required for the glass fiber sampling tube. Like the charcoal, the glass fiber is in the two sections, a 7 mm front sampling section and a 5 mm back section to detect breakthrough. NIOSH recommends sampling at least 60 liters of air to detect trace amounts of isocyanates as low as 0.02 micrograms. The data from the USAF OEHL surveys showed that breakthrough did not occur until the quantity of HDI detected exceeded 18 micrograms. These limits allow the detection of HDI levels ranging from 0.3 $\mu\text{g}/\text{m}^3$ to 300 $\mu\text{g}/\text{m}^3$ for a 60-

liter sample. For a 20 liter, 10 minute ceiling limit determination, levels ranging from 1 $\mu\text{g}/\text{m}^3$ to 900 $\mu\text{g}/\text{m}^3$ can be detected, or up to approximately six times the ceiling limit. The NIOSH recommended, 10-hour workshift, 40-hour workweek, TWA for HDI is 35 $\mu\text{g}/\text{m}^3$ and the recommended ceiling limit for any 10-minute period is 140 $\mu\text{g}/\text{m}^3$.

2. Stability

The NIOSH procedure cautions against possible interference during sampling. Nitro reagent on glass fiber is unstable in the presence of light and is unstable to a lesser extent during storage in the dark. The deterioration of the reagent results in a positive interference caused by the presence of a peak during HPLC, which coincides with the HDI-urea peak. To eliminate the possibility of this type of interference, tubes are prepared in the USAF OEHL analytical laboratory and delivered to the base by the next day for immediate use. Each tube is refrigerated before and after use and covered with aluminum foil to protect it from exposure to light. During the course of the surveys, the USAF OEHL analyzed tubes that had been refrigerated as long as five days before and five days after sampling with no indication of interference or deterioration. The NIOSH method recommends storage no longer than seven days at room temperature in the dark and four weeks at -21°C .

3. Chemical Interferences

Both positive and negative chemical interferences are also possible. Any chemical that will react with the isocyanate group can cause a negative interference; and any compound that has the same retention time during HPLC as the urea-derivative of the isocyanate can interfere positively. No interferences of either type were identified during the spray paint surveys.

4. Precision

Table II shows the HDI levels of five samples collected from the same area in the spray paint hangar at Randolph AFB. The average amount of HDI present was 19.58 μg with a standard deviation of ± 2.71 μg . The RSD is 14%. The calculated average concentration was 69 $\mu\text{g}/\text{m}^3$ with a standard deviation of ± 8 $\mu\text{g}/\text{m}^3$.

The samples, which were separated by no more than four feet, were located at Point A in Figure I. All the Survey III samples in Area A were collected for 140 minutes at 2 Lpm during touch-up painting of a T-38 aircraft. Although 60 liters is the recommended sampling volume for determining the TWA for HDI, higher volumes were used in this case to detect breakthrough and establish the limits of the method. Breakthrough did occur in two samples as shown in Table II. However, even at its limits, these data show the method to be reasonably precise.

TABLE II. HDI LEVELS FROM AREA A
(SURVEY III)

Sample	HDI, μg	HDI, $\mu\text{g}/\text{m}^3$
1	17.52	62
2	23.79*	84
3	20.73*	73
4	17.39	62
5	18.48	66
Mean	19.58	69
Std. Dev.	2.71	8

*Breakthrough occurred. HDI levels are the sum of the front and back sections.

