Evaluation of Protective Gloves
Used In the Collision Repair Industry

Diana Ceballos

A dissertation submitted in partial fulfillment
of the requirements for the degree of

Doctor of Philosophy

University of Washington

2009

Program Authorized to Offer Degree:
Environmental and Occupational Health Sciences

University of Washington
Graduate School

This is to certify that I have examined this copy of a doctoral dissertation by

Diana Ceballos

and have found that it is complete and satisfactory in all respects,
and that any and all revisions required by the final
examining committee have been made.

Chair of the Supervisory Committee:

Michael G. Yost

Reading Committee:

Michael G. Yost

Michael S. Morgan

Michael S. Morgan

S. G. Whittaker

Stephen G. Whittaker

Date: 07-15-2009

In presenting this dissertation in partial fulfillment of the requirements for the doctoral degree at the University of Washington, I agree that the Library shall make its copies freely available for inspection. I further agree that extensive copying of the dissertation is allowable only for scholarly purposes, consistent with "fair use" as prescribed in the U.S. Copyright Law. Requests for copying or reproduction of this dissertation may be referred to ProQuest Information and Learning, 300 North Zeeb Road, Ann Arbor, MI 48106-1346, 1-800-521-0600, to whom the author has granted "the right to reproduce and sell (a) copies of the manuscript in microform and/or (b) printed copies of the manuscript made from microform."

Signature Diana Ceballos
Date 07-15-2009

University of Washington

Abstract

Evaluation of Protective Gloves Used In the Collision Repair Industry

Diana Ceballos

Chair of the Supervisory Committee:
Professor Michael G. Yost
Department of Environmental and Occupational Health Sciences, School of Public Health

This dissertation describes studies that were a collaborative effort to determine priority research to address isocyanate exposure in the Washington State collision repair industry. This work focuses on addressing dermal protection needs by assessing the effectiveness of gloves commonly used by autobody painters, through the use of a permeation panel. Dermal exposure to isocyanates is significant in these shops, and can contribute to the development of occupational asthma. Limited and conflicting information is available on the effectiveness of protective gloves for spray painters. Conventional permeation testing methods do not work with low volatility, low water-solubility agents, complex mixtures, or materials that polymerize or cure, like isocyanate-based paint. In chapter 2, we describe an objective color scale technique, developed to assess isocyanate surface contamination by using computerized image analysis tools. This technique has great potential for dermal exposure assessment, and proved valuable for measuring glove permeation with the permeation panel. Chapter 3 provides an overview of the dermal protection currently used in Washington State's collision repair industry including a discussion of gloves commonly used by painters. Chapter 4 summarizes a comparison of current isocyanate analytical methods used to determine isocyanate concentrations in a representative sample of commercial hardener. This isocyanate analytical method comparison elucidates the challenges of measuring isocyanates, and ultimately helped validate the results from the permeation panel experiments. Chapter 5 describes the development of a permeation panel to test the efficacy of dermal protective clothing against

sprayed coatings. The panel is a novel field-testing device that can provide objective permeation data and can test several materials at once, under actual spray-coating conditions. The permeation panel could also be used to measure other permeants, such as solvents and other sprayed coatings. Finally, in chapter 6, several protective gloves commonly used by painters were evaluated against aliphatic isocyanate paints used in the collision repair industry. This provides the basis for initial recommendations for the selection of protective gloves when spray painting.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Table Number Page

ACKNOWLEDGEMENTS

First and foremost, the author would like to thank God for the opportunity to work in such a stimulating field guided by exceptional mentors, colleagues, and collaborators. Secondly, sincere thanks to Prof. Michael Yost: committee chair, advisor, and mentor. Without him, this work would not have been possible. His brilliant mind, wisdom, humility, great heart, and admirable sense of humor helped the author grow as a scientist navigating the graduate school maze.

Also, the author would like to acknowledge:

- Dr. Stephen Whittaker for agreeing to be a committee member. He has been a mentor and friend, who tirelessly helped and motivated. Steve facilitated the author's internship at SHARP, leading to this dissertation and meaningful on-going collaboration. Much of this dissertation came from his great ideas. His help in the field and incredible patience editing drafts and presentations were indispensable.
- Janice Camp for agreeing to be a committee member. She has been a mentor and friend who helped identify internships and provided constant support and motivation.
- Dr. Michael Morgan and Dr. Richard Gammon for agreeing to be committee members. Their advice, editing, and support provided positive direction throughout this process.
- Carolyn Reeb-Whitaker for her friendship and support. The author is grateful for Carolyn's contributions with the design of the permeation panel experiments, reviewing manuscripts, motivation, and assistance in the field.
- The Department's EH Lab for their generous and patient support of the project's chemical analysis needs. Special thanks to Russell Dills, who tirelessly helped with wise advice, clever ideas, and assistance finding resources.
- The WISHA Lab for their help and support providing supplies and chemical analysis. Special thanks to Lisa Weiland for her advice and supplying hardener samples.
- Dr. Leena Nylander-French and her lab (especially Linda Gaines, Kenny Fent, Sheila Flack, and Jen Thomasen) for the unique opportunity to assist in the field and collaboration in different projects.
- Dr. Dhimiter Bello for assisting on the inter-method protocol, providing chemical analysis expertise, collaboration, and reviewing a manuscript.
- Tom Klingner (Colorimetric Laboratories, Inc.) for his guidance.

- Robert Anderson for his help in collecting samples.
- Mary Cushmac (Environmental Protection Agency) for her expert advise.
- Biostatistics Consulting Group (UW) and Joyce Fan (SHARP Program) for their valuable help with the statistical analysis.
- Robert Streicher for his advice and reviewing of a manuscript.
- Marc Beaudreau for building the permeation panel prototype and his ingenious ideas for the final panel.
- Ming-Yi Tsai for brainstorming ideas to build the permeation panel.
- Jeff Brandon for technical advice and impeccable workmanship building the permeation panel and cells.
- Venetia Runnion for her friendship and editing.
- Collaborating labs for their efforts, lab analyses, and support for the inter-method study.
- Participating Puget Sound Spray Painting Training Facilities and Shops. Special thanks to the spray-paint trainer who shared his knowledge and time, helping this project be a reality.
- The Department's grad students. Special thanks to Eric Coker, Danielle Parette, and Jackelin Tran, for their invaluable help in the field. Also thanks to Rick Neitzel for his help with biostatistics.
- The Department's professors. Special thanks to Chris Simpson for the opportunity to work as a research scientist. Also thanks to Lee Monteith for reviewing a manuscript.
- The Department's staff. Special thanks to Rory Murphy, Monica Leibrant, and Patty Foster for their help and friendship.
- The Yost lab for their help, patience, and company.
- Funding by the ERC, NORA, and the SHARP Program.
- Family and friends for their love and constant support. Special thanks to the author's parents Elkin and Beatriz for their emotional and financial support. Thanks especially to Beatriz for her loving care of the author's daughter. Special thanks to the author's husband Neal for his love, listening, and selfless day-to-day generosity. Thanks for his help editing and technology assistance. The author is indebted for his contribution to this dissertation by drawing the design of the permeation cells. Thanks also to the author's daughter, Isabela, for being a motivation and inspiration in her life.

DEDICATION

To my loving husband.

Chapter 1

INTRODUCTION

The collision repair industry in the Puget Sound is composed of numerous small businesses, many of which have ineffective health and safety practices. Paint spraying and mixing painting processes, besides being an inhalation hazard, contribute to a painter's dermal exposure. Isocyanates are present in high concentration in the final "clear" coat. Isocyanates are known irritants and sensitizers (Redlich *et al.* 2007). These substances are also a leading cause of work-related asthma in Washington State (Whittaker and Reeb-Whitaker 2009). Of particular concern are the findings in animal studies that respiratory sensitization may be initiated by dermal exposure (Erjefalt and Persson 1992; Rattray *et al.* 1994, Bello *et al.* 2007a). While the majority of painters wear respirators while spray-painting, they do not necessarily wear gloves that protect their skin. Little information currently is available on the effectiveness of protective gloves for spray painters because no systematic investigation has ever been conducted. The currently available information is largely focused on comfort, elasticity, or solvent resistance, rather than resistance to isocyanates. Compatibility charts provided by manufacturers and suppliers regarding diisocyanate monomers and oligomers protection are limited and conflicting. This is not surprising since isocyanates have chemical characteristics that make testing difficult with standard methods used to test protective clothing. We developed a novel field device for testing the efficacy of gloves for protection against isocyanate sprayed coatings.

This study had the following specific aims:

1. Review the literature to understand the usage and importance of isocyanates in the collision repair industry, as well as the health concerns associated with the dermal route of exposure;
2. Summarize our field observations and questionnaire data on dermal protection in the Washington State collision repair industry and compare usage of different PPE with SHARP's needs assessment findings;
3. Review our development of an objective color scale and analysis algorithm for isocyanates;

4. Critically compare different chemical methods currently used to analyze the isocyanates present in clear coat hardeners by conducting an analytical method comparison study;
5. Evaluate chemical protective gloves, specifically nitrile and latex, for resistance to isocyanates using a permeation system:
    a. Design and construct permeation panels suitable for use in controlled spray applications;
    b. Characterize the permeation system;
    c. Select a representative set of glove materials and paint formulations for testing with the permeation system based on manufacturer's literature, and existing data from the field survey of auto body shops;
    d. Conduct colorimetric and quantitative screening permeation tests of glove materials for selected paint formulations;
    e. Conduct quantitative permeation rate experiments for selected glove materials;
    f. Summarize permeation test panel findings and provide recommendations for future studies.

1.2. Background

Isocyanates are highly reactive organic chemicals containing the functional group – N=C=O. More than 6 million tons of isocyanates are produced annually worldwide and this number increases between 10 and 15% per year (Tremblay *et al.* 2003). The total number of workers currently exposed to isocyanates is not known. NIOSH's estimate of 280,000 U.S. workers exposed or potentially exposed to isocyanates (NIOSH 1996) and it is increasing given the growth of this industry (Bello *et al.* 2007a). Isocyanates are classified based on the number of NCO (e.g. monoisocyanates, diisocyanate, or polyisocyanates) or the type of molecules bound to the functional group (e.g. aromatic and saturated or aliphatic). The diisocyanate monomers are important because the two NCO groups allow them to undergo direct polymerization reactions with alcohols to form polyurethanes. In addition, diisocyanates monomers are used in prepolymerization reactions to form commercially important polyisocyanates. Polyisocyanates formed by the condensation of up to 15 monomeric isocyanates are also called oligomers. Polyisocyanates still contain multiple free NCO groups and can further react with other active hydrogen compounds, such as polyfunctional alcohols (polyols) or amines, to form polymeric products of even greater complexity. The chemical structures of some major isocyanates of commercial importance are found in Bello *et al.* (2004) and Bayer Corporation (1997).

For the purpose of this discussion, terms are defined as follows (Streicher *et al.* 2000):

- Diisocyanate monomer: the difunctional isocyanate species from which polyisocyanates and polyurethanes are derived. Common examples include 1,6-hexamethylene diisocyanate (HDI), 2,4- and/or 2,6-toluene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), and isophorone diisocyanate (IPDI).
- Polyisocyanates: species possessing free isocyanate groups and derived from monomeric isocyanates either by directly linking these monomeric units (a homopolymer) or by reacting these monomers with di- or poly-functional alcohols or amines (a co-polymer).
- Prepolymer: species possessing free isocyanate groups, prepared from the reaction of polyol with an excess of di- or polyisocyanate. Commercially available isocyanate products frequently contain prepolymers in lieu of more volatile isocyanate monomers.
- Oligomeric isocyanate (oligomers): relatively low molecular weight polyisocyanates (containing up to about 15 monomeric units). Common examples of HDI oligomers include biuret, isocyanurate and uretidone. For the purpose of this dissertation, the words polyisocyanates and oligomers will be used interchangeably.
- Intermediates: species possessing free isocyanate groups formed during use of an isocyanate product by partial reaction of the isocyanate species with a polyol.

Exposure to isocyanates is irritating to the skin, mucous membranes, eyes, and respiratory tract (Streicher *et al.* 2000). The most common adverse health outcomes associated with exposure to both monomeric and oligomer forms is asthma due to sensitization. Less prevalent are contact dermatitis (both irritant and allergic forms) and hypersensitivity pneumonitis (HP) (Streicher *et al.* 2000). Isocyanate-induced asthma appears to be a multifactorial disease involving the immune system, airway epithelium, and genetic factors. (Liu and Wisnewski 2003). The only effective intervention for workers with isocyanate-induced sensitization (asthma) or HP is cessation of all isocyanate exposure. This typically is accomplished by removing the worker from the work environment where isocyanate exposure occurs. After sensitization, exposures to levels below an occupational exposure limit or standard can produce an asthmatic response that may be life threatening (Streicher *et al.* 2000).

Isocyanate exposures can occur at work, even with the use of personal protective equipment (Bello *et al.* 2007b and Fent *et al.* 2008). Numerous occupations involve risk of isocyanate exposure, including polyurethane foam makers, plastic molders, upholstery and furniture workers, spray painters, wire coating workers, rubber workers, insulation installer, and workers in foundries and transportation equipment manufacturing (Liu and Wisnewski 2003). Also, many consumer products contain isocyanates such as glues, foam insulation, and polyurethane coatings (Bello *et al.* 2007a).

Animal studies suggest that skin contact is an efficient route to induce sensitization, with subsequent inhalation challenge resulting in asthma-like responses (Erjefalt & Persson 1992; Rattray *et al.* 1994; and Bello *et al.* 2007a). Several lines of evidence support a similar role for human isocyanate skin exposure (Bello *et al.* 2007a). Sufficient evidence already exists to justify greater emphasis on the potential risks of isocyanate skin exposure and the importance of preventing such exposures at work and during consumer use of certain isocyanate products (Bello *et al.* 2007a). Indirect evidence from a growing number of case reports and clinical and epidemiologic studies suggests that isocyanate skin exposure occurs in the workplace and can increase the risk for sensitization and isocyanate asthma (Bello *et al.* 2007a). Further, isocyanate asthma can occur in settings where measured isocyanate respiratory exposures are below the level of detection, even when sensitive analytical methods are used (Bello *et al.* 2007a).

Historically, the focus to minimize isocyanate-induced health effects has been on inhalation exposures. To reduce the vapor hazards associated with the lower molecular weight diisocyanates, prepolymer and polyisocyanate forms were developed and have replaced the monomers in many product formulations (Streicher *et al.* 2000). Use of less volatile isocyanates as well as improved hygiene practices, have resulted in reductions in inhalation exposures to volatile monomer (Bello *et al.* 2004), thereby potentially increasing the relative importance of skin exposure. Isocyanate skin exposure could contribute a significant proportion of the total body burden of isocyanates (Bello *et al.* 2004 and 2007a). Workers are still being exposed to high isocyanate air concentrations (Sparer *et al.* 2004). In the U.S. regulations for these chemicals are not sufficiently adequate to ensure that good practices are enforced (Bello *et al.* 2004). This lack of regulations stems partially from the challenges in the sampling, analysis, and metrics (or units) for isocyanates, especially for polyisocyanates (Bello *et al.* 2004).

1.3. Isocyanates and the Collision Repair Industry

1.3.1. Occupational Isocyanate Exposure and Disease Risk in the Collision Repair Industry

Polyurethane paints containing isocyanate hardeners were introduced in the US car refinishing market in the late 1960s and began to be widely used in the 1980s. In 1999 there were ~35,000 automotive refinishing facilities in the USA, employing ~207,000 people (Woskie *et al.* 2004). Between 2,200 and 2,800 production employees are potentially exposed to isocyanates in Washington State's collision repair industry. About 1,155 auto repair facilities were identified in King County alone in late 1999 (Marshall *et al.* 2002) but all of these facilities did not necessarily paint. The Safety & Health Assessment & Research for Prevention (SHARP) program at the Washington State Department of Labor & Industries identified a total of 1,258 collision repair shops in Washington State with 2,168 production employees, 828 were painters and 1,340 were collision techs (SHARP 2005 and Whittaker and Reeb-Whitaker 2009).