5. Accuracy

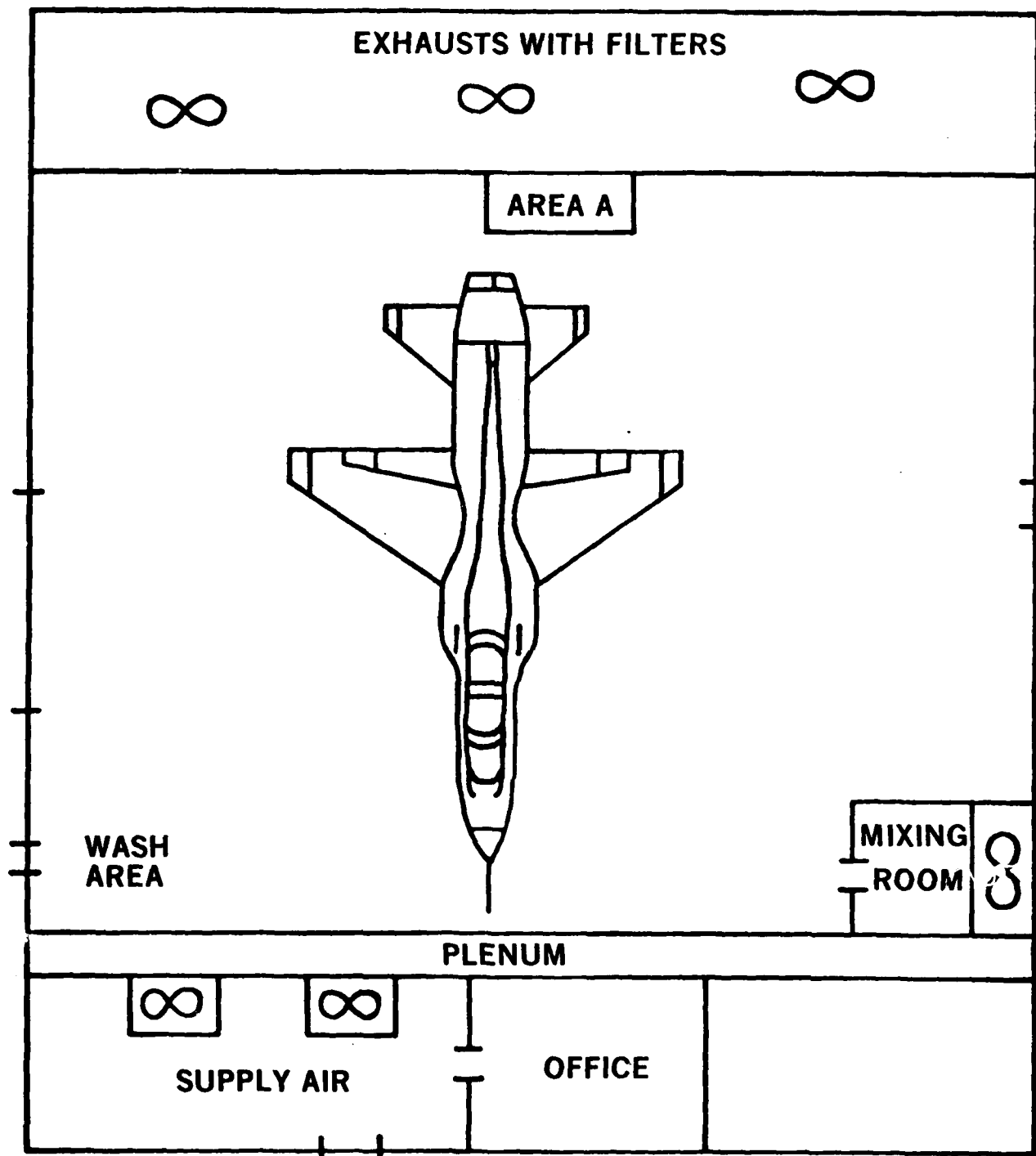
Although the accuracy of the method could not be directly determined under uncontrolled field conditions, the following sampling procedures were used to estimate accuracy:

a. Comparison of HDI Levels Sampled at 1 Lpm and 2 Lpm

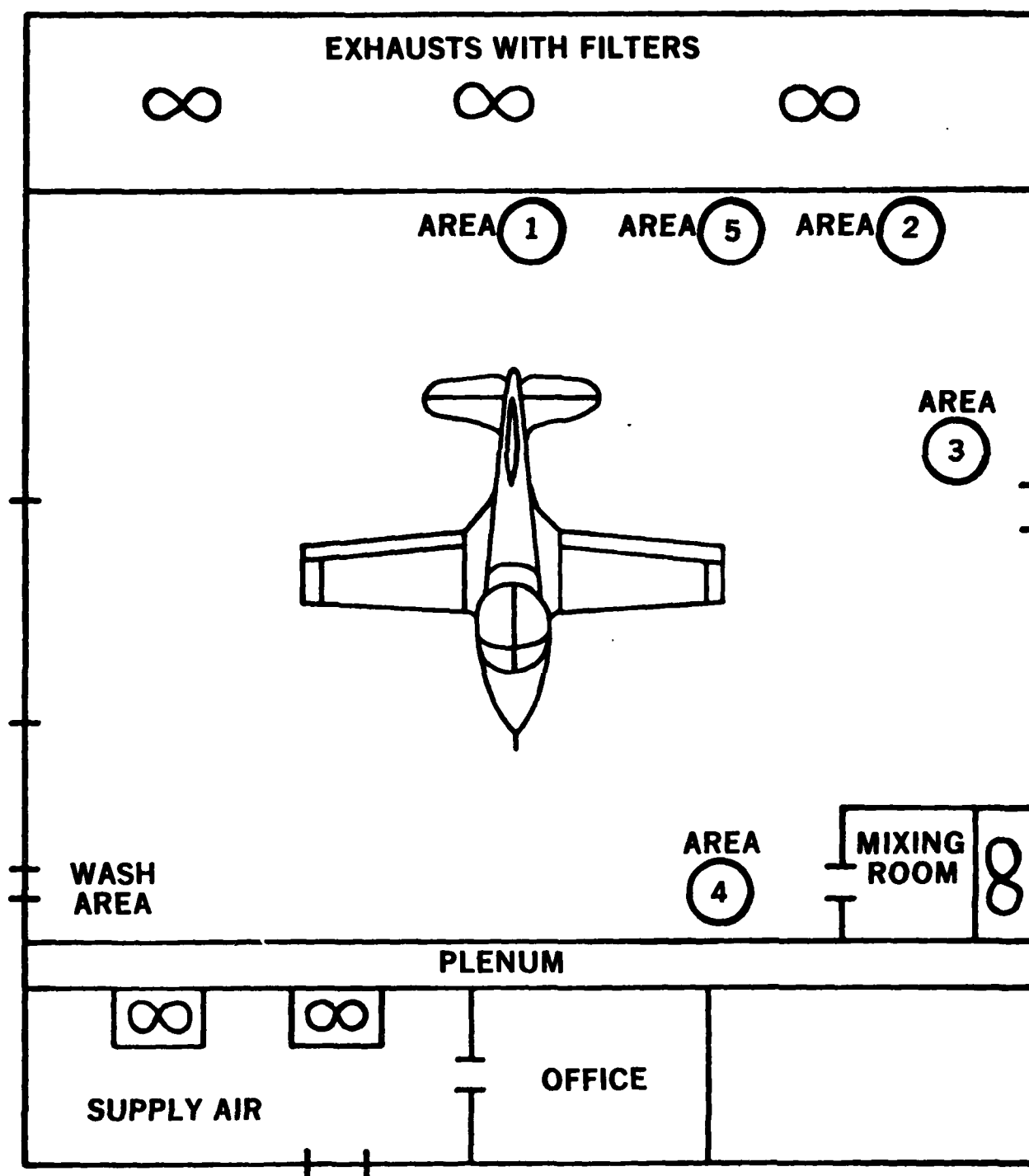
There was no significant difference between HDI levels collected on single sampling tubes at 1 and 2 Lpm for the microgram quantities shown in Table III. The sampling tubes, as listed, were in consecutive order, in Area A (Figure I), with no more than 6 inches separating each tube; each sample was collected for 102 minutes.

TABLE III. COMPARISON OF HDI LEVELS AT 1 LPM AND 2 LPM
(SURVEY II)

Paired Sample Groups Area A	Rate, Lpm	HDI, μg	HDI, $\mu\text{g}/\text{m}^3$
	1	4.905	48
	1	3.787	37
	2	10.006	49
	2	7.127	35



**FIGURE I. SAMPLING AREA, SURVEYS II AND III
HANGER 48, RANDOLPH AFB**



**FIGURE II. SAMPLING AREAS, SURVEY I
HANGER 48, RANDOLPH AFB**

b. Detection of Breakthrough

To detect large amounts of isocyanate which may have passed through the sampling train unreacted, trains were set-up at sampling rates of 1 and 2 lpm, in which the sampling tube containing the nitro-coated glass fiber was followed by an impinger containing nitro/toluene reagent (Survey I). In no case was isocyanate detected in the impinger.

c. Characterization of HDI as an Aerosol/Vapor

While the sampling tube is presumably collecting all of the HDI, it is possible that if HDI exists as an aerosol, it may remain unreacted in trapped paint particles. The data in Table IV show that most of the HDI monomer detected is in the form of an aerosol. During sampling in Area A of the paint hangar (Figure I), the glass fiber sampling tubes were paired with sampling trains in which a glass fiber tube was preceded by an uncoated 37 mm glass fiber prefilter. The level of the HDI monomer detected on the single glass fiber sampling tube is 5 to 20 times greater than the level detected on the glass fiber sampling tube preceded by the prefilter.