Production workers in the collision repair industry may be exposed to a wide range of chemical hazards, including metals, organic solvents, and, most notably, isocyanates. Isocyanates are a particular concern because their widespread use in this industry (NIOSH 1996) is a leading cause of work-related asthma (Liu & Wisnewski 2003). Isocyanates appear as catalyst hardeners in two-part polyurethane paint systems, primers, sealers, and basecoats. However, the final "clear coat" usually involves higher concentrations than primer/sealer (Sparer *et al.* 2004) and may result in higher exposures. Spraying these products can create a significant inhalation hazard for aerosolized isocyanates (EPA 2005; Sparer *et al.* 2004). Dermal exposures also may occur during handling of pre-mixed or mixed paint products and during spraying and clean-up.

The American Thoracic Society estimated that 15% of adult asthma may be attributable to occupational exposure (American Thoracic Society 2003). Occupational disease surveillance in the United Kingdom identified isocyanates as the most common causative agents for work-related asthma (WRA) in the period 2002-2004 (HSE 2005a). The UK's Surveillance of Work-related and Occupational Respiratory Disease (SWORD) suggests that "vehicle spray painters" had the second-highest rate of WRA (HSE 2005b) for the period 2002-2004. The WRA rate for vehicle painters (86 WRA cases per 100,000 workers per year) was 86-fold greater than the rate determined for "all occupations" (1 case per 100,000 workers per year). Further, the West Minlands Thoracic Society's Rare Respiratory Disease Registry Surveillance Scheme of Occupational Asthma (Shield) reported that isocyanates were the commonest offending agents responsible for 21% of occupational asthma reports for the period of 1991 and 2005 (Bakerly *et al.* 2008).

SHARP reviewed Washington State's workers' compensation data from 1995 through 2002 (SHARP 2003). The automotive repair industry exhibited the second-highest rate of compensable State Fund asthma claims: 20.3 compensable claims per 100,000 full-time equivalents (FTE) per year, a rate almost ten times the overall incidence rate of 2.2 per 100,000 FTE per year. Additionally, the rate for all asthma claims (compensable as well as non-compensable) filed in this industry (32.5 claims per 100,000 FTE per year) was three times the overall rate of 9.8 claims per 100,000 FTE per year. Although the causative agent(s) were not described, it is likely that exposure to isocyanates in two-part paint systems was largely responsible for this respiratory disease.

SHARP also administers Washington State's WRA surveillance system (SHARP 2000, 2003), which is partially funded by NIOSH. WRA cases are received from two sources: Washington State's workers' compensation database and reporting physicians. A careful review of cases identified from September 2000 to July 2005 identified a total of 937 workers' compensation claims filed for WRA, and 12 of these cases were filed by workers conducting collision repair (identified by reviewing text associated with the claims file). Of these 12 cases, eight had confirmed exposures to isocyanates that were identified as contributing factors in the workers' asthma. An additional two cases had possible isocyanate exposures while the remaining two workers were unlikely exposed to isocyanates.

1.3.2. Clear coat Application in the Collision Repair Industry

Clear coats are the non-pigmented top-coats that are applied over base-coat paints. Clear coats improve the vehicle coating systems' general appearance and durability. Clear coats are typically polyurethane coatings based on a combination of a polyol resin and isocyanate "pre-polymers". The most common isocyanates used in clear coats are 1,6-hexamethylene diisocyanate (HDI) monomer and its oligomers (e.g., uretidone, biuret, and isocyanurate), although some formulations may also contain monomeric and polymeric isophorone diisocyanate (IPDI).

In the auto body shop, painters typically combine three constituents to yield the final clear coat mixture. The first constituent is the "clear", which contributes the polyols (plus other solids and organic solvents). The second constituent is the "hardener", which contains the isocyanates. The final constituent is the "reducer" or "thinner", which lowers the viscosity of the mixture for spray application. The painter applies this three-part mixture to the painted surface with a spray gun. The reaction between the polyols and isocyanates results in polymerization of the clear coat mixture to yield a polyurethane coating. It is not possible to predict the surface chemistry of individual products with any certainty because the manufacturers consider the precise composition of clear coat systems and the role of individual constituents to be proprietary information.

Many additives in the paint are used, with thinners being the most common. Several different types of thinners are specified for the same paint, each having a unique evaporation rate. The slow thinner is for high ambient temperatures and the quick or faster thinner is for low ambient temperatures. For example, a slow thinner must be used at high temperatures so that only a small amount of thinner evaporates during the time the paint leaves the spray gun and reaches the surface being painted (Toyota Motor Corporation 1991).

1.4. Measuring Isocyanates

This section will focus on an overview of methods used for air, surface, and skin sampling of isocyanates in the workplace, in particular related to collision repair industry. Even though measurement of other biological samples, such as urine (Pronk *et al.* 2006a, Trelles Gaines *et al.* 2009), have been studied, we will not discuss these methods because they are outside of the scope of this dissertation.

1.4.1. Isocyanate Air Sampling

Although several standardized methods exist for the measurement of aliphatic diisocyanate monomers (e.g. OSHA 42, OSHA PV2034, NIOSH 5522, NIOSH 5521), only a few methods are standardized to measure oligomeric isocyanates (e.g. OSHA PV2030) or total isocyanates (e.g. NIOSH 5525). Quantifying oligomers is much more complex. There are currently three potential approaches used to quantify and express concentrations of oligomers: the pure product mass, the NCO group concentration or mass, and the monomer equivalent mass (Bello *et al.* 2004). However, the Iso-Chek method bases its measurement according to the physical state of the species. This dual system is intended to collect aerosols on a reagentless front filter and collect vapors on a reagent-coated back filter consequently monomers and oligomers are analyzed separately (Streicher *et al.* 2000).

The reactivity of isocyanates dictates that samples must be derivatized for stabilization and enrichment (Henneken *et al.* 2007). There are many derivatization reagents and analytical methods for isocyanates. Some derivatization reagents include 1-(2-pyridyl)piperazine or PPZ, 9-(methylaminomethyl)anthracene or MAMA, 1-(2- methoxyphenyl)piperazine or 2-MP, and dibutyl amine or DBA. Henneken *et al.* (2007) critically compared several commonly-used sampling and analytical methods for isocyanates and concluded that although the OSHA method for isocyanates analysis still uses 1-(2-pyridyl)piperazine or PPZ, 9-(methylaminomethyl)anthracene or MAMA) and 1-(2- methoxyphenyl)piperazine or 2-MP) exhibit greater stability and sensitivity. Streicher *et al.* (2000) also recognizes that PPZ can exhibit stability problems but this can be counteracted by storing filters in the freezer before sampling. However, Streicher *et al.* (1996) and Bello *et al.* (2002) evaluated three parameters for the different derivatization reagents: 1) chemical reactivity, 2) analytical sensitivity and 3) response factor across multiple isocyanate species. These authors reported that the reagent, 1-(9- anthracenylmethyl)piperazine or MAP outperforms other reagents in its class (especially 2-MP, PPZ, and MAMA). Tremblay *et al.* (2003) provided further evidence that significant differences may exist for methods that rely on these derivatization reagents.

The complex and non-volatile molecules resulting from the derivatization reaction with isocyanates makes liquid chromatography the best option for chemical analysis. Typical detectors for isocyanate analysis include ultraviolet (UV), fluorescence (FL), electrochemical (EC), mass spectrometry (MS), and tandem MS or MS/MS (NIOSH 2004, Streicher *et al.* (2000). UV has been coupled with FL, like in the case of OSHA 42/47 and NIOSH 5525 (NIOSH 2004). UV has also been coupled with EC detection, for example for method NIOSH 5521. FL has been coupled with EC for method NIOSH 5522 (NIOSH 2004). A disadvantage of the EC detector is incompatibilities with HPLC gradient elution; EC detectors are especially sensitive to changes in mobile phase (Streicher *et al.* 2000). DBA has been used exclusively with LC/MS-MS analysis for the measurement of monomers and oligomers (Pronk *et al.* 2006b, Bobeldijk *et al.* 2008). LC/MS-MS has also been reported with the use of 2-MP derivatization reagent for the measurement of HDI and IPDI monomers in air samples (Gagnes *et al.* 2005 and Boutin *et al.* 2006). LC-MS with 2-MP has been also used for the measurement of HDI monomer in tape stripping (Fent *et al.* 2006) as well as for HDI monomer and oligomers in tape stripping, air, and bulk samples (Fent *et al.* 2008). There has not been, to our knowledge, a report of the coupling of MS with other detectors.

Recent methods have emerged using LC/MS (Fent *et al.* 2008) or modified versions of standard methods such as modified NIOSH 5525 (Bello *et al.* 2002, NIOSH 2003). Methodological improvements have focused on improving sensitivity and measuring oligomers with more specificity. Because isocyanates are sensitizers, the ability to detect them at relatively low air concentrations is important (Bello *et al.* 2002). Methods that have reported excellent limits of detection include LC-MS-MS (Boutin *et al.* 2006 and Bobeldijk *et al.* 2008) as well as LC-MS (Fent *et al.* 2008). Much of the challenge associated with measuring oligomers is that there are no commercial oligomer standards. Isocyanate oligomers are not available for purchase in pure form, so even established methods call for purification of commercial products to generate oligomer standards (e.g. OSHA PV2030 or OSHA PV2125).

Comparing performance of different isocyanate methods is challenging, especially for oligomer species because, as already mentioned, standards are not commercially available. The Skarping group, for example, developed an LC-MS-MS DBA system for HDI monomer and HDI oligomers (Bobeldijk *et al.* 2008). The standards were prepared as described by Karlsson *et al.* (2005), which for HDI oligomers used isocyanate products reacted with labeled DBA and characterized by LC. Pronk *et al.* (2006a, 2006b) described using procedures by Karlsson *et al.* (2005) for the production of standards. However, further purification was described by Fent *et al.* (2008) in the production of their standards. The urea derivative of HDI was synthesized according to NIOSH method 5521 while the oligomers were purified in house. Purification included crystallization, filtration, lyophilization, and HPLC-UV separation. Standards were also characterized by nuclear magnetic resonance spectrometer.

1.4.2. Isocyanate Surface Sampling

A promising direct-reading test for the presence of unpolymerized isocyanates is a reagent impregnated surface sampling pad, developed by CLI (SWYPE, Colorimetric Laboratories Inc., Des Plaines, IL). Using a proprietary chemical reaction, these pads employ a simple and sensitive colorimetric response to identify surfaces contaminated with isocyanates. The pad changes color from yellow to orange/red proportionally with the concentration of the isocyanate functional group (NCO) (Bello *et al.* 2007b, Liu *et al.* 2000, Liu *et al.* 2007, OSHA 1997a, and OSHA 1999).

Other surface sampling techniques rely on wipe pads that are later analyzed with same methods used for air sampling (OSHA 2002). An example is OSHA method W4002, in which wipes impregnated with dioinized water are used for surface sampling with the help of a wetting agent (isopropyl alcohol and water) and analyzed using the OSHA 42 method (OSHA 1989). Another example is wipe pads impregnated with polypropylene glycol and analyzed by NIOSH 5525, as reported by Bello *et al.* (2007b).

1.4.3. Isocyanate Skin Exposure Sampling

Skin wipe samples taken on potentially exposed areas of an employee's body are a useful technique for demonstrating exposure to a recognized hazard (OSHA 1997b). For water-soluble chemicals, a wipe pad moistened with deionized water can be used to wipe the skin (OSHA 1997b). In the case of isocyanates, pads are usually moistened with polypropylene glycol instead to improve recovery (Bello *et al.* 2008). Other techniques include tape-stripping, which use a surgical tape applied to the surface of the skin of an exposed worker. When removed, the tape-strip removes one layer of corneocytes, including chemicals contained in the cell layer. Hence successive tape-strips can serve to explore the extent of percutaneous penetration (Fent *et al.* 2006). Wipe-sampling or tape-stripping is usually conducted on the dorsal side of each hand and on the dorsal and volar sides of each arm. Isocyanate skin exposure has also been documented qualitatively with colorimetric techniques in several work settings (Liu *et al.* 2000; Bello *et al.* 2008). Lastly, extraction from nitrile gloves used underneath protective gloves was used to measure hand skin exposure to isocyanates (Pronk *et al.* 2006a)

1.4.4. Metrics and Regulations

As discussed by Bello *et al.* (2004), most occupational exposure limits (OELs) are for isocyanate monomers and only a few exist for polyisocyanates. The Occupational Safety and Health Administration (OSHA) has ceiling Permissible Exposure Limits (PELs) for TDI and MDI monomers, but no 8-hr-time weighted average (TWA) standard for diisocyanates monomers or polyisocyanates. NIOSH has ceiling and full-shift TWA recommended exposure limits (RELs) for several diisocyanate monomers, but none for polyisocyanates. The American Conference of Governmental Industrial Hygienists (ACGIH) has full-shift TWA threshold limit values (TLVs) for a variety of monomers with a short-term exposure limit (STEL) set only for TDI monomer. ACGIH has no polyisocyanate TLVs. The OSHA, ACGIH, and NIOSH OELs for diisocyanate monomers are all expressed as the monomer mass concentration. The Bayer Corporation has established Manufacturer's Guideline Limits (MGL), which were later adopted by the Oregon State OSHA. Limits include an 8-hr PEL of 0.5 mg/m3 and a ceiling limit of 1 mg/m3 for the HDI-based biuret and isocyanurate only (HDI monomer excluded), expressed as pure product mass concentration (Bello *et al.* 2004).

The United Kingdom Health and Safety Executive (UK-HSE) regulates isocyanates using total NCO mass as the exposure metric. This approach combines all monomers and polyisocyanates into a single total isocyanate standard, which is expressed as micrograms NCO group/m^3. The UK-HSE sets the maximum exposure limits at 20 μg NCO/m^3 for the full shift and 70 μg NCO/m^3 for a 15-min short-term exposure limit (STEL) (Bello *et al.* 2004). The Australian National Occupational Safety and Health Commission has also adopted the UK-HSE maximum exposure limits for isocyanates (Bello *et al.* 2004). The Swedish standard is set at 20 (TWA) and 44 (5-min STEL) mg NCO/m^3 (equal to 90 and 200 μg pure HDI-biuret mass/m^3, respectively) (Bello *et al.* 2004).

There are currently no surface contamination criteria or quantifications for skin absorption included in OSHA standards (OSHA 1997b). Chemicals that pose a health hazard through skin exposure are commonly assigned two qualitative descriptors: a "skin" notation, referring to absorption of the chemical through the skin, and/or a "sensitizer" notation for an agent with the potential to produce sensitization regardless of the exposure route (respiratory, skin, or conjunctiva) (Bello *et al.* 2007a). In the United States, although NIOSH recommends prevention of isocyanate skin exposure, skin exposure is not regulated. No "skin" notation exists for diisocyanates monomers or polyisocyanates, except for the NIOSH (2005) recommendation for IPDI (Bello *et al.* 2007a).

Recommendations for the prevention of skin exposure are now being made in Material Safety Data Sheets (MSDS) and are beginning to appear in the medical literature (Bello *et al.* 2007a). Wider dissemination and improved hazard communication of this information by occupational and environmental health professionals, as well as better personal protection among workers, are needed. Inclusion of "skin" notation may encourage such protection for all isocyanates (diisocyanates monomers and polyisocyanates) (Bello *et al.* 2007a).

1.5. Performance of Chemical Protective Clothing

Several factors can be tested to assess efficacy of chemical protective clothing, including degradation, penetration, and permeation (Anna 2003). For the most part, test methods should mimic workplace conditions as closely as possible, in particular temperature. The exposure by the chemical should also be on the normal outside surface only (Anna 2003). Some tests specific for glove performance beyond permeation include (Anna 2003): cut resistance (ASTM F 1790), puncture resistance (EN 388, clause 6.4), abrasion resistance (ASTM D 3889), chemical degradation resistance (new method), liquid-tight integrity (ASTM D 5151), and heat degradation resistance (ISO 17493). In this dissertation we will focus on the measurement of permeation.

1.5.1. Standard Methods to Assess Permeation of Protective Gloves

The measurement of chemical permeation resistance is specified in the different standard test methods offered by ASTM, CEN, and ISO (Anna 2003):

- American Society for testing and materials (ASTM) test methods:
    - ASTM F739, test method for resistance of protective clothing materials to permeation by liquids or gases under conditions of continuous contact
    - ASTM F 1383, test method for resistance of protective clothing materials to permeation by liquids and gases under conditions of intermittent contact
    - ASTM F 1407, test method for resistance of chemical protective materials to liquid permeation-permeation cup method.
- European committee on standardization (CEN) test methods:

  - EN 369, protective clothing – protection against liquid chemicals – test method: resistance of materials to permeation by liquids
  - EN 374-3, protective gloves against chemicals and microorganisms – part 3: determination of resistance to permeation by chemicals
- International standards organization (ISO) test method:
  - ISO 6529, protective clothing – protection against liquid chemicals- determination of resistance of air – impermeable materials to permeation by liquids.

In each of the tests (except ASTM F 1407), a similarly designed test cell is used for mounting the material specimen. The test cell consists of two hemispherical halves divided by the material specimen. One half of the test cell serves as the "challenge" side where the chemical is placed for contacting the material chamber. The other half is used as the "collection" side that is sampled for the presence of chemical permeating through the material specimen. The basic procedure in each test is to charge a chemical into the challenge side of the test cell and to measure the concentration of a test chemical in the test cell as a function of time (Anna 2003).

Permeation is the process of a chemical that diffuses through the solid test material pores or molecular gaps. Permeation is affected by both chemical solubility and diffusivity through the test material (Anna 2003). Material permeation resistance is generally characterized using two test results: breakthrough time and permeation rate (Anna 2003). Permeation rate provides information on the amount of mass that permeates the material per unit time per unit area while breakthrough time provides information on the time at which the permeant is first measured at the inner surface. Gloves with lower permeation rates and longer breakthrough times offer more protection against a chemical (Boman *et al.* 2004). More frequent changes may be an acceptable trade-off for choosing a glove with a shorter breakthrough time (Klingner and Boeniger 2002). Over extended periods of use, gloves will likely become contaminated on the inside by repeated doffing and donning (Garrod *et al.* 2001; Sanderson *et al.* 1995; and NIOSH 2001). The breakthrough time, for example, indicates the potential useable time: if the glove is removed before the breakthrough time, there is no exposure. The steady-state permeation is a state that is reached when the permeation rate becomes virtually constant (Boman *et al.* 2004). If the glove is worn beyond the breakthrough time, the steady state permeation rate help estimate dermal exposure (Berardinelli, 1988).

1.5.2. Isocyanate Permeation of Protective Gloves

Gunderson *et al.* (1989) suggested that isocyanates may be carried by solvents through protective clothing. Liu *et al.* (2000) is the only published article with recommendations regarding protective clothing while spray painting. Colorimetric wipe sampling revealed considerable contamination on skin and penetration through latex gloves after a single painting task (Liu *et al.* 2000). Regulatory agencies have recommended nitrile gloves when handling isocyanates (OSHA 1999; EPA 1999). However, EPA cautions that nitrile gloves may not be protective in strong solvents such as methyl ethyl ketone (MEK) and suggest that butyl rubber may be more protective. None of these documents address the effects of glove thickness.

There is growing evidence of the extent of isocyanate dermal exposure for autobody painters when their skin is protected or unprotected. Liu *et al.* (2000) found dermal exposure to isocyanates in workers using latex gloves. Fent *et al.* (2006; 2008) detected isocyanates on tape strips on the dorsal side of each hand and on the dorsal and volar side of each arm from unprotected auto-body painters. Fent *et al.* (2006) repoted HDI monomer while Fent *et al.* (2008) reported dermal exposures to HDI monomer and HDI oligomers. Bello *et al.* (2008) used skin colorimetric and quantitative wipe techniques and found HDI and HDI oligomers in the skin of autobody painters under protective gloves. The majority of workers (88%) in the Bello *et al.* (2008) study used latex gloves. Pronk *et al.* (2006a) used nitrile gloves under painter's gloves to measure permeation and reported isocyanate exposure under gloves on both hands of auto body and industrial spray painters, with the highest median hand exposure detected during paint mixing. Gloves and protective clothing are presumed to protect against isocyanate skin exposure, with nitrile gloves considered preferable to latex (Bello *et al.* 2007a, EPA 1999). However, data on the workplace performance of protective gloves are limited, there is evidence that solvents (Collin-Hansen *et al.* 2006) can also be detected underneath painters gloves.

Besides peer-reviewed and government publications, online literature from glove manufacturers provides conflicting information about protection from isocyanates. Nitrile rubber is recommended for the use of polyurethane coating systems by PPG (1997). Most manufacturers recommend heavy weight chemical protective gloves for use with toluene diisocyanate (TDI) or methylene diphenyl 4,4'-diisocyanate (MDI). Few recommend gloves specifically for handling HDI or IPDI. Most collision repair shops use disposable gloves because they are cheaper and graded as 'acceptable' in supplier-provided glove compatibility charts.

1.6. Rationale for the Dissertation

The overall goal of this dissertation is to investigate the efficacy of gloves used by autobody painters against isocyanates to provide glove use recommendations to the collision repair industry painters. This was motivated by the collaboration with the Washington State Department of Labor & Industries' SHARP Program, whose ultimate goal is to reduce work-related asthma among autobody painters. SHARP is planning to use social marketing tools to aid education and behavior change to improve work practices (Whittaker and Reeb-Whitaker 2009). Before SHARP can do this work, they need to understand what protective clothing are most appropriate for this industry. In order to test gloves, a permeation system was developed for this dissertation (Chapter 5). However, before the experiments could provide valuable results, key information was collected through several supporting projects, as follows:

1) Information on the typical painter' work practices to inform the development of the permeation system (lead to project in Chapter 3)
2) Information on the most commonly used gloves by painters in the collision repair industry to help inform our decision as to what materials to test with the permeation system (led to project in Chapter 3)
3) Information on the most commonly used clear coat formulations by painters in the collision repair industry to help inform our decision as to what materials to test in the inter-method comparison and with the permeation system (lead to project in Chapter 4).
4) Develop an objective analysis method for the colorimetric surface wipe sampling technique so that it could be used for the permeation system experiments (lead to project in Chapter 2)
5) Understand current isocyanate analytical methods and relative performance with the EH lab OSHA method to validate results from the objective colorimetric method and permeation system (lead to project in Chapter 4)

Dermal protection survey data were collected during field visits as part of a larger University of North Carolina (UNC) - Chapel Hill project funded by NIOSH, grant: "Dermal Exposure to 1,6-Hexamethylene Diisocyanate". The University of Washington (UW) provided field support for this project in a collaborative effort between the UNC and SHARP. As a side project, SHARP collaborated with the UW to evaluate isocyanate surface contamination in collision repair shops (Ceballos *et al.* 2007). A semi quantitative colorimetric approach was used to assess surface contamination by assigning a color scale ranging from 0 (no contamination) to 3 (heavy contamination). The need for a more objective method of detection was necessary and lead to the development of an objective color scale for isocyanate loading (Chapter 2). During the field studies, observations of dermal protection use highlithed the need to improve work practices (Chapter 3). Further, a knowledge gap regarding materials that protected the skin against isocyanates was identified (Chapter 1 and 6). The surface sampling technique was used for preliminary permeation testing and to aid the development of the permeation measurements described in Chapter 5. Simultaneously, while deciding on the quantitative method to use for the permeation panel, the isocyanate analytical method comparison study was started (Chapter 3). Finally, the testing of the most common gloves and clear coat formulations used by painters is described in Chapter 6.

1.7. Organization of the Dissertation

The next 5 chapters (Chapter 2-6) of this dissertation are written as individual scientific publications. I am first author on each of these papers.

- Chapter 2 was published as: Diana M. Ceballos, Michael G. Yost, Stephen G. Whittaker, Janice Camp, and Russell Dills. Objective Color Scale for the SWYPE Surface Sampling Technique Using Computerized Image Analysis Tools. Accepted by the Journal of Occupational & Environmental Hygiene.
- Chapter 3, which will be submitted for publication shortly as: Ceballos D, Fent K, Whittaker SG, Gaines LG, Thomasen J, Flack SL, Nylander-French L, Yost M, and Whitaker C. Survey of Dermal Protection in the Washington State Collision Repair Industry.
- Chapter 4, which will be submitted for publication shortly as: Ceballos, D., Whittaker, S.G., Yost, M., Dills, R., Bello, D., Thomasen, J., Nylander-French, L., Whitaker, C., Peters, P., Suydam, W. , and Weiland, E. Determination of Isocyanate Concentrations in a Sample of Commercial Hardener – An Isocyanate Analytical Method Comparison Study.
- Chapter 5 and 6 which will be submitted for publication shortly as companion papers: Chapter 5 paper will be named: Development of a Permeation Panel to Test the Efficacy of

Dermal Protective Clothing Against Sprayed Coatings. Chapter 6 paper will be named: Evaluation Of Protective Gloves Against Aliphatic Polyisocyanate Paints Used In The Collision Repair Industry

- Chapter 7 provides a summary of the presented papers by interconnecting them and draws some final conclusions. Recommendations for future studies are also included. This chapter will not be published as a separate paper.

1.8. Notes to Chapter 1

Anna DH. Chemical Protective Clothing, 2nd edition. (2003), 530 pages

American Thoracic Society (2003): American Thoracic Society statement: Occupational contribution to the burden of airway disease. Am. J. Respir. Crit. Care. Med. 167(5):787–797

Bakerly ND, VC Moore, AD Vellore, *et al.* (2008): Fifteen-year trends in occupational asthma: data from the Shield surveillance scheme. Occup. Med. 58:169–174

Bayer Corporation. (1997): The chemistry of polyurethane coatings: A general reference manual. Pittsburgh, PA: Bayer Corporation.

Bello D, Streicher RP, Woskie SR. (2002) Evaluation of the NIOSH draft method 5525 for determination of the total reactive isocyanate group (TRIG) for aliphatic isocyanates in autobody repair shops. National Institute for Occupational Safety and Health. J. Environ. Monit. 4(3): 351-360

Bello D, Woskie SR, Streicher RP, Liu Y, Stowe MH, Eisen EA, *et al.* (2004): Polyisocyanates in occupational environments: a critical review of exposure limits and metrics. Am. J. Ind. Med. 46(5):480–491

Bello D, Herrick CA, Smith TJ, Woskie SR, Streicher RP, Cullen MR, Liu Y, and Redlich CA (2007a): Skin Exposure to Isocyanates: Reasons for Concern. Environmental Health Perspectives. Environ. Health Perspect. 115(3):328–335

Bello D, Sparer J, Redlich CA, *et al.* (2007b): Slow curing of aliphatic polyisocyanate paints in automotive refinishing: a potential source for skin exposure. J. Occup. Environ. Hyg. 4(6):406-11

Bello D, Redlich CA, Stowe MH, *et al.* (2008): Skin exposure to aliphatic polyisocyanates in the auto body repair and refinishing industry: II. A quantitative assessment. Ann. Occup. Hyg. 52(2):117-124

Boman A, Estlander T, and Wahlberg JE: Protective Gloves for Occupational Use. 2nd Ed. CRD Press. Published by Informa Health Care, (2004). 343 pgs.

Bobeldijk I, Karlsson D, Pronk A, *et al.* (2008): Validation of Transferability of DBA Derivatization and LC–MS/MS Determination Method for Isocyanates via an Interlaboratory Comparison. Ann. Occup. Hyg. 52(8):757–763

Boutin1 M, Dufresne A, Ostiguy C, And Lesage J (2006): Determination of Airborne Isocyanates Generated During the Thermal Degradation of Car Paint in Body Repair Shops. Ann. Occup. Hyg. 50(4):385–393

Ceballos DM, Yost MG, Whittaker SG, and Camp J (2007): "Isocyanate Surface Sampling in the Puget Sound Collision Repair Industry." Abstract. Poster 45 presented at the American Industrial Hygiene Conference & Expo, Philadelphia, PA. June 3-6, 2007

Collin-Hansen I, Stowe M, Ibrahim K, *et al.* (2006): Field evaluation of gloves and protective clothing against organic solvents during auto body spray painting [Abstract]. In: American Industrial Hygiene Association Conference 2006, Chicago, IL. Available at http://www.aiha.org/abs06/po119.htm [accessed 19 January 2007]

U.S. Environmental Protection Agency (EPA) Nov (1999): Choosing the right gloves for painting cars. U.S. Environmental Protection Agency. Publication EPA/744-F-00-005. Updated June 2000. Available at http://www.epa.gov/dfe/pubs/auto/gloves/gloves.pdf

U.S. Environmental Protection Agency (EPA) (2005): Revised Automotive Refinishing Industry Isocyanate Profile. U.S. Environmental Protection Agency. January 2005. Available at www.epa.gov/opptintr/dfe/pubs/auto/profile/index.htm, accessed October 2005

Erjefalt I and Persson CG (1992): Increased sensitivity to toluene diisocyanate (TDI) in airways previously exposed to low doses of TDI. Clin. Exp. Allergy. 22(9):854-62

Fent K, Jayaraj K, Gold A, Ball L, and Nylander-French L (2006): Tape-strip sampling for measuring dermal exposure to 1,6-hexamethylene diisocyanate. Scan. J. Work. Environ. Health. 32(3):225–231

Fent KW, Jayaraj K, Ball LM, and Nylander-French LA (2008): Quantitative monitoring of dermal and inhalation exposure to 1,6-hexamethylene diisocyanate monomer and oligomers. J. Environ. Monit. 10(4):500-7. Epub 2008 Feb 21.

Gagne S, Lesage J, Ostiguy C, Cloutier Y, Van Tra H (2005): Quantitative determination of hexamethylene diisocyanate (HDI), 2,4-toluene diisocyanate (2,4-TDI) and 2,6-toluene diisocyanate (2,6-TDI) monomers at ppt levels in air by alkaline adduct coordination ionspray tandem mass spectrometry. J. Environ. Monit. 7(2):145-150

Garrod AN, Phillips AM, and Pemberton JA (2001): Potential exposure of hands inside protective gloves - a summary of data from non-agricultural pesticide surveys. Ann. Occup. Hyg. 45:55-60

Gunderson EC, Kingsley BA, Witham CL, and Bromberg DC. (1989): A practical study in laboratory and workplace permeation testing. Appl. Ind. Hyg. 4(12):324-329

Henneken H, Vogel M, and Karst U. (2007): Determination of airborne isocyanates. Anal. Bioanal. Chem. 387(1):219-36. Epub 2006 Nov 14

Health and Safety Executive (HSE) (2005a): Work-related Asthma. HSE Statistics. Viewed at www.hse.gov.uk/statistics/causdis/asthma.htm, accessed November 2005

Health and Safety Executive (HSE) (2005b): Table THORR05: Occupational asthma: estimated number of cases reported by chest and occupational physicians to SWORD/OPRA and estimated rates per 100,000 workers per year, by occupation. HSE. Available at www.hse.gov.uk/statistics/Tables/thorr05.htm, accessed November 2005

Karlsson D, Dahlin J, Marand A, Skarping G, and Dalene M. (2005): Determination of airborne isocyanates as di-n-butylamine derivatives using liquid chromatography and tandem mass spectrometry. Anal. Chim. Acta. 534:263-269

Klingner TD and Boeniger MF (2002): A critique of assumptions about selecting chemical resistant gloves: a case for workplace evaluation of glove efficacy. AOEHJ 17(5):360-367. Available at: http://www.clilabs.com/clidownloads.htm (file: GLOVEPAP1-final.pdf), accessed July 2006

Liu Q and Wisnewski AV (2003): Recent developments in diisocyanate asthma. Ann. Allergy Asthma Immunol. 90:35-41

Liu YC, Sparer J, Woskie SR, *et al.* (2000): Qualitative Assessment of Isocyanate Skin Exposure in Auto Body Shops: A Pilot Study. Am. J. Ind. Med. 37(3):265-274

Liu Y, Bello D, Sparer JA, *et al.* (2007): Skin Exposure to Aliphatic Polyisocyanates in the Auto Body Repair and Refinishing Industry: A Qualitative Assessment. Ann. Occup. Hyg. 51:429-439

Marshall M, Li K, Kaufman M, Lawrence B, and McKenrick L (2002): Auto Repair Industry Evaluation Report. Published by the Local Hazardous Waste Management Program Public Health – Seattle & King County. Environmental Health Division. December 23, 2002.