TABLE IV. DETERMINATION OF HDI VAPOR AND
AEROSOL CONCENTRATIONS, $\mu\text{g}/\text{m}^3$
(SURVEY III)

Group	Uncoated 37 mm Prefilters—Coated Fiber	Coated Fiber
1	8	62
2	4	84
3	10	73
4	13	62
5	13	66

d. Comparison of Glass Fiber Sampling Tubes and Filters

NIOSH suggests that a flat filter coated with nitro-reagent is a more efficient way to sample for aerosol. Table V shows results from paired samples using the coated glass fiber sampling tubes from Area A and closed faced cartridges with nitro-coated 37mm glass fiber filters. The sampling tubes are clearly superior with an average HDI concentration of 69 $\mu\text{g}/\text{m}^3$, compared to 23 $\mu\text{g}/\text{m}^3$ for the 37 mm filters.

TABLE V. COMPARISON OF HDI CONCENTRATIONS DETECTED ON
COATED FIBER AND COATED 37 mm FILTER, $\mu\text{g}/\text{m}^3$
(SURVEY III)

Group	Coated 37 mm Filters	Coated Fiber
1	22	62
2	17	84
3	26	73
4	28	62
5	21	66

e. Comparison of Glass Fiber Sampling Tubes and Impingers

An attempt to compare the glass fiber tube and the impinger sampling methods resulted in a few data points showing no consistent, significant difference at low HDI levels (Table VI, Figure II). For longer sampling periods paint visibly collected on the walls of the impinger and at the outlet of the impinger sampling tip. The data from most of the sampling trains using toluene containing impingers were invalid because of pump failure caused by toluene leakage or because of the presence in the samples of diethylhexyl phthalate, the plasticizer in Tygon^R tubing, which was dissolved by the toluene.

TABLE VI. COMPARISON OF HDI LEVELS USING NITRO-COATED GLASS FIBER
SAMPLING TUBES AND TOLUENE/NITRO REAGENT IMPINGERS
(SURVEY I)

Impinger Nitro Method				TUBE NITRO METHOD		
Area	Flow Rate, Lpm	Total Volume, Liters	$\mu\text{g}/\text{m}^3$	Flow Rate, Lpm	Total Volume, Liters	$\mu\text{g}/\text{m}^3$
A1	2	170	<0.005	0.95	81	0.039
A2	2.1	178.5	0.009	1	85	0.009
A3	2.05	174.3	<0.005	1	85	0.013
A4	1.95	161.5	<0.005	0.95	81	<0.005
A5	2	73*	0.024	1	85	0.012

*Pump stopped during sampling.

B. MDI Sampling During Foam-in-Place Operations

The original intent of field testing the glass fiber sampling tube for MDI or TDI was simply to confirm the results of the NIOSH laboratory validation, which showed the method to be both accurate and precise for TDI and MDI sampling. However, the data from the foam-in-place survey at Kelly AFB do not substantiate the accuracy and precision of the method for MDI collection and suggest the need for further sampling.

During foam-in-place operations, MDI has been shown in the literature to exist normally as an aerosol, while TDI because of its higher vapor pressure, usually exists as a vapor (5). For these reasons, NIOSH validated the nitro-coated glass fiber sampling tube method for TDI vapor and used 13 mm nitro-coated glass fiber filters for MDI aerosol. However, the data collected at Kelly AFB indicate that for the conditions encountered during this particular survey, MDI existed as a vapor and that neither the glass fiber tube nor the 37 mm glass fiber filter was a satisfactory sampling method under these conditions.

The sampling trains used during the foam-in-place survey at Kelly AFB were similar to the trains set up during the spray paint surveys, in which single, nitro-coated glass fiber sampling tubes were paired with trains consisting of sampling tubes preceded by uncoated 37 mm prefilters and with single, nitro-coated 37 mm filters, all collected at 2 Lpm for 96 minutes. During the foam-in-place operation, an MDI 7005 tape monitor supplied a direct-reading, continuous strip chart recording of MDI levels.

As shown in Table VII, MDI levels on the single sampling tube do not vary significantly from the levels detected on sampling tubes preceded by an uncoated prefilter. These results indicate that MDI existed as a vapor and may explain the breakthrough evident despite the very low microgram quantities detected during the survey (Table VIII); vapor collection is generally more efficient at lower flow rates. The vapor nature of the MDI also probably explains the nondetectable MDI levels using nitro-coated 37 mm filters. The MDA 7005 tape monitor, sampling at a rate of 1.0 Lpm, over the same time period averaged 1.75 ppb MDI. If the sampling tubes were to detect MDI vapor levels of 1.75 ppb, the microgram amount of MDI present should have been approximately 3.5 micrograms, rather than the less than one-half microgram amount actually detected.

V. CONCLUSIONS

A. HDI Sampling During Aircraft Spray Painting

The data show that only 5-20% of the HDI monomer detected is in the form of free vapor with the remaining 80-95% of the reacting monomer entrapped in paint droplets. While no detectable quantities of HDI pass through the glass fiber sampling tube, it is not possible to determine in a limited field testing situation how much of the HDI present on the glass fiber is actually reacting and what effect a change in variables such as particle size distribution, sample loading, temperature, humidity, etc., would have on the accuracy of the method. Also it is not known what practical significance the

TABLE VII. MDI, $\mu\text{g}/\text{m}^3$ FOAM-IN-PLACE, KELLY AFB
(SURVEY IV)

Group	Uncoated 37 mm Prefilter-Coated Fiber	Coated Fiber	Coated 37 mm Filter
1	3	ND	ND
2	2	2	ND
3	2	1	ND
4	1	3	ND

TABLE VIII. MDI, μg , FOAM-IN-PLACE, KELLY AFB
(SURVEY IV)

Group	Section	Uncoated 37 mm Prefilter-Coated Fiber	Coated Fiber	Coated 37 mm Filter
1	FRONT	0.330	0.299	
	BACK	0.208	0.157	
	TOTAL	0.538	0.456	ND
2	FRONT	0.302	0.287	
	BACK	0.096	0.139	
	TOTAL	0.398	0.426	ND
3	FRONT	0.201	0.246	
	BACK	0.200	ND	
	TOTAL	0.401	0.246	ND
4	FRONT	0.281	0.393	
	BACK	ND	0.188	
	TOTAL	0.281	0.581	ND

actual or detected levels of HDI vapor, or HDI aerosol have in terms of either toxicity or respiratory protection. Nevertheless, the method does provide reasonably precise and reproducible results in a field testing situation. It can be adapted to routine, base-level use with a minimum of difficulty. Overall, the field evaluation shows that with proper handling the glass fiber sampling tube can provide a consistent method for monitoring HDI levels during

spray paint operations up to 8.5 times the TWA and 6 times the ceiling limit at the recommended sampling volumes.

B. TDI/MDI Sampling During Foam-in-Place Operations

The results of the foam-in-place survey at Kelly AFB suggest the need for additional sampling. Future surveys should compare collection of both TDI and MDI at 1 and 2 Lpm, determine the vapor/aerosol nature of the isocyanate, and compare the efficiency of collection of sampling tubes versus flat filters for either vapor or aerosol. The MDA tape monitor method is a proven method for monitoring TDI vapor, although it requires special calibration for accurately monitoring MDI aerosol.

VI. RECOMMENDATIONS

Use of the nitro-coated glass fiber sampling tube method outlined in NIOSH Method P&CAM 326 as the best method currently available for monitoring isocyanate levels during spray painting operations.

Continued use of the MDA 7005 tape monitor when isocyanates are used in operations other than spray painting.