The National Institute for Occupational Safety and Health (NIOSH) (1996): NIOSH Alert: Preventing Asthma and Death from Diisocyanate Exposures. National Institute of Occupational Safety and Health. Cincinnati, OH. DHHS (NIOSH) Publication No. 96-111. 1996. Available at http://www.cdc.gov/niosh/asthma.html, accessed March 2009

The National Institute for Occupational Safety and Health (NIOSH) (2001): Recommendations for Chemical Protective Clothing: A Companion to the NIOSH Pocket Guide to Chemical Hazards. Available at http://www.cdc.gov/niosh/ncpc/ncpc2.html, accessed March 2009

The National Institute for Occupational Safety and Health (NIOSH) (2003): NIOSH Manual of Analytical Methods. P. C. Schlecht and P. F. O'Connor, (eds). NIOSH, Cincinnati, OH, 4th edn., Method 5525, Isocyanates, total (MAP), Issue 1, 3rd supplement, 2003, 154. Available at http://www.cdc.gov/niosh/nmam/pdfs/5525.pdf, Cincinnati: National Institute for Occupational Safety and Health, accessed June 2008

The National Institute for Occupational Safety and Health (NIOSH) (2004): A Summary of Health Hazard Evaluations: Issues Related to Occupational Exposure to Isocyanates, 1989 to 2002. Available at http://www.mass.gov/envir/ota/pubs/wbfull.pdf, accessed July 2006

The National Institute for Occupational Safety and Health (NIOSH) (2005): NIOSH Pocket Guide to Chemical Hazards. Publication No. 2005-149. Cincinnati, OH:National Institute for Occupational Safety and Health. Available at http://www.cdc.gov/niosh/npg/, accessed 12 January 2007

Occupational Safety & Health Administration (OSHA) (1989): OSHA 42 Analysis Method "Diisocyanates" Available at http://www.osha.gov/dts/sltc/methods/organic/org042/org042.html, Accessed July 15, 2006

Occupational Safety & Health Administration (OSHA) (1996): "Centers for disease control and prevention, NIOSH health hazard evaluation report 95-0311-2593. Martin's Carstar, Inc., Lakewood, Colorado" Available at http://www.osha.gov/SLTC/autobody/docs/cdc002.html#Isocyanates, Accessed July 15, 2006

Occupational Safety & Health Administration (OSHA) (1997a): "Aromatic isocyanate surface contamination sampling and evaluation techniques" Available at http://www.osha.gov/SLTC/isocyanates/mrl_inte.html, Accessed July 15, 2006

Occupational Safety & Health Administration (OSHA) (1997b): OSHA Technical manual, Occupational Skin Exposure Chapter 2. Available at http://www.osha.gov/dts/osta/otm/otm_ii/otm_ii_2.html, Accessed July 15, 2006

Occupational Safety & Health Administration (OSHA) (1999): Sampling for surface contamination. In: OSHA Technical Manual, Section II, Chapter 2. Salt Lake City, Utah: OSHA Technical Center, p 1-16.

Occupational Safety & Health Administration (OSHA) (2002): 1,6-Hexamethylene Diisocyanate sampling and analytical method W 4002. "1,6-Hexamethylene Diisocyanate" Available at http://www.osha.gov/dts/sltc/methods/validated/w4002/w4002.html, Accessed July 15, 2006

PPG Industries (1997): PPG Two-Component Polyurethane Coating Systems Guidelines for Safe Use. PAM 9379 8/97

Pronk A, Yu F, Vlaanderen J, Tielemans E, *et al.* (2006a): Dermal, inhalation, and internal exposure to 1,6-HDI and its oligomers in car body repair shop workers and industrial spray painters. Occup. Environ. Med. 63(9):624-31

Pronk A, Tielemans E, Skarping G, *et al.* (2006b): Inhalation exposure to isocyanates of car body repair shop workers and industrial spray painters. Ann. Occup. Hyg. 50(1):1-14

Rattray NJ, Botham PA, Hext PM, *et al.* (1994): Induction of respiratory hypersensitivity to diphenylmethane-4 4'-diisocyananate (MDI) in guinea pigs. Influence of route of exposure. Toxicology. 88:15-30

Redlich CA, Bello D, and Wisnewski AV (2007): Isocyanate exposures and health effects. In: Environmental and occupational medicine (Rom WN, ed). Philadelphia, PA 2007: Lippincott-Raven, 502-516

Sanderson WT, Ringenburg V, and Biagini R (1995): Exposure to commercial pesticide applicators to the herbicide Alachlor. Am. Ind. Hyg. Assoc. J. 56:890-897

Safety & Health Assessment & Research for Prevention, (SHARP) Washington State Department of Labor and Industries (2000): Workers' Compensation Based Surveillance of Asthma, Hospitalized Burns, and Adult Blood Lead Levels in Washington State, 1994-1998. SHARP report 64-1-2000. Olympia, Washington. July 2000

Safety & Health Assessment & Research for Prevention, (SHARP) Washington State Department of Labor and Industries (2003): Work-Related Asthma in Washington State: A Review of Worker's Compensation Claims from 1995-2002. SHARP report 64-6-2003. Olympia, Washington. December 2003

Safety & Health Assessment & Research for Prevention, (SHARP) Washington State Department of Labor and Industries (2005): Health and Safety in Washington State's Collision Repair Industry: A Needs Assessment. Technical report 69-4-2005. SHARP, Olympia, Washington, December 2005

Sparer J, Stowe MH, Bello D, Liu Y, Gore *et al.* (2004) Isocyanate exposures in autobody shop work: the SPRAY study. J. Occup. Environ. Hyg. 1(9):570-81

Streicher RP, Arnold JE, Ernst MK, and Cooper CV. (1996): Development of a novel derivatization reagent for the sampling and analysis of total isocyanate group in air and comparison of its performance with that of several established reagents. Am. Ind. Hyg. Assoc. J. 57(10): 905-913

Streicher RP, Reh CM, Key-Schwartz RJ, *et al.* (2000): Determination of airborne isocyanate exposure: considerations in method selection. Am. Ind. Hyg. Assoc. J. 61(4):544-56. Review.

Trelles Gaines LG, Fent KW, Flack SL, *et al.* (2009): Urine 1,6-Hexamethylene Diamine (Hda) Levels Among Workers Exposed To 1,6-Hexamethylene Diisocyanate (HDI). In preparation

Tremblay P, Lesage J, Ostiguy C, and Tra HV. (2003): Investigation of the competitive rate of derivatization of several secondary amines with phenylisocyanate (PHI), hexamethylene-1,6-diisocyanate (HDI), 4,4'-methylenebis(phenyl isocyanate) (MDI) and toluene diisocyanate (TDI) in liquid medium. Analyst. 128(2):142-149

Toyota Motor Corporation (1991): Toyota Fundamental Painting Procedures. Pub. No. BRM024E. Edited by Body & Paint Service Division. Published by Overseas Service Division. Japan.

Whittaker SG and Reeb-Whitaker C (2009): Characterizing the Health and Safety Needs of the Collision Repair Industry. J. Occup. Environ. Hyg. 6(5):273 282

Woskie SR, Sparer J, Gore RJ, *et al.* (2004): Determinants of isocyanate exposures in auto body repair and refinishing shops. Ann. Occup. Hyg. 48(5):393-403

Chapter 2

OBJECTIVE SURFACE COLORIMETRIC SAMPLING

2.1. Introduction

Isocyanates are a leading cause of work-related asthma (Bakerly *et al.* 2008), and workers in the automotive collision repair industry are at high risk for isocyanate exposures (Bello *et al.* 2007a; SHARP 2005, Whittaker and Reeb-Whitaker 2009). Workers may be exposed to isocyanates through inhalation as well as skin contact. Recent studies suggest that dermal exposure may cause allergic sensitization of the respiratory tract (Bello *et al.* 2007; Herrick *et al.* 2002; Pauluhn 2008; and Rattray *et al.* 1994). Isocyanates are present in high concentrations as catalyst hardeners in several automotive coatings, most particularly in the final "clear coat" of two-part polyurethane paint systems (Whittaker and Reeb-Whitaker 2009). The most common isocyanate constituents of commercial hardeners are polyisocyanate forms of hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) (Sparer *et al.* 2004). Contamination of work surfaces is potentially an important source of isocyanate exposure in shops. Spills of isocyanate-containing hardeners are frequent, especially in the paint mixing room (Bello *et al.* 2005, Ceballos *et al.* 2007 - Appendix B.1). Overspray and freshly painted parts can also be a source of isocyanate surface contamination (Bello *et al.* 2007).

A promising direct-reading test for the presence of unpolymerized isocyanates is the reagent impregnated surface sampling pad, developed by CLI (SWYPE, Colorimetric Laboratories Inc., Des Plaines, IL). Using a proprietary chemical reaction, these pads employ a simple and sensitive colorimetric response to identify surfaces contaminated with isocyanates. The pad changes color from yellow to orange/red proportionally with the concentration of the isocyanate functional group (NCO) (Bello *et al.* 2007b). As designed, the pads provide only a quanlitative measure of surface contamination. This technique is a valuable immediate response tool in the field for workers in the collision repair industry as well as industrial hygiene practitioners. A more objective measure of the SWYPEs response would be beneficial for focusing workplace interventions and more extensive exposure assessment efforts.

Colorimetric pads have been described as a screening tool for surface contamination with both aliphatic and aromatic isocyanates in autobody shops (Bello *et al.* 2007a; Bello *et al.* 2007b; OSHA 1996, 1997 and 1997b; Liu *et al.* 2000). However the chemistry underlying the

SWYPEs for aliphatic and aromatic compounds are different; the test systems are optimized to provide maximum sensitivity and color stability for the respective chemical classes. The SWYPEs used in this study were optimized only for the aliphatic species, which are the predominant isocyanates present in paints and coatings.

Surface contamination and skin exposures to aliphatic isocyanates in autobody shops have been documented using SWYPEs semi-quantitatively by assigning a color scale ranging from 0 (no contamination) to 3 (heavy contamination) (Liu *et al.* 2000). In later studies, Liu *et al.*(2005 and 2007) described a color scale that ranged from 0 to 5. In addition to a qualitative assessment of the colorimetric response, Liu *et al.* (2005) performed a comparison with quantitative wipe sampling - before and after cleaning contaminated surfaces. These authors determined that SWYPEs were as efficient as the wipe pads analyzed using the NIOSH 5525 method for verifying isocyanate surface decontamination (Liu *et al.* 2005).

Bello *et al.* (2007b) also used a semi-quantitative color scale for SWYPEs from 0 to 5 and performed side-by-side sampling with wipes analyzed using the NIOSH 5525 method. Using this strategy, Bello *et al.* (2007b) demonstrated that the SWYPE color scale showed good agreement with quantitative wipes ($r^2 > 0.8$) and found that complete curing of automotive coatings on painted surfaces may take several days. Liu *et al.* (2007) described an extensive field validation of the SWYPE versus quantitative wipes and suggested the need for an objective assessment of the colorimetric response.

The use of a portable scanner to capture digital images represents a simple method to obtain an objective SWYPE color scale. This method has the benefit of recording the colorimetric response under reproducible lighting conditions. The scanner digitizes the color images as separate red (R), green (G), and blue (B) components, which can subsequently be viewed as red-green-blue (RGB) histograms. Although this approach has been used in a variety of applications (Gaiao *et al.* 2006; Misimi *et al.* 2007; and Pilin *et al.* 2007), we are not aware of any studies that have used RGB analysis to quantify colorimetric surface sampling results.

The aims of this present study are to: 1) develop an objective color scale and analysis algorithm for the colorimetric response of SWYPEs to unpolymerized isocyanates and 2) validate the objective color scale against an established quantitative wipe method.

2.2. Methods

2.2.1. Materials

The colorimetric wipe method used Surface SWYPEs (used one year before expiration date) 2.5 x 2.5 cm for aliphatic isocyanates and developing solution (Colorimetric Laboratories, Inc., Des Plaines, IL). Preparation of standards used reagent grade toluene, Desmodur N 3400 aliphtic polyisocyanate (Bayer Material Science LLC, Pittsburgh, PA), and Chromabase 7775S activator-reducer (DuPont, Wilmington, DE). Quantitative wipes used Ghost Wipes (Environmental Express, Cat. # 4210, Mt. Pleasant, SC), reagent grade isopropyl alcohol, and 1-(2-pyridyl) piperazine (Aldrich, Product #: 408166-5mL, St. Louis, MO).

2.2.2. Characterization of the SWYPE Colorimetric Response

Selection of Isocyanate Standard

Desmodur N 3400 was used for the initial characterization of the colorimetric response. This solvent-free product is used widely as the source of polyisocyanates in commercial hardener formulations. According to the manufacturer's literature, Desmodur N 3400 is a homopolymer of HDI with a purity of greater or equal to 95%. The manufacturer's certificate of analysis for this product (dated 2/9/2009) reported 21.55% NCO (specifications within a range of 21.1-22.5% NCO). For the purposes of this study, the total mass of N 3400 product was assumed to be equivalent to the mass of isocyanates.

Preparation of Standards

Approximately 100 mg of N 3400 was dissolved in 10 ml of toluene and serial dilutions were prepared using toluene as the solvent. Aluminum foil surfaces were spiked with 20-100 μL of N 3400 standards and allowed to dry for approximately 2 minutes. Standard surfaces were prepared in the range of 0-200 μg bulk N 3400 loadings (0, 3.5, 31, 62, 124, and 186 μg). In order to assess the method's sensitivity, a lower range of N 3400 standards was also prepared (0, 3.5, 4, 5, 6, 10, and 35 μg).

Aluminum Foil SWYPE Sampling

The SWYPE surface sampling procedure followed the manufacturer's recommended procedures, with minor modifications. Briefly, 2-3 sprays of mineral oil (developing solution) were applied to 100 cm^2 areas of aluminum foil that had been loaded with N 3400, as described above. After 30 seconds, the surface was wiped with a circular motion, starting at the perimeter and working towards the center. Nitrile gloves were used and changed frequently to avoid cross contamination. The loaded SWYPE was then wrapped immediately in a commercially available plastic film for ease of handling and storage – this last step is an addition to the manufacturer's recommendations.

RGB Analysis

The ScanJet G4010 Photo Scanner (Hewlett Packard, Berkshire, UK) was allowed to warm up according to the manufacturer's instructions. Photographs (reflective images) of SWYPE samples were captured against a white background using a color-calibrated scanner with VueScan Scanning Software (Hamrick Software, Phoenix, AZ). In order to ensure reliable color rendition, a reference color calibration file was created (an International Color Consortium [ICC] profile) using the inCamera Photo Shop plug-in (PictoColor Corporation, Burnsville, MN) and a ColorChecker color rendition chart (Gretag Macbeth, Grand Rapids, MI). Alternatively, there are commercial printed color calibration charts, like IT8, that work directly with VueScan without the use of external plug-ins. An example of an IT8 commercially available is the Fuji Velvia by Wolf Faust (Coloraid.de, Frankfurt, Germany).

SWYPEs were scanned between 3 and 20 minutes after loading (we had previously determined that the colorimetric response did not change when SWYPEs were stored for up to 20 minutes in plastic wrap). Scanned images were saved to an attached laptop computer as raw TIFF files and analyzed using Adobe Photoshop (Adobe Systems Incorporated, San Jose, CA). In order to avoid color deviation after color conversion, TIFF files were used instead of other compressed formats such as joint photographic experts group (JPEG).

The source images were color calibrated by transforming them to match the scanner's ICC profile. First the sources were assigned to the calibrated ICC profile, and then converted to Adobe Photoshop's default space (working RGB: sRGB IEC61966-2.1). Calibrated images were then zoomed to 100-200% and SWYPE areas were selected using Adobe Photoshop's polygonal selection tool. The resulting SWYPE RGB histogram data for each channel were transferred to a Microsoft Excel file; the loading responses were described using median color intensity values.

A series of experiments was conducted to determine the precision, reproducibility, and extraction efficiency of the SWYPE RGB analysis. Precision was evaluated by determining the error associated with the polygonal selection tool used for image analysis; the same SWYPE image area was selected three independent times and RGB values were recorded for comparison. The reproducibility of the RGB response was determined by evaluating three replicates of the same standards at six loading levels. Surface extraction efficiency was estimated by comparing direct loading of a standard on the SWYPE followed by 700 μL oil versus wiping of controlled loading on aluminum foil at low (3.4 μg) and high (350 μg) loading levels.

2.2.3. Cross-Validation of the SWYPE with the Standard W4002 Method

Selection of Hardener

A commercial hardener product (Chromabase 7775S) was used in the cross-validation experiments. The manufacturer's MSDS for this hardener lists aliphatic polyisocyanate resin and several organic solvents, such as esters and aromatic hydrocarbons (47% by weight solids). Laboratory analysis of this product (OSHA 42 method) confirmed that Chromabase 7775S contains polyisocyanate forms of both HDI and IPDI (>11% NCO measured by HPLC (OSHA 1989, Bello *et al.* 2004).

Cross-Validation Approach

Side-by-side measurements with the SWYPE and W4002 methods were performed at bulk hardener loadings ranging from 0 to 500 μg (0, 97.4, 243.5, 389.6, and 487 μg of bulk hardener). Aluminum foil loading and SWYPE sampling and analysis were performed as described above.

W4002 Method Sampling Procedure

The standard method W4002 (OSHA 2002) was followed, with slight modifications. Briefly, Ghost Wipes were stored in sealed plastic bags and handled with clean, gloved fingers. Using a disposable pipette, the Ghost Wipe was moistened with 0.5 mL of wetting reagent (50:50 isopropyl alcohol : water solution). Using firm pressure, the outer edge of the 100 cm^2 aluminum foil surface was wiped, progressing towards the center while making concentric squares of decreasing size. The Ghost Wipe was folded with the loaded surface facing inward, and the wiping was repeated. The Ghost Wipe was then placed in a vial containing 5 mL of 1-(2-pyridyl) piperazine derivatizing solution and shaken vigorously for one minute. Vials were stored in a cooler and sent to the laboratory for OSHA 42 HPLC analysis (OSHA 1989). The Ghost Wipes were gently compressed to extract the derivatizing solution for analysis.

Accuracy was calculated for both the W4002 methods and SWYPE RGB analysis by comparing measured loading to predicted loading at different levels using a jackknife approach (Efron 1982). Predicted loading was systematically recomputed while omitting one observation at a time from the calibration. Plotting this computed set of "observations" illustrates the bias and the variance of the predictions.

Experiments were also conducted to determine the reproducibility and extraction efficiency of the W4002 Method. Reproducibility was determined by evaluating duplicates of the same standards at two loading levels (97.4 μg and 243.5 μg). Surface extraction efficiency was estimated by comparing direct loading on the Ghost Wipe versus sampling controlled loadings on aluminum foil at a medium loading level (243.5 μg).

2.3. Results

The SWYPE color scale using N 3400 is presented in Figure 2.1. A visual color scale ranging from 0 to 3 was applied, as previously described by Liu *et al.* (2000). RGB histograms were created for each SWYPE, where the X-axis represents color intensity in the RGB channels and the Y-axis represents the pixel frequency. The loading of the SWYPE was proportional to color change. The green and blue median peaks of the histograms decreased in color intensity with increasing isocyanate loading, while red intensity remained essentially unchanged. Both mean and median could be used for the calibration but median values were chosen because they represent the peak in the histogram.

The calibration curve for SWYPE loading with N 3400 is presented in Figure 2.2 (data in Appendix B.2). Over the range tested (0 to 186 μg N 3400), a quadratic curve ($r^2 = 0.98$) or an exponential decay to a non-zero asymptote ($r^2 = 0.99$) adequately described the relationship between mass loaded and median color intensity of the summed green and blue pixels. Analysis in this paper used a quadratic fit for all calibrations. Clearly, as the SWYPE loading increased and the reagent on the SWYPE is depleted, the green and blue pixel density asymptotically approaches a low value, causing red to predominate.

The lowest loading level in which a visual color change could be observed with N 3400 was 6-10 μg of bulk product, as has been reported previously (Liu *et al.* 2000). However, RGB analysis revealed a statistically significant increase in color intensity relative to the blank at 3.5 μg of bulk product ($p = 0.0208$). The variability associated with the image analysis area selection tool and zoom in the range of 100-200% was minimal; the coefficient of variation percentage (%CV) was 0.02-0.09. The precision of the RGB response was in the range of 0-9%CV. Surface recovery of the N3400 from the aluminum foil surface was >90%.

We determined that slight variations in the SWYPE sampling procedure affect the colorimetric response. For example, both precision and recovery were improved when a spray bottle was used to apply the oil to an aluminum surface, compared to using a pipette (unpublished observations). In addition, applying oil directly to the SWYPE resulted in total color saturation at 100 μg of N 3400, whereas no total color saturation was observed at 2,400 μg N 3400 when oil was placed on the aluminum foil surface. We suggest that applying oil to the surface with the spray bottle likely facilitates dilution of isocyanates and subsequent absorption to the SWYPE.

Calibration of the W4002 method was achieved (up to $r^2 = 0.99$) by associating loading with the total mass of isocyanate species identified in the commercial 7775S hardener using the OSHA 42 method (data in Appendix B.3.). The aluminum surface recovery for the W4002 method was >80%. The detection limit was 0.18 μg/sample for HDI, 0.17 μg/sample for IPDI, and 3.2 μg/sample for total oligomers.

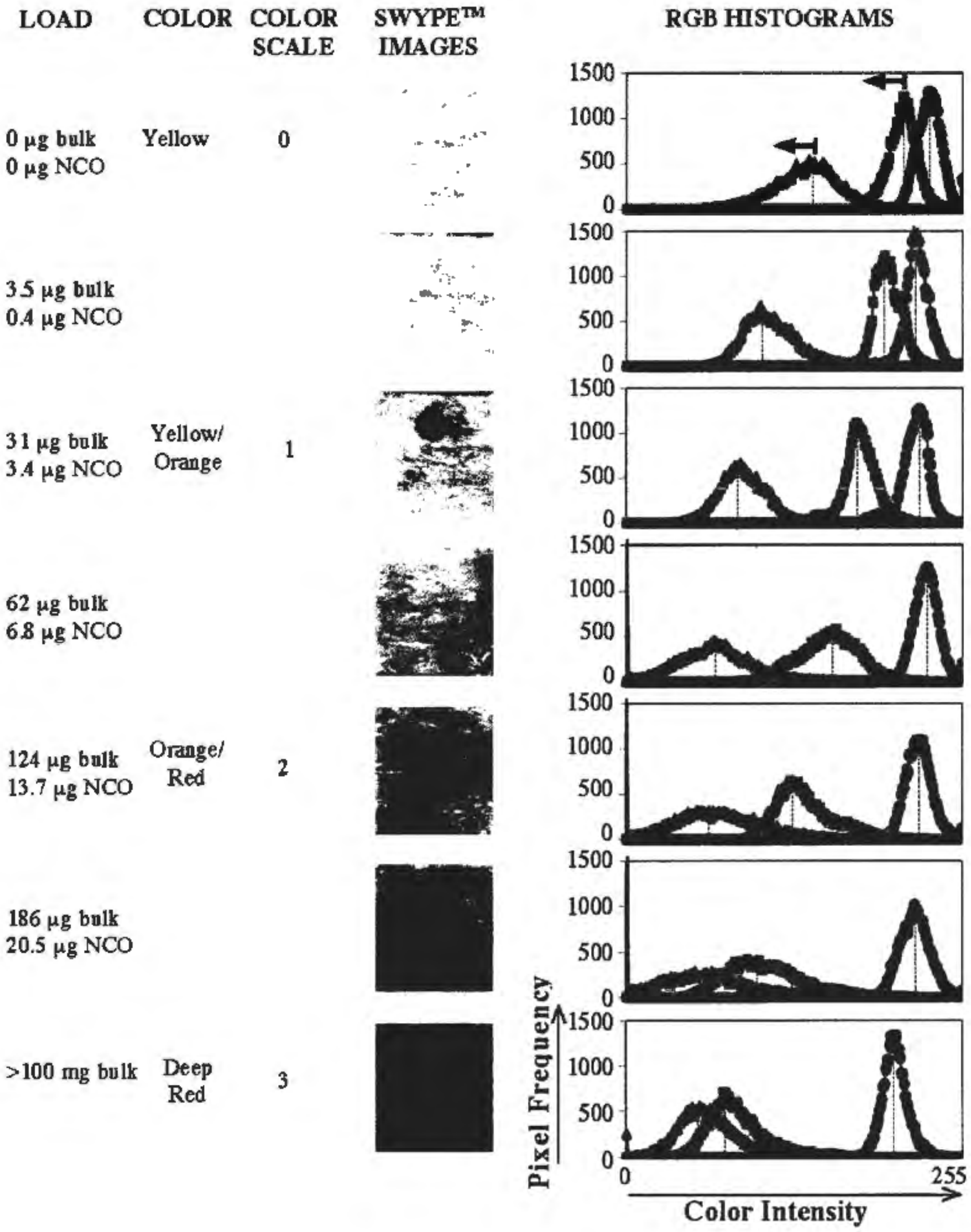


Figure 2.1. SWYPE Color Gradient (Desmodur N 3400) and RGB Histograms. The loading of the SWYPE was proportional to color change. The green and blue median peaks of the histograms decreased in color intensity with increasing isocyanate loading, while red intensity remained essentially unchanged.

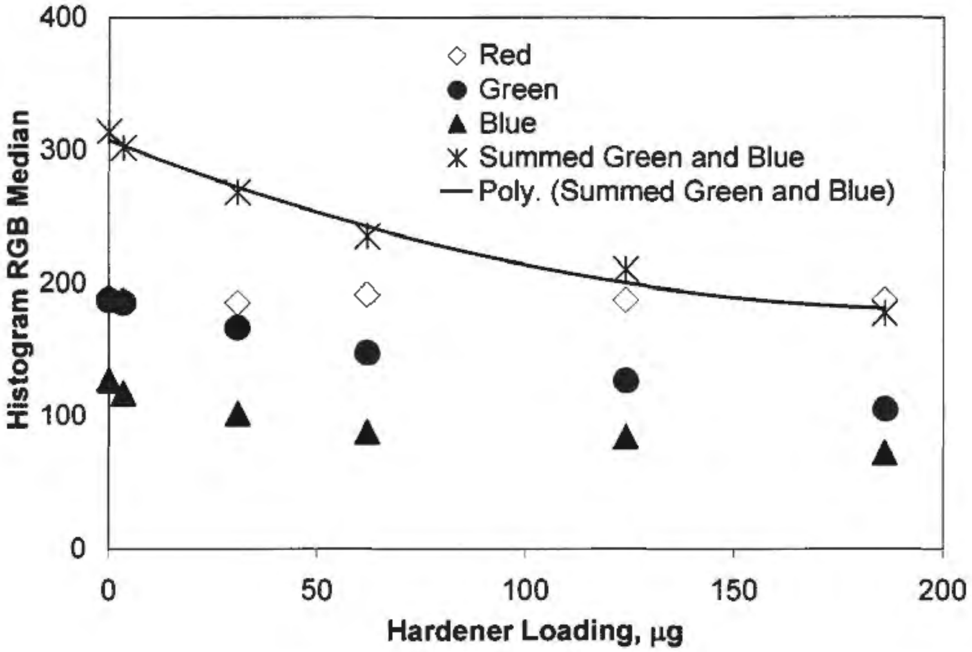


Figure 2.2. SWYPE RGB Analysis Calibration (Desmodur N 3400). The intensity of the green and blue responses decreased markedly as hardener bulk loading increased. A quadratic curve ($r^2 = 0.98$) adequately described the relationship between mass loaded and median color intensity of the summed green and blue pixels.

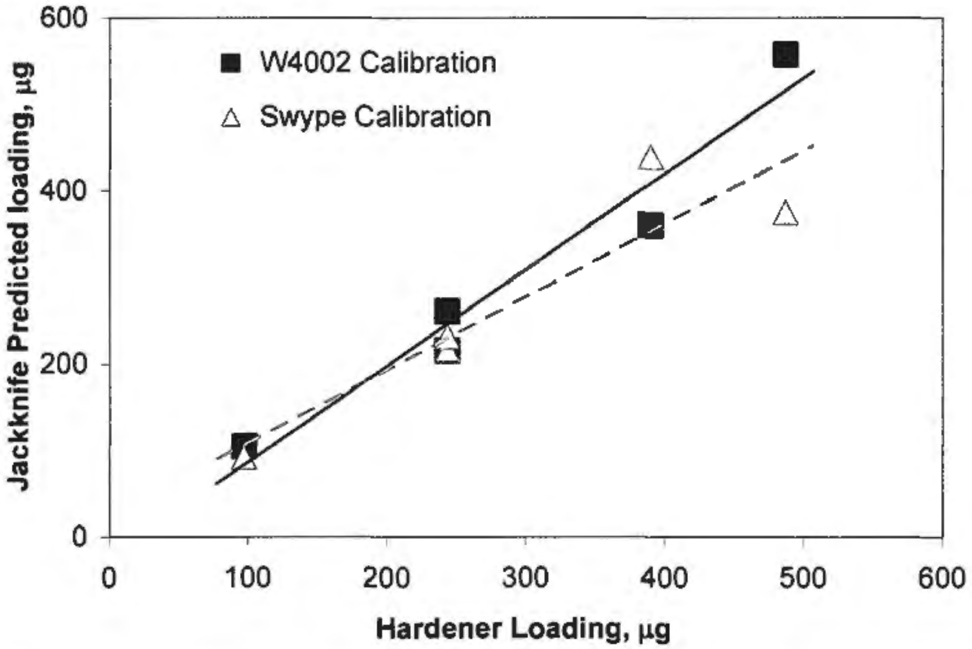


Figure 2.3. SWYPE RGB Analysis Cross-Validation with Quantitative W4002 Wipe Method (Chromabase 7775S). Similar loading predictions were achieved with both methods when using the jackknife approach; slopes close to 1 (1.1 and 0.84 for W4002 and SWYPE, respectively) suggest good agreement. SWYPE's RGB analysis saturation at highest loading reflects depletion of the reagent and limitations of the quadratic model.

Application of the bulk commercial 7775S hardener yielded similar loading predictions for the SWYPE RGB quadratic calibration (data in Appendix B.4) and W4002 linear calibration when using the jackknife approach (Figure 2.3); the average accuracy was >93% for both methods. The similarities in the slopes for both methods (1.1 and 0.84 for W4002 and SWYPE, respectively) also suggest good agreement. The SWYPE's highest loading (487 μg) showed some saturation and predicted a lower mass than expected. Linear correlation of the predicted loading for the SWYPE RGB analysis ($r^2 = 0.85$) was lower than that for the W4002 method ($r^2 = 0.95$). The linear correlation between the two methods was $r^2 = 0.69$.

2.4. Discussion

The first goal of this study was to develop an objective color scale and analysis algorithm for the colorimetric response of SWYPEs to unpolymerized isocyanates. Using N 3400 as a calibrant, we demonstrated that the relationship between isocyanate loading and the RGB response was a quadratic or an exponential decay to a non-zero asymptote, with an $r^2 > 0.90$. Quadratic fit was chosen because it is more practical than the exponential decay, especially when there are few data points in the calibration.

The detection limit was 3 μg/sample (or 0.03 μg/cm^2), which is in agreement with values reported by the manufacturer and OSHA (1997 and 1997b). The RGB analysis detection limits were significantly lower than is achievable via visual detection (10 μg/sample or ~0.1 μg/cm^2) (Liu *et al.* 2000). Replicates had a coefficient of variation <9%, which is reasonable considering the inherent variability of the surface sampling process. Extraction efficiency was >90% on aluminum surfaces. Image area selection did not add significant error to the RGB analysis.