APPENDIX 1

C

MATERIAL SAFETY DATA SHEET						OSHA Approval No. 45-R0138
SECTION I	MANUFACTURER'S NAME AND FIRM (Federal Supply Code for Manufacturers) DEFT CHEMICAL COATINGS 33461					EMERGENCY PHONE NO. 714-549-8911
	ADDRESS (Number, Street, City, State, and ZIP Code) 17451 Von Karman Avenue, Irvine, California 92714					
	CHEMICAL NAME AND SYNONYMS Polyurethane Catalyst component			TRADE NAME AND SYNONYMS Defthane Catalyst		
	CHEMICAL FAMILY Polyurethane isocyanate catalyst			FORMULA 03-4-40 Catalyst		
	FEDERAL STOCK NUMBER (FSN) 8010-00-181-8281			GROSS WEIGHT (LBS) 8282		OUTSIDE PACKAGE DIMENSIONS (Inches)
SECTION II - HAZARDOUS INGREDIENTS	MIL-STD-131/NATIONAL FIRE PROTECTION ASSOCIATION STD 704M SIGNAL FLAMMABILITY X HEALTH REACTIVITY SPECIFIC HAZARD					
	PAINTS, PRESERVATIVES, AND SOLVENTS	%	THRESHOLD LIMIT VALUE (Dose)	ALLOYS AND METALLIC COATINGS	%	THRESHOLD LIMIT VALUE (Dose)
	PIGMENTS			BASE METAL		
	CATALYST			ALLOYS		
	VEHICLE			METALLIC COATINGS		
	SOLVENTS			FILLER METAL PLUS COATING OR CORE FLUX		
	ADDITIVES			OTHERS		
	OTHERS					
	HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES				%	THRESHOLD LIMIT VALUE (Dose)
	Methyl Ethyl Ketone				40	200
Xylene				5	100	
Ethylene glycol mono ether acetate				20	100	
Hexamethylene diisocyanate monomer				0.5	.02	
SECTION III PHYSICAL DATA	BOILING POINT (°F)		175-331°F		SPECIFIC GRAVITY (H ₂ O=1)	
	VAPOR PRESSURE (mm Hg)		28.6		PERCENT VOLATILE BY VOLUME (%)	
	VAPOR DENSITY (AIR=1)		heavier		EVAPORATION RATE (ether=1)	
	SOLUBILITY IN WATER		none			
SECTION IV - FIRE AND EXPLOSION HAZARD DATA	APPEARANCE AND ODOR clear thin water white organic liquid - odor of methyl ethyl ketone					
	FLASH POINT (Method used) 28°F Tag Open Cup ASTM D 1310		FLAMMABLE LIMITS	LOWER EXPLOSIVE LIMIT 1.7	UPPER EXPLOSIVE LIMIT not available	
	EXTINGUISHING MEDIA carbon dioxide, foam or dry chemical					
	SPECIAL FIRE FIGHTING PROCEDURES - a self contained breathing apparatus should be worn. Do not use water stream which might spread fire. Water spray					
	UNUSUAL FIRE AND EXPLOSION HAZARDS OF LOG. Caution against application to hot surfaces and use in areas where sparks or open flames may be present.					

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SECTION V HEALTH HAZARD DATA	THRESHOLD LIMIT VALUE			See Section II
	EFFECTS OF OVEREXPOSURE			
	Moderate eye irritant. Possible irritation of skin by solvents.			
	Irritation or narcosis can result from inhalation of solvent vapors.			
	EMERGENCY AND FIRST AID PROCEDURES Skin contact - wipe off with a rag then thorough rinsing with water and washing with mild soap and water.			
Eye contact - flush 10 minutes with water and consult an eye physician.				
Inhalation - remove to fresh air.				
SECTION VI REACTIVITY DATA	STABILITY	UNSTABLE		CONDITIONS TO AVOID - avoid sparks from being struck with steel object or static electricity.
		STABLE	X	Avoid open flame in vicinity. Avoid exposure to heat.
	INCOMPATIBILITY (Materials to avoid) - avoid contact with water, alcohols and other compounds which react with isocyanates.			
	HAZARDOUS DECOMPOSITION PRODUCTS			
SECTION VII SPILL OR LEAK PROCEDURES	HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
		WILL NOT OCCUR	X	
	STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED			
	Absorb with oil absorbing compound or dry rags. Flush with large volume of water.			
SECTION VIII - SPECIAL PROTECTION INFORMATION	WASTE DISPOSAL METHOD			
	Dispose in tightly closed container and finally dispose by sanitary landfill.			
	RESPIRATORY PROTECTION (Specify type)			
	VENTILATION	LOCAL EXHAUST use adequate ventilation with exhaust fan		SPECIAL
SECTION IX SPECIAL PRECAUTIONS		MECHANICAL (General)		OTHER
	PROTECTIVE GLOVES		yes	EYE PROTECTION
				yes
	OTHER PROTECTIVE EQUIPMENT Use cartridge type respirator with particulate filters. (MSD Catalog No. CR84306)			
SECTION X TRANSP. DATA	PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING			
	Material is sensitive to moisture and should be kept in tightly closed containers.			
	OTHER PRECAUTIONS - avoid prolonged inhalation of vapors. Where ventilation is poor a fresh air supply mask is recommended.			
SECTION X TRANSP. DATA	PROPER SHIPPING (Article) NAME			DOT CLASSIFICATION
	DOT ARTICLE - Paint product			Flammable liquid
	DOT LABEL	DOT MARKING	EMERGENCY ACCIDENT PRECAUTIONS AND PROCEDURES	
	RED		Section V	
SECTION X TRANSP. DATA	DOT PLACARD	PRECAUTIONS TO BE TAKEN IN TRANSPORTATION		
	Flammable	Normal precautions.		