The second goal of this study was to validate the SWYPE RGB response against an established quantitative wipe method. Cross-validation using a commercial hardener product demonstrated that the RGB analysis yielded comparable results to method W4002. The average accuracy for both methods was >93%. Extrapolation using the quadratic curve was not appropriate at high SWYPE loadings because the reagent was depleted. Predictions using an exponential decay to a non-zero asymptote curve would be better, but many more calibration levels would be needed to solve the equation accurately.

Liu *et al.* (2007) published a laboratory comparison of side-by-side spiked SWYPE and quantitative wipes analyzed by modified method NIOSH 5525. The scatter data resembled a quadratic shape, similar to the SWYPE calibration using the RGB methodology. The lack of reproducibility and accuracy in the Liu *et al.* (2007) study likely reflects the subjectivity of the visual color scale grading. Liu *et al.* (2007) reported a SWYPE linear relationship at <5 μg NCO (equivalent to 22.86 μg polyisocyanates), which flattens out at >13 μg NCO (equivalent to 59.43 μg polyisocyanates). SWYPE data from Liu *et al.* (2007) reflect unexplained saturation at low loading levels that differs from our findings. The sensitivity reported (3.2 μg polyisocyanate) agrees with results presented in this current study.

Liu *et al.* (2007) also provided a field comparison of the colorimetric pads (both surface and skin wipes) versus quantitative wipes. To address the inherent limitations of the SWYPE, a large number of paired samples were compared (n = 249), and the side-by-side surface areas were 25 cm^2. Quantitative data were grouped in categories of color intensity scoring and geometric means were used for comparison. Reasonable agreement between the methods was demonstrated. The SWYPE was found to be highly specific (0-7% false positives) but less sensitive than HPLC (68-72% false negatives). A similar field validation for the RGB analysis would be desirable but outside the scope of this publication.

We recognize several intrinsic limitations with SWYPEs. The SWYPE color change is not specific to a particular isocyanate; the SWYPEs react with both monomeric and polyisocyanate forms of any aliphatic isocyanate. Consequently, different hardener formulations may yield different colorimetric responses, reflecting variations in isocyanate and solvent content. Thus, the objective color scale presented in this study may not be representative of all possible hardeners found in auto body shops.

While hardeners N 3400 contains twice the amount of %NCO compared to hardener 7775S, the bulk masses required to obtain equivalent visual and RGB colorimetric responses in SWYPEs were more than double: the calibration for 7775S required 5 times more bulk mass than N 3400. One explanation for this difference between the products is that 7775S contains only 47% solids by weight, whereas N 3400 is a pure material. In addition, it is likely that the color reaction elicited by a specific hardener does not depend solely on the isocyanate content of a product; other product-specific factors include: 1) the formula weights of the isocyanates; 2) the number of NCO groups per molecule for the isocyanates; 3) the molar ratios of the compounds; and 4) the percent by weight of NCO-containing compounds.

The detection limits achieved in the field may be higher than those determined in the laboratory because the colorimetric response may be affected by physical characteristics of the sampled surface and the presence of surface contaminants (e.g., pigmented paints, dust, lubricating oil, and carbon composites) (Liu *et al.* 2000). The mineral oil developing solution may represent a slip hazard in the workplace and may also contaminate automotive paints and other products. Finally, the SWYPE sampling method is "destructive" of the sample; the surface of interest may only be sampled once accurately, unlike direct spectroscopic methods which do not react with the isocyanate bonds.

Quality of the scanned image is critical to the RGB methodology, so any sample degradation before scanning could give erroneous results. However, we determined that scanning can be performed without color degradation up to 20 minutes after sampling when plastic wrap was used immediately. From laboratory observations, the color on a SWYPE without plastic wrap and at normal atmospheric conditions degrades in less than 15 minutes after sampling, whereas no degradation was observed when plastic wrap was used. It should also be noted that reflective image analysis provides only data associated with the SWYPE's outer surface, as would be the case with visual scoring. However the color response is three-dimensional because the SWYPE is 1-2 mm thick. Regardless, since the RGB analysis measures the average of the color over an area, uneven color surfaces did not appear to alter the objective scoring of the SWYPEs significantly. This was clear when comparing the SWYPEs used to calculate the extraction efficiency (>90%). Directly spiked SWYPEs were unevenly colored while spiked surfaces provided more homogeneous colored SWYPEs. Overall, we conclude that the RGB analysis calibration is superior to the semi-quantitative method used by Liu *et al.* (2000) because it is objective and more reproducible. A list of characteristics for both methods is shown in Table 2.1.

There are several opportunities to extend the use of the RGB analysis to other colorimetric methods, in particular those that test skin contamination. To face some of the challenges that other colorimetric methods may bring, modifications to the scanning process could aid further color resolution. Options include using a bandwidth-specific light source and the use of photographic filters such as Wratten filters (Imai and Berns). Some scanners, such as the one used for this current study, have more than three available channels. Consequently, all channels could be used if using a software application that provides a raw output for each channel.

RGB analysis using a commercial flatbed scanner offers clear advantages over other methods for quantifying the colorimetric response. For example, the use of a spectrophotometer would require extraction of the color from the pad and the degree of extraction would add another variable to the analysis. In addition, spectrophotometers are relatively expensive and require a higher degree of technical expertise to operate. Another advantage of the described methodology is that scanned SWYPE images are amenable to archiving and future re-analysis. Creating a library of commercially available hardener calibrations would facilitate field sampling. The investigator could wipe, store, and analyze field samples within minutes. Visual photos and numerical estimates of loading could provide businesses with useful information for training or intervention. As high-quality scanners become more compact, RGB analyses are likely to become even more practical in field settings.

2.5. Conclusions

We acknowledge that quantitative analytical chemistry methods typically provide more sensitivity, specificity, and accuracy than colorimetric methods. However, the proposed RGB analysis combined with the SWYPE is an improvement over existing qualitative or semi-quantitative colorimetric isocyanate SWYPE tests. The RGB analysis of the SWYPE has the main advantages of preserving images of the samples as well as reducing reader-to-reader variability.

The RGB method provides a simple and powerful tool with which to objectively assess the extent of surface contamination with unpolymerized isocyanates. The method is relatively rapid, inexpensive, and requires the use of only portable consumer-grade equipment in the field, unlike the quantitative analysis using Ghost Wipes. This method has advantages over subjective semi-quantitative method used to date. This methodology should find wide application for characterizing surface contamination in auto body shops and other workplaces in which isocyanates are used in coatings and other commercial products.

Table 2.1. Comparison of the Semi-Quantitative and Objective RGB SWYPE Methods

Characteristic	**Semi-Quantitative Method**[a, b]	**Objective RGB Method**
Sensitivity	▪ 10-25 μg/sample very light color and 50 μg/sample as more easily observed[a].	▪ 3 μg/sample (same as reported by manufacturer).
Reproducibility	N/A	▪ >90%
Extraction efficiency	N/A	▪ >90%
Accuracy	▪ Qualitative reference to negative and positive contaminated SWYPES.	▪ >90%
Calibration	▪ Visual color scale ranging from 0 (no contamination) to 3 (heavy contamination).[a, b] Color gradient reference chart sometimes used.	▪ A calibration curve created from a series of reference RGB histograms derived from scanned images of SWYPES loaded with an isocyanate-containing product.
Instrument needs	▪ None	▪ Commercial portable scanner and portable computer.
Time used for calibration	▪ N/A unless a printed color reference chart (0 to 3 visual scoring) is prepared (1 hour).	▪ 1 hour for standard solutions preparation, 1 hour for SWYPE standard preparation and scanning, 1 hour for RGB analysis and calibration calculations.
Time used for sampling	▪ 1 minute sampling and 3 minutes for color development.	▪ 1 minute sampling, 3 minutes for color development and plastic wrapping, and 2 minutes for scanning. Note: scanner warm up is only few seconds when first turned on.
Time used for analysis	▪ Seconds	▪ 2-5 minutes
Main advantages	• Fast and easy for detection of isocyanate contaminated areas. • Not much training required.	• Scanner provides constant light source for assigning color. • Objective color scale. • Color assessment can be done within 20 minutes from sampling. • Loading assessment can be done during or after field visit. • Archiving of the sample and standard scans for future reference or reanalysis.
Main disadvantages	• Subjective due to lighting and the reader. • Sample degrades so color assessment should be done immediately after color develops.	• Needs a calibration for each hardener so best if used in shops were only one or two hardeners are used.

[a] Liu *et al.* 2000
[b] Liu *et al.* 2007

2.6. Notes to Chapter 2

Bakerly ND, Moore VC, Vellore AD, et al. (2008): Fifteen-year trends in occupational asthma: data from the Shield surveillance scheme. Occup. Med. (Lond) 58(3):169-74

Bayer Material Science LLC: DESMODUR N 3400 Aliphatic Polyisocyanate [Product Bulletin] Pittsburgh, Pa.: Bayer MaterialScience, (2002)

Bello D, Woskie SR, Streicher RP, et al. (2004): Polyisocyanates in occupational environments: a critical review of exposure limits and metrics. Am. J. Ind. Med. 46(5):480-91

Bello D, Woskie SR, Streicher RP, et al. (2005): A laboratory investigation of the effectiveness of various skin and surface decontaminants for aliphatic polyisocyanates. J. Environ. Monit.7:716- 721

Bello D, Herrick CA, Smith TJ, et al. (2007a): Skin Exposure to Isocyanates: Reasons for Concern. Environ. Health Perspect. 115(3):328-35

Bello D, J Sparer, CA Redlich, et al. (2007b): Slow curing of aliphatic polyisocyanate paints in automotive refinishing: a potential source for skin exposure. J. Occup. Environ. Hyg. 4(6):406-11

Ceballos DM, Yost MG, Whittaker SG, and Camp J (2007): "Isocyanate Surface Sampling in the Puget Sound Collision Repair Industry." Abstract. Poster 45 presented at the American Industrial Hygiene Conference & Expo, Philadelphia, PA. June 3-6, 2007

Efron B: The jackknife, the bootstrap, and other resampling plans, In The Society of Industrial and Applied Mathematics CBMS-NSF Monographs, 38 (1982)

Gaiao N, VL Martins, S Lyra, et al. (2006): Digital image-based titrations. Anal. Chim. Acta. 570(2):283-90

Herrick CA, Xu L, Wisnewski AV, et al. (2002): A novel mouse model of diisocyanate-induced asthma showing allergic-type inflammation in the lung after inhaled antigen challenge. J. Allergy Clin. Immunol. 109(5):873-878

Imai FH and Berns RS: "High-Resolution Multi-Spectral Image Archives - A Hybrid Approach." Available at: http://www.cis.rit.edu/people/faculty/berns/PDFs/cic6_Imai.pdf, Accessed July 20, 2006

Liu Y, Sparer J, Woskie SR, et al. (2000): Qualitative Assessment of Isocyanate Skin Exposure in Auto Body Shops: A Pilot Study. Am. J. Ind. Med. 37(3):265-274

Liu Y, Stowe MH, Bello D, et al. (2005): "Surface and skin decontamination of aliphatic isocyanates: a field study." Abstract for Poster 66 presented as part of the International Conference Occupational and Environmental Exposures of Skin to Chemicals. Stockholm, Sweden, June 12-15, 2005. Available at http://www.cdc.gov/niosh/topics/skin/OEESC2/AbPost066Liu.html, Accessed August 7, 2006

Liu Y, Bello D, Sparer JA, et al. (2007): Skin Exposure to Aliphatic Polyisocyanates in the Auto Body Repair and Refinishing Industry: A Qualitative Assessment. Ann. Occup. Hyg. 51:429-439

Misimi E, Mathiassen JR, and Erikson U (2007): Computer vision-based sorting of Atlantic salmon (Salmo salar) fillets according to their color level. J. Food Sci. 72(1):S030-5

Occupational Safety & Health Administration (OSHA) (1989): OSHA 42 Analysis Method "Diisocyanates" Available at http://www.osha.gov/dts/sltc/methods/organic/org042/org042.html, Accessed July 15, 2006

Occupational Safety & Health Administration (OSHA) (1996): "Centers for disease control and prevention, NIOSH health hazard evaluation report 95-0311-2593. Martin's Carstar, Inc., Lakewood, Colorado" Available at http://www.osha.gov/SLTC/autobody/docs/cdc002.html#Isocyanates, Accessed July 15, 2006

Occupational Safety & Health Administration (OSHA) (1997): "Aromatic isocyanate surface contamination sampling and evaluation techniques". Available at http://www.osha.gov/SLTC/isocyanates/mrl_inte.html, Accessed July 15, 2006

Occupational Safety & Health Administration (OSHA) (1997b): OSHA Technical manual, Occupational Skin Exposure Chapter 2. Available at http://www.osha.gov/dts/osta/otm/otm_ii/otm_ii_2.html, Accessed July 15, 2006

Occupational Safety & Health Administration (OSHA) (2002): 1,6-Hexamethylene Diisocyanate sampling and analytical method W 4002. "1,6-Hexamethylene Diisocyanate" Available at http://www.osha.gov/dts/sltc/methods/validated/w4002/w4002.html , Accessed July 15, 2006

Pauluhn J (2008): Brown Norway rat asthma model of diphenylmethane-4,4'-diisocyanate (MDI): impact of vehicle for topical induction. Regul. Toxicol. Pharmacol. 50(1):144-54

Pilin A, Pudil F, and Bencko V (2007): Changes in colour of different human tissues as a marker of age. Int. J. Legal Med. 121(2):158-62

Rattray NJ, Botham PA, Hext PM, et al. (1994): Induction of respiratory hypersensitivity to diphenylmethane-4 4'-diisocyanante (MDI) in guinea pigs. Influence of route of exposure. Toxicology. 88:15-30

Safety & Health Assessment & Research for Prevention, (SHARP) Washington State Department of Labor and Industries (2005): Health and Safety in Washington State's Collision Repair Industry: A Needs Assessment. Technical report 69-4-2005. Olympia, Washington, (2005). Available at http://www.lni.wa.gov/Safety/Research/Collision/Repair/Default.asp, Accessed March 17, 2007

Sparer J, Stowe MH, Bello D, et al. (2004): Isocyanate exposures in autobody shop work: the SPRAY study. J. Occup. Environ. Hyg. 1(9):570-81

Whittaker SG and Reeb-Whitaker C (2009): Characterizing the Health and Safety Needs of the Collision Repair Industry. J. Occup. Environ. Hyg. 6(5):273-282

Chapter 3

SURVEY OF DERMAL PROTECTION IN AUTOBODY SHOPS

3.1. Introduction

Washington State collision repair has been described as a male-dominated industry comprised chiefly of small, non-unionized, family-run businesses (SHARP 2005 and Whittaker and Reeb-Whitaker 2009). SHARP surveyed 700 collision repair shops in Washington State (SHARP needs assessment study) and found that many shops face numerous safety and health challenges, resulting from a combination of misinformation within the industry, insufficient funds to address workplace health and safety concerns, and social barriers to enforcing best practices within the shops. Most notably, inappropriate selection and use of respirators, gloves, and other protective clothing likely contributes significantly to isocyanate exposures. While most painters wear respirators while spray-painting, they do not necessarily wear dermal protective clothing. When using gloves, most painters use relatively thin, disposable latex and nitrile. These observations agree with that of the SPRAY study in Connecticut, which studied 27 auto body shops (among the 500 in the State in 1999). This major epidemiological study of spray-painting in autobody shops in the late 1990s/early 2000s found very similar characteristics of the shops and the way they operate. Similar choices were also found for dermal protective use (Sparer *et al.* 2004).

Since information particular to auto paints and dermal PPE protective efficacy is not always available, other factors besides performance may play a major role when choosing dermal PPE in the collision repair industry. Human factors, for example, describe how PPE affects the wearer in terms of functionality, fit, comfort, and overall well-being (Anna 2003). Most human factor properties represent tradeoffs with protection, for example, barriers to chemicals versus thermal comfort. Common human factors for dermal chemical protective clothing includes: material potential for skin irritation, thermal insulation and breathability, mobility and range of motion, donning and doffing ease, and hand motion. This last factor assesses the effects of gloves on specific functions of the hand used to perform tasks or manipulations, such as dexterity (the ability for the individual glove wearers to manipulate small or large objects with their hands), tactility (the ability of the individual glove wearer to sense by touch differences in surfaces), and grip (the ability of the individual glove wearers to grasp objects under both dry and wet conditions) (Anna 2003). In the case of eye protection the most important human factor is clarity or field of vision; for respirators it is ease of communications (Anna 2003).

Training, risk perception, beliefs in susceptibility to disease, and behaviors can affect personal exposure (Geer *et al.* 2006 and 2007). Geer *et al.* (2006) and Vaughan (1993) found that self-protective behavior was most likely if workers were informed about the risks, believed that precautionary methods were effective, and had a greater perception about their own ability to control exposure. Geer *et al.* (2006) and Quandt *et al.* (1998) documented lack of knowledge with regard to the risk of skin absorption of chemicals. Comfort is another important factor affecting workers' PPE use (Akbar-Khanzadeh 1998). The most frequently cited factors contributing to discomfort or dissatisfaction wearing PPE were related to the workers' belief that the PPE was not needed, created a new hazard, interfered with their work, was too heavy, was hard to wear, prohibited breathing or communicating, irritated skin, put pressure on the body, and was of an undesirable type or model.

This current research was a collaborative effort between the University of North Carolina - Chapel Hill and the Washington State Department of Labor & Industries' SHARP Program. The UNC-SHARP field study was funded by a NIOSH grant [survey funded by NIOSH, R01 OH 007598 "Dermal Exposure to 1,6-Hexamethylene Diisocyanate", Dr. Nylander-French, PI]. Field assistance was provided by the University of Washington. In brief, an industrial hygiene survey was combined with measurements of exposure through all potential routes, with measurements of biologically available dose and exposure modeling. Only data from Washington State' painters were included in this publication. This study was mainly designed to understand the role of dermal exposure as a route for systemic exposure and develop strategies to measure and minimize dermal exposure (Fent *et al.* 2008, 2009). As previously described by Liu *et al.* (2000), this investigation revealed that dermal exposure occurred even when painters used dermal PPE such as coveralls and gloves (Fent et al 2009). This study also indicated that skin exposures were high for painters not wearing dermal PPE (Fent *et al.* 2008). Recommendations from this study are mainly geared towards improvement of engineering controls in these shops to reduce breathing zone concentrations and overspray (Fent *et al.* 2008). However, because painters could not always rely on engineering controls, it is important to understand dermal PPE use before any future interventions to reduce dermal exposure.

The aims of this study were to 1) provide an overview on the state of the collision repair industry in Washington State with regard to dermal protective equipment use and 2) identify the factors affecting painter's dermal PPE choices. Spray painters' dermal PPE use data in Washington State were based on the results of industrial hygiene surveys administered during the UNC-SHARP field study. Survey data and field observations were summarized to yield information on dermal PPE frequency and type. In addition, demographic, health, and work determinants were evaluated for their effect on painters' PPE choices. These results were compared to data derived from SHARP's needs assessment (Whittaker and Whitaker 2009).

3.2. Methods

An industrial hygiene survey was administered at the onset of the 2006-2007 UNC-SHARP field study in Washington State's collision repair industry.

3.2.1 Recruitment of Painters

The protocol used to recruit auto painters for study participation in the Puget Sound area of Washington State has been described previously (Fent *et al.* 2009). In brief, initial contact was made with shop owners and managers to determine their interest in allowing the study to be conducted in their shops. Contact was made through trade association meetings, recruitment letters, and telephone calls. Subject recruitment, study design, and data handling procedures were approved by the Institutional Review Boards of UNC and Washington State. Researchers met with the potential subjects (i.e., the painters) at the shop - individually or as a group - and the objectives and procedures of the study were explained. Participation was entirely voluntary. Upon agreeing to participate in the study, the subject was asked to sign a consent form and a questionnaire was administered. Information was provided to the shop owners and study participants concerning work-related asthma and best practices for spray painting before conducting the exposure study. The criteria for recruitment of subjects were 18 to 65 years of age and English-speaking (to avoid translation costs). The target was to recruit at least 30 subjects for the study. A modest financial incentive to participate was offered at the end of each sampling period. Investigators maintained the linkage between the study participants and their corresponding exposure information in the strictest confidence.

3.2.2. Study Design

Survey and exposure assessment used a repeated-measurement strategy. Sampling was conducted a total of three times in approximately three-month intervals over a period of 9–12 months. During each sampling period, we collected auto body spray painters' survey data, biological specimens (urine, blood, and skin tape strips), and wipe samples of different work surfaces for unpolymerized isocyanates. The methods and results relevant to the exposure and biomarker measurements are published elsewhere (Fent *et al.* 2008 and 2009).

3.2.3. Industrial Hygiene Survey

A questionnaire was administered to the subjects at the beginning of each visit. Demographic, health, and work factors were included in the survey. Demographic factors included age, race, and skin type. Health determinants included weight and height to calculate BMI as well as questions on smoking status, allergies, rash after painting, and asthma. Work determinants included years spray painting, paint jobs per week and per month, as well as type and frequency of PPE use. Painters were asked if they used any of a variety of respirators. Some questions were geared towards maintenance of PPE, such as how frequently respirator filters were changed. In terms of spray booth maintenance practices, painters were asked regarding ceiling and floor change-out schedules as well as when filters were last changed. Data on spray booth type and airflow was not collected in the IH survey, this information was collected while sampling and it was only task specific (Fent *et al.* 2008).

Glove and coverall data were recorded in a survey form without relying exclusively on the painter's direct answers but complementing information with physical evidence. For example, if painters reported the use of a certain type of glove, then investigators would ask them to show the box of the gloves they used. Once the box was inspected, then the brand and specifications of the gloves used were noted when possible. Information about these dermal protective products was also verified through manufacturer's web sites.

3.2.4. Statistical Analysis

Only data from the first of up to three visits were included in this study because this first visit was the best representation of the painters' use of PPE (i.e. it avoided any influence from the investigators). This first visit represented a cross-sectional picture of the collision repair industry. Data from the first visit were used for all variables except coverall make. This exception was necessary because, during the first visit, the information on the make of coveralls was recorded for only 8 subjects. To compensate for the lack of information, we used make of coverall data from all three visits. In order to avoid any bias, each painter' coverall information was categorized as "ever" or "never" use of make of coveralls. For example, if a painter had ever used, during the three visits, a coverall then we noted the coverall make as "ever" used. Frequency on the make of coveralls was based on the "ever" counts.

Demographic, health, and work determinants were summarized at the painter level (total 33 subjects) and at the shop level (total 25 shops). Survey data for one of the subjects was missing, giving a total of 32 observations. Average values among painters within a shop for each variable were calculated to obtain data per shop. Data at the shop level were compared to SHARP's needs assessment data (Whittaker and Whitaker 2009). Data analysis used Microsoft Office Access 2003, Microsoft Office Excel 2003, SPSS version 15.0 (SPSS Inc. Chicago, IL), and Stata version 10 (Stata CORP LP, College Station, TX). Data were managed according to the IRB's requirements and kept in the strictest confidence. Individual painters were assigned a specific anonymous code in the questionnaire database. The key that provided the linkage between the painters' assigned codes and their identities was maintained under lock and key.

For quantitative variables, skewness<1 and kurtosis<3 criteria were used to select variables for further analysis. For categorical variables with all categories above 5 counts, chi-square analysis was determined. Transformations were explored for all variables that did not survive. Outcome variables were dichotomized to allow logistic regression analysis and determine the odds ratio (OR) and 95% confidence intervals (CI) for those factors affecting the outcomes. Outcome variables studied were: frequency of glove use (high or low-medium use), frequency of coverall use (high or low-medium use), type of glove use (latex or nitrile), and thickness of glove use (thin or medium-thick). Since information on the make of coverall was obtained using the "ever or never" approach, this variable was not studied as an outcome variable.

Of the 46 original variables, 8 dichotomous transformations were performed with a final 14 variables surviving for analysis. These 14 demographic, health, or work determinants were studied against each outcome for association. Among the determinants analyzed, 6 were associated with the outcome variables, as follows: 1) smoker status (never or ever smoker), 2) time spray painting (years in the profession), 3) frequency of glove use (high or low-medium use), 4) BMI, 5) frequency of respirator filter change schedule (changed every 0-2 weeks or higher), and 6) number of paint jobs per month.

Bivariate analysis was performed to establish significant relationship by Pearson's correlation, t-test, chi-square, or Fisher's test. Bivariate logistic regression analysis was then performed, followed by multivariate logistic regression analysis. Since the study sample size was fairly small, frequency of the outcome variables was checked to ensure that they were greater than 10 for each category to assure stability of the logistic regression. Model fit was assessed by the Cox & Snell R^2 value provided by the model. For multivariate models, a forward stepwise approach was performed to confirm that the variable added to the model allowed significance at the 5%. Exact logistic regression was calculated to confirm logistic regression odds ratio (OR) (when p values were at the 5% significance) because exact logistic regression may be more appropriate for a small sample size, like the ones studied here. To assure that painter' observations were independent of shop, a random sample was obtained to verify OR values by randomly taking a worker per shop (a total of 25 observations). Multivariate logistic regression models are described here as hypothesis generating efforts rather than predictive models.

3.3. Results

3.3.1. Industrial Hygiene Survey Baseline Characteristics

A total of 25 shops were visited with a total of 33 painters; there were 1-3 painters per shop. Only one painter was missing survey information. All painters were male, age ranged from 21 to 59 years, with an average of 34 years old. By comparison, SHARP needs assessment (Whittaker and Whitaker 2009) also reported a high percentage of male employees with only 3 percent of shops with one female painter. Most painters in the UNC-SHARP field study were white (78.1%) with a skin type that tans easily (40.6%). Twenty eight percent of painters were smokers. Five painters (15.6%) reported seasonal allergies, 2 painters (6.2%) reported asthma, and 2 painters (6.2%) reported breathing problems after painting. Only one painter reported a rash after painting. In overall, painters reported an average of 11.6 years in the profession with 3 painters (9.4%) reporting painting for less than 1 year and 25% of the painters reporting less than 4 years in the job. Two of the painters (6.2%) were very experienced, with more than 31 years spray painting. Survey data are presented in Appendix C.

Painters reported an average of 66.8 paint jobs per month with a minimum of 5 jobs per month and a maximum of 200 jobs per month. The paint-jobs-per-month data collected was collinear with paint-jobs-per-week (Pearson correlation r^2=0.969) inferring that shops had a fairly steady flow of cars throughout the month. Survey baseline characteristics by worker and by shop and comparison to survey from SHARP (Whittaker and Whitaker 2009 and SHARP 2005) was summarized in Table 3.1a and 3.1b.

3.3.2. Industrial Hygiene Survey PPE Use

The type of PPE used during our field visits was tabulated in Table 3.2. The type of glove used most frequently was latex (46.9%), many used nitrile (34.4%), two painters did not use gloves (6.2%), and one painter used other kinds of gloves (3.1%). Although some painters claimed that only thin gloves provided adequate dexterity, we observed that 9 painters (28.2%) used medium to thick latex, nitrile, or neoprene gloves (0.127mm – 0.305mm). Among latex users, 52.9% of painters used thin latex, 5.9% used medium thickness latex, and 11.8% used thick latex. Among nitrile users, 27.3% of painters used thin nitrile and 45.5% used medium thickness nitrile. Gloves used were from many different manufacturers with highest use of Microflex (40%). The most common type of respirator used was replacable half-face air purifying respirator (34.4%) followed by disposable half-face air purifying respirator (28.1%). The type of PPE used by worker and shop is summarized in Table 3.2. Respirator filters were last changed on an average of every other week and on a frequency of 32 times per year. Respirator facepieces were last changed on average of 22 weeks, with a frequency of every 8 weeks per year.

Among coverall makes, Shoot Suit Inc. (Battle Ground, WA) were most common (44% of painters ever used it) followed by SAS Safety Corp. (Long Beach, CA) (26.5% of painters ever used them). Coveralls were used on an average of 10 weeks (N=8), with some painters using them for up to a year, and usually without laundering.

The survey also asked painters about the PPE frequency of use (summarized in Table 3.3). Results from Table 3.3 do not agree necessarily with that of Table 3.2 because there was painters that used more than one type of respirator. It was reported that 22 painters (68.8%) always wore gloves and 20 painters always wore coveralls (62.5%). Fifty percent of painters reported never using long sleeves and 25% reported always using hats (25%). Six painters reported using eye protection (18.8%). The half-face respirator with replaceable cartridges was the respirator reported to be used always (62.5%) followed by disposable half-face respirator (9.4%) and powered air purifying respirator (PAPR) (9.4%).

Survey results reported that shops changed booths' ceiling and floor filters on an average of 3 and 23 times per year, respectively. Painters reported to last changing ceiling and floor filters 22 and 3 weeks ago, respectively.

3.3.3. Field Observation

Although most nitrile gloves used by painters were thicker than latex, in one instance, we observed a painter using low quality thin nitrile gloves that were perforated from manufacturing. On another occasion, a painter spray painted a side mirror by holding the part with his hand, resulting in direct spraying of his gloved hand. We also observed that gloves were changed frequently, usually between paint jobs. Each paint job ranged in duration from 3 to 40 min. However, some of the painters who used thicker gloves reused them for several days. Only few painters used long gloves (12 inch, measured from the tip of the middle finger to the base of the glove), called extended cuff gloves. Shorter gloves (9 inch cuff) usually left some of the wrist/arm area exposed to overspray because there was a space between the glove and the sleeve of the coverall. Lastly, field observations with painters did not find the use of multiple gloves or barrier creams. Paint suits or coveralls were reused for long periods of time (up to a year). This occurred even though some coveralls are disposable. Coveralls and hoods used by painters were not usually laundered.

Most painters said that glasses and goggles were uncomfortable and could interfere with the use of half-face respirators. Painters also suggested that eye protection obscured vision when fogged or over sprayed. We only observed eye protection when painters used full-face respirators or hoods.

Respiratory protection program were inadequate in most shops. None of the painters wearing half-face and full-face respirators with cartridges performed a daily fit-checking during the day of our visit. We also observed, in some instances, interferences with half-face respirators that could disrupt the seal. These interferences were created by painters' facial hair or hood.

Most painters had the autonomy to choose their own protective equipment because managers wanted them to have the freedom and comfort they wished within a certain budget. This had positive consequences, such as painters exploring different brands and products, but also negative consequences, such as not enough enforcement and lack of dermal PPE. These observations agree with those of SHARP (Whittaker and Whitaker 2009).

As reported by Sparer *et al.* (2004), spray booths remain the primary means of engineering conrols for airborne isocyanate exposure in this industry. Many shops had local exhaust ventilation for paint mixing rooms but unlike that reported by Sparer *et al.* (2004) most mixing rooms may have had insufficient ventilation, suggested by a strong solvent smell. Further, we observed that painters did not typically wear respirators while mixing clear coats.

Sparer *et al.* (2004) reported that the most common administrative controls in autobody shops are: use of booths, maintenance, housekeeping, and training. We did not collect enough information to list the number of spray-booths or curtain areas (or semi booths) per shop, but we did observe that booths and semi-booths were used, depending on the nature and length of the spraying application. We observed that many spray booths were not cleaned regularely, with floor vents obstructed, doors ajar, among other factors that indicate a need for better housekeeping and maintenance. When we conducted the survey, many painters did not recall any training taken place during the last year.

3.3.4. Predictors of PPE Use

A summary of the PPE determinants that were significantly associated with the outcome variables is presented in Table 3.4 and 3.5. Frequencies of glove use, frequency of coverall use, and smoker status were the variables that had more than 10 painters in each dichotomized category and were also significantly correlated. These conditions were important to assure stability of the logistic regressions. From Table 3.4 and 3.5, smoker status was repeatedly associated with the outcome variables. Ever smokers tended to use gloves and coveralls more frequently (Pearson chi-square p_{gloves}=0.05 and $p_{coveralls}$=0.01). Also, on the average, painters that used coveralls more frequently painted more jobs per month: 78 jobs per month, versus painters that used coveralls less frequently, 34 jobs per month (independent t-test p=0.038, 95%CI: -85.164 to -2.669).