MATERIAL SAFETY DATA SHEET						OMB Approval No. 45-M0338				
SECTION I	MANUFACTURER'S NAME AND PSCH (Federal Supply Code for Manufacturers)					EMERGENCY PHONE NO.				
	DEFT CHEMICAL COATINGS 33461					714-549-8911				
	ADDRESS (Number, Street, City, State, and ZIP Code)									
	17451 Von Karman Avenue, Irvine, California 92714									
	CHEMICAL NAME AND SYNONYMS				TRADE NAME AND SYNONYMS					
	Polyurethane topcoat, base component				Defthane					
SECTION II - HAZARDOUS INGREDIENTS	CHEMICAL FAMILY		FORMULA							
	Polyurethane enamel, aliphatic		03-W-40, Color 17875, MIL-C-832863							
	FEDERAL STOCK NUMBER (FSN)		GROSS WEIGHT (LBS)		OUTSIDE PACKAGE DIMENSIONS (Inches)					
	8010-00-181-8281 & 8281									
	MIL-STD-131/NATIONAL FIRE PROTECTION ASSOCIATION STD 704M SIGNAL									
	FLAMMABILITY ☒ HEALTH ☐ REACTIVITY ☐ SPECIFIC HAZARD ☐									
SECTION III - PHYSICAL DATA	PAINTS, PRESERVATIVES, AND SOLVENTS		%	THRESHOLD LIMIT VALUE (Units)	ALLOYS AND METALLIC COATINGS		%	THRESHOLD LIMIT VALUE (Units)		
	PIGMENTS				BASE METAL					
	CATALYST				ALLOYS					
	VEHICLE				METALLIC COATINGS					
	SOLVENTS				FILLER METAL PLUS COATING OR CORE FLUX					
	ADDITIVES				OTHERS					
	OTHERS									
	HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES							%	THRESHOLD LIMIT VALUE (Units)	
	Methyl ethyl ketone							10	200	
	Ethyl Acetate							10	400	
SECTION IV - FIRE AND EXPLOSION HAZARD DATA	Ethylene glycol mono ethyl ether acetate							20	100	
	BOILING POINT (°F)		169-331°F		SPECIFIC GRAVITY (H ₂ O=1)		1.37			
	VAPOR PRESSURE (mm Hg)		15.0		PERCENT VOLATILE BY VOLUME (%)		53.44			
	VAPOR DENSITY (AIR=1)		heavier		EVAPORATION RATE (ether=1)		slower			
	SOLUBILITY IN WATER		none							
	APPEARANCE AND ODOR									
White paint, odor pleasant-pungent										
SECTION IV - FIRE AND EXPLOSION HAZARD DATA	FLASH POINT (Method used)		28°F Open cup ASTM D 1310		FLAMMABLE LIMITS		LOWER EXPLOSIVE LIMIT 1.6		UPPER EXPLOSIVE LIMIT not available	
	EXTINGUISHING MEDIA									
	Carbon dioxide, foam or dry chemicals									
	SPECIAL FIRE FIGHTING PROCEDURES - do not use water stream which might spread fire. Water spray or fog can be used effectively.									
	UNUSUAL FIRE AND EXPLOSION HAZARDS									
	Caution against application to hot surfaces and use in areas where sparks or open flames may be present									

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SECTION V HEALTH HAZARD DATA	THRESHOLD LIMIT VALUE See Section II		
	EFFECTS OF OVEREXPOSURE Moderate eye irritant. Possible irritation of skin by solvent.		
	Irritation or narcosis can result from inhalation of solvent vapors.		
	EMERGENCY AND FIRST AID PROCEDURES Skin contact - wipe off with a rag then thorough rinsing with water and washing with mild soap and water.		
	Eye contact - flush 10 minutes with water and consult an eye physician.		
SECTION VI REACTIVITY DATA	Inhalation - remove to fresh air.		
	STABILITY	UNSTABLE	CONDITIONS TO AVOID - avoid sparks from being struck with steel object or static electricity.
		STABLE	Avoid open flame in vicinity. Avoid exposure to heat.
	INCOMPATIBILITY (Materials to avoid)		
	HAZARDOUS DECOMPOSITION PRODUCTS		
SECTION VII SPILL OR LEAK PROCEDURES	HAZARDOUS POLYMERIZATION	MAY OCCUR	CONDITIONS TO AVOID
		WILL NOT OCCUR	
	STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED		
	Absorb with oil absorbing compound or dry rags. Flush with large volume of water. Avoid sparks or open flame.		
SECTION VIII - SPECIAL PROTECTION INFORMATION	WASTE DISPOSAL METHOD		
	Dispose of clean-up rags by wetting with water and keep in a closed container. Dispose in tightly closed metal container and finally dispose by sanitary landfill.		
	RESPIRATORY PROTECTION (Specify type) Good ventilation		
	VENTILATION	LOCAL EXHAUST Use adequate ventilation with exhaust fan	SPECIAL
		MECHANICAL (General)	OTHER
SECTION IX SPECIAL PRECAUTIONS	PROTECTIVE GLOVES		EYE PROTECTION
	yes		yes
	OTHER PROTECTIVE EQUIPMENT		
	PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING		
	Use normal storing precautions as with paint. Keep away from heat, sparks or open flames.		
SECTION X TRANSP. DATA	OTHER PRECAUTIONS		
	Avoid prolonged inhalation of vapor.		
	PROPER SHIPPING (Article) NAME DOT ARTICLES - Paint product		DOT CLASSIFICATION Flammable Liquid
	DOT LABEL Red	DOT MARKING	EMERGENCY ACCIDENT PRECAUTIONS AND PROCEDURES See Section V
	DOT PLACARD Flammable	PRECAUTIONS TO BE TAKEN IN TRANSPORTATION Normal precautions.	

LITERATURE CITED

1. Birch, S.R., Industrial Hygiene Survey - 47th FMS Aircraft Painting Facility, Laughlin AFB TX, OL AA USAF OEHL, Kelly AFB TX, Report No. 77-2, March 1977.
2. Bishop, E. C., Evaluation of Aircraft Touchup Painting, Mather AFB CA, USAF OEHL Report No. 81-41, May 1981.
3. Burnett, R.D., and P. Diamond, Industrial Hygiene Evaluation of Spray Applications of Polyurethane Coatings, USAF EHL, McClellan AFB CA, Report No. 73-10, Nov 1973.
4. Criteria for Recommended Standard--Occupational Exposure to Diisocyanates, Publication No. 78-215, Rockville MD, USD (HEW), PHS, NIOSH, Sep 1978.
5. Dharmarajan V., and H. Weill, Physical State of Airborne p-p'-diphenyl methane diisocyanate (MDI) and its Measurement, Am. Ind. Hyg. Assoc. J, 39:737-44, 1978.
6. Prather, J.B., Industrial Hygiene Evaluation - Aircraft Painting Facility, Bldg 692, McClellan AFB CA, USAF OEHL Report No. 81-10, February 1981.
7. Toluene 2,4-Diisocyanate--Physical and Chemical Analysis Branch, Analytical Method No. P&CAM 326, NIOSH Manual of Analytical Methods, DHEW (NIOSH) Publication No. 80-125, Cincinnati, U.S. DHEW, PHS, CDC, NIOSH, 1980, Vol. 6, pp. 326-1/326-11.
8. Tucker, S.P., and J.E. Arnold, Sampling and Determination of 2,4-Bis(carboxylamino) toluene and 4,4-Bis(carboxylamino) diphenyl methane in Air. NIOSH, Cincinnati, Ohio, Unpublished.
9. Vogt, C.R.H., C.Y. Ko, and T.R. Ryan, Modification of an Analytical Procedure for Isocyanates to High Speed Liquid Chromatography. Cincinnati, USDHEW, PHS, CDC, NIOSH, 1976.