Further, those determinants that were significantly associated with the outcome variables studied were further scrutinized with logistic regression (Table 3.4 and 3.5). Painters who always used gloves were more likely to have ever smoked (OR=10.7, p=0.01, 95%CI: 1.743-65.271, Cox & Snell R^2=0.223). Similarly, painters that always used coveralls were more likely to have ever smoked (OR=4.7, p=0.049, 95%CI: 1.006-21.652, Cox & Snell R2=0.122). Painters who always used coveralls were more likely to use gloves (OR=7.9, p=0.061, 95%CI: 1.4771-43.4783, Cox & Snell R^2=0.185). When adjusted by the number of paint jobs per month, the OR increased even higher (OR=21.74, p=0.011, 95%CI: 2.02-250.00, Cox & Snell R^2=0.318). To assure that painter' observations were independent of shop, an OR value was obtained with one painter randomly selected per shop. No significant difference was observed between the OR obtained from all observations and the OR obtained by randomly selecting one painter per shop (Table 3.4 and 3.5).

Thickness of gloves was an outcome variable with less than 10 painters for each dichotomized category, so it was not included in Table 3.4. However, a simple bivariate analysis indicated that most painters that frequently changed their respirator filters (more than every 2 weeks) used thin gloves (Pearson chi square p=0.035). Another association not highly significant but nevertheless interesting was that heavier painters with an average BMI of 28.4 preferred thinner gloves than lighter painters with an average BMI 25.7 (independent t-test p=0.084, 95%CI: -0.4343 to 6.3865). As reference, a BMI of 24.9 is considered "normal" weight, so the lighter group was borderline "normal". Similarly, painters with an average of 30.1 BMI used coveralls less frequently than painters with an average of 27 BMI (independent t-test p=0.073, 95%CI: -0.28 to 5.83).

Although not significantly, type of glove was associated with smoker status (Pearson chi square p=0.098), which meant that nitrile users may be more likely to have ever smoked. It was also associated not significantly with years of spray painting (independent t-test p=0.122, 95%CI: -13.93 to 1.745), which suggested that nitrile users may have likely painted for longer. Finally, type of glove and frequency of glove use were also correlated (Pearson chi square p=0.079), which indicated that painters using nitrile gloves were more likely to use gloves frequently.

Table 3.1a. Baseline Characteristics, Quantitative Variables

			UNC-SHARP 2006		SHARP 2005
Factor	**Variable**		**Painters**	**Shops**	**Shops**
Demographic	Age	N	32		
		Range	21-59		
		Mean	33.9		
		SD	8.8		
Health	BMI	N	32		
		Range	21.5-38.8		
		Mean	28		
		SD	3.8		
Work	Years spray painting	N	32	25	38
		Range	0-35	0-32	1-50
		Mean	11.6	11.1	16
		SD	9.4	8.6	10.2
	Times painting per month	N	32	25	490
		Range	5-200	5-160	0-400
		Mean	66.8	67	41.9
		SD	52.4	43.1	46.3

Table 3.1b. Baseline Characteristics, Categorical Variables

Factor	Variable	Category	UNC-SHARP 2006	
			Painters	**Shops**
			N (%)	**N (%)**
Demographic	Race	White	25 (78.1)	22 (78.6)
		Black	0 (0)	0 (0)
		Hispanic	3 (9.4)	2 (7.1)
		Asian	1 (3.1)	1 (3.6)
		Native American	1 (3.1)	1 (3.6)
		Mixed	2 (6.2)	2 (7.1)
		Other	0 (0)	0 (0)
	Skin Type	Burns very easily	4 (12.5)	4 (13.8)
		Burns easily	11 (34.4)	11 (37.9)
		Tans easily	13 (40.6)	11 (37.9)
		Brown	4 (12.5)	3 (10.3)
		Black	0 (0)	0 (0)
Health	Current Smokers		9 (28.1)	
	Past Smokers		9 (28.1)	
	Seasonal allergies		5 (15.6)	
	Year round allergies		2 (6.2)	
	Asthma		2 (6.2)	
	Breath problems after paint		2 (6.2)	
	Rash after paint		1 (3.1)	

Table 3.2. Type of PPE Use

Variable	Category	UNC-SHARP 2006		SHARP 2005
		Painters	Shops	Shops
		N (%)	N (%)	N (%)
Glove type	Latex	15 (46.9)	13 (50)	253 (51)
	Nitrile	11 (34.4)	10 (38)	195 (40)
	Other	1 (3.1)	1 (4)	80 (17)
	None	2 (6.2)	2 (8)	11 (2)
Glove thickness	Thin 2-5 mil	12 (37.5)	12 (52.2)	
	Medium 6-8 mil	6 (18.8)	6 (26)	
	Thick >8 mil	3 (9.4)	3 (13)	
Glove make	Microflex	6 (40)	6 (50)	
	Gloveworks	2 (13.3)	1 (8)	
	Others	7 (46.7)	5 (42)	
Coverall make*	Shoot Suit	15 (44.1)	14 (43.8)	
	SAS Safety	9 (26.5)	8 (25.1)	
	PPG	2 (5.9)	2 (6.3)	
	Mipa	2 (5.9)	2 (6.3)	
	Others	6 (17.6)	6 (18.8)	
Respirator type	Air line half or full-face	2 (6.2)	2 (7.4)	40 (26.5)
	Air line helmet or hood	4 (12.5)	4 (14.8)	18 (12)
	Powered air purifying respirator	2 (6.2)	2 (7.4)	8 (5.3)
	Full face air purifying respirator	1 (3.1)	1 (3.7)	16 (10.6)
	Disposable half-face air purifying respirator	9 (28.1)	7 (25.9)	46 (30.5)
	Replaceable half-face air purifying respirator	11 (34.4)	11 (40.7)	23 (15.2)

*Ever or never use within the three field visits

Table 3.3. Frequency of PPE Use

	# Painter (%)			
Variable	**Never**	**Seldom**	**Usually**	**Always**
Gloves	1 (3.1)	1 (3.1)	8 (25)	22 (68.8)
Long sleeves	16 (50)	4 (12.5)	2 (6.2)	10 (31.2)
Coveralls	6 (18.8)	2 (6.2)	4 (12.5)	20 (62.5)
Hat	14 (43.8)	6 (18.8)	4 (12.5)	8 (25)
Goggles	17 (53.1)	8 (25)	1 (3.1)	6 (18.8)
Air line half or full-face	27 (84.4)	1 (3.1)	1 (3.1)	3 (9.4)
Air line helmet or hood	28 (87.5)	0 (0)	0 (0)	2 (6.2)
Powered air purifying respirator	28 (87.5)	0 (0)	0 (0)	3 (9.4)
Full face air purifying respirator	30 (93.8)	0 (0)	0 (0)	1 (3.1)
Disposable half-face air purifying respirator	27 (84.4)	0 (0)	0 (0)	3 (9.4)
Replaceable half-face air purifying respirator	5 (15.6)	3 (9.4)	4 (12.5)	20 (62.5)

Table 3.4. Dermal PPE Determinants for Frequency of Glove Use

				Bivariate Analysis		
Sample Size	**Categories**	**Determinant**		**chi-square/t-test**	**Logistic Regression***	**Exact Logistic Regression****
		Smoker Status				
		Never	Ever: past or present			
All Workers	Never or Seldom or Usually N=10	N=8	N=2	Pearson chi-square p=0.05	OR=10.7, p=0.01, 95%CI: 1.743-65.271, Cox&Snell R^2=0.223	OR=9.8,Suff. 16, 2*Pr(Suff.)=0.0154, Pr>=score=0.0084, 95%CI: 1.4122-120.4064
	Always N=22	N=6	N=16			
Randomly selected: 1 worker per shop	Never or Seldom or Usually N=7	N=6	N=1	Pearson chi-square p=0.09	OR=15.6, p=0.022, 95%CI: 1.481-164.376, Cox&Snell R^2=0.253	OR=13.7,Suff. 13, 2*Pr(Suff.)=0.0283, Pr>=score=0.0213, 95%CI: 1.221851-770.8694
	Always N=18	N=5	N=13			

*SPSS version 15.0 **Stata version 10

Table 3.5. Dermal PPE Determinants for Frequency of Coverall Use

				Bivariate Analysis		
Sample Size	**Categories**	**Determinant**		**chi-square/t-test**	**Logistic Regression***	**Exact Logistic Regression****
		Frequency of Glove Use				
		Never or Seldom or Usually	Always			
All Workers	Never or Seldom or Usually N=10	N=7	N=3	Pearson chi-square p=0.01	OR=7.9, p=0.061, 95%CI: 1.4771-43.4783, Cox&Snell R^2=0.185	OR=7.33,Suff. 17, 2*Pr(Suff.)=0.0310, Pr>=score=0.0184, 95%CI: 1.158579-61.78006
	Always N=22	N=5	N=17			
Randomly selected: 1 worker per shop	Never or Seldom or Usually N=7	N=5	N=2	Pearson chi-square p=0.045	OR=6.5, p=0.058, 95%CI: 0.937-45.106, Cox&Snell R^2=0.148	OR=5.96,Suff. 13, 2*Pr(Suff.)=0.1237, Pr>=score=0.0752, 95%CI: 0.6980436-82.56087
	Always N=18	N=5	N=13			
		Smoker Status				
		Never	Ever: past or present			
All Workers	Never or Seldom or Usually N=12	N=8	N=4	Pearson chi-square p=0.043	OR=4.7, p=0.049, 95%CI: 1.006-21.652, Cox&Snell R^2=0.122	OR=4.424, Suff. 14, 2*Pr(Suff.)=0.0973, Pr>=score=0.0683, 95%CI: 0.8075456-29.00737
	Always N=20	N=6	N=14			
Randomly selected: 1 worker per shop	Never or Seldom or Usually N=10	N=6	N=4	Pearson chi-square p=0.188	OR=3, p=0.194, 95%CI: 0.571-15.766, Cox&Snell R^2=0.067	OR=2.86, Suff. 10, 2*Pr(Suff.)=0.3661, Pr>=score=0.2406, 95%CI:0.43663-21.61548
	Always N=15	N=5	N=10			

*SPSS version 15.0 **Stata version 10

3.4. Discussion

3.4.1. Study Limitations

The data collected with this field study only represents a portion of the collision repair shops in the Puget Sound area. However, comparison of protective clothing usage observed in the field with that reported in the Needs Assessment survey data (Whittaker and Whitaker 2009), which included over 400 collision repair shops in the Puget Sound, confirmed that the population studied during the UNC-SHARP field study was representative of Washington State.

We did not categorize shops by size because this was hard to measure using the variables collected in the survey. Shop size may be related to the number of painters, number of booths in the shop, used area of the business, and revenue per month (Woskie *et al.* 2004). However, it was difficult to assess shop size in our study because all shops were different and what applied to some did not apply to all. For example, when using number of painters to assess shop size, we found challenges because some large businesses had several painters, while the shops with the highest number of cars painted per month only had one painter. Analysis was performed at the worker level because not enough determinants at the shop level were recorded and we were not able to assess shop size accurately.

No other health determinants besides BMI were analyzed because of the small sample size. The authors acknowledge that health determinants may play a role in the painters' perception of risk and frequency and type of PPE choices and we recommend that larger studies be conducted to understand their effect.

Unfortunately, no questions in the industrial hygiene survey were directly geared towards understanding reasons behind the choices for PPE in painters. Data of this type were only gathered based on observations or conversations during the field studies.

3.4.2. Industrial Hygiene Survey

The 33 auto painters surveyed (25 shops) were all male, mostly white (78%), mostly young (mean 34 years), slightly overweight (mean BMI 28), fairly experienced painters (mean 12 years painting), and with a high volume of paint jobs per month (mean 67). These results agreed with those described by SHARP (Whittaker and Whitaker 2009). A high percentage of painters were smokers (28.1%), if compared with the 17% Washington State average in adults reported by the Department of Health (2009).

Survey data and observations from the UNC-SHARP field study suggested that painters used inadequate protective clothing, such as thin food-grade latex gloves. The most frequently used glove type was latex (46.9% of painters and 50% of shops). SHARP had also found a high frequency of latex glove use within shops (51%) (Whittaker and Whitaker 2009); Sparer *et al.* (2004) reported 89% of workers wearing latex gloves. Approximately 35% of painters (38% of shops) used nitrile gloves during the UNC-SHARP field study. Similarly, SHARP reported 40% of shops and Sparer *et al.* (2004) reported 25% of shops using nitrile. Although Sparer *et al.* (2004) study was conducted in 37 auto body shops in Connecticut (the SPRAY study), the results are comparable to the data presented here. A lower percentage of latex use and higher nitrile use was found in Washington compared to Connecticut State. Washington State study was performed later than the Connecticut study so this glove trend may be caused by dissemination of information that nitrile is more protective than latex when spray painting, with educational materials like that of EPA (1999).

A higher percentage of painters used medium to thick gloves than we anticipated. This was encouraging; however, we observed that those using thicker gloves tended to use them for longer periods of time because of their higher cost. Even though using thicker gloves is more protective, if the gloves are reused inadequately it may actually increase the painter's exposure to isocyanates. Measuring urinary metabolites, Creely *et al.* (2006) reported that misuse of protective gloves might actually increase a worker's exposure.

Although NIOSH (2004) recommends the use of elbow-length gloves while using isocyanate products, we did not observe any in use while mixing or spray painting. Most painters reported never using long sleeve shirts (under coveralls) (50%), which was not surprising considering that many used coveralls over street cloths and temperatures are high when inside the booth. Although Creely *et al.* (2006) and Jepsen *et al.* (1985) reported the use of gloves under secondary chemical protective gloves for the application of isocyanate-based paints in the vehicle manufacturing industry, we did not see these in use during our field visits.

We observed that the majority of painters used coveralls (62.5%) and that the coveralls were highly reused, some times until they were falling apart. These observations match Sparer *et al.* (2004), with 80% of painters reporting use of coveralls. Bello *et al.* (2007) reported that auto spray paint could take several days to cure completely, suggesting that coveralls may retain reactive isocyanates for several hours or days after painting. The presence of paint in coveralls may increase exposure. Disposing of coveralls daily could be a solution; however, this would be an issue for employers because frequent replacement would translate to higher costs. NIOSH (2004) recommends to dispose or launder protective clothing after each use (e.g. at the end of the work shift). However, we observed only a few shops where protective clothing was laundered by the employer.

Covering the head may reduce dermal exposure due to overspray. However, we observed that painters that used hats or hoods would usually wear them every day. Some times hats or hoods were made of absorbent fabrics such as cotton, which if not washed daily could increase exposure. On other occasions, the hoods were part of the coveralls in which case the fabric was usually not absorbent.

Very few automobile painters used eye protection (18.8%). Based on field observations, painters that had their eyes protected were using full-face respirators. Workers may not be informed or concerned with chemicals that are absorbed through the eyes and may not consider the physical hazards associated with using a pressurized spray gun. Increasing the use of full-face respirators would increase both eye protection and dermal protection because less skin is exposed, especially when the respirator has a hood or helmet. We observed that the bare skin of the face and neck in painters using half-face respirators were highly exposed to overspray.

Painters using half-face respirators did not use eye protection because they perceived safety glasses and goggles to be an impediment to spray painting. This worker behavior agrees with observations found by Akbar-Khanzadeh (1998). The use of safety peel-off lens covers on respirators, hoods, or goggles are an alternative for painters whose main concern is visibility while painting. Covers are disposable and protect lens against paint and chemical overspray but are expensive. We did not observe the use of safety peel-offs during our field visits.

All painters used a respirator. Similar findings were reported by Sparer *et al.* (2004), with 100% of the 37 shops studied reporting using respirators. However, since the majority of workers used negative-pressure respirators or APRs (72%), there is a need to increase the use of positive-pressure respirators in this industry. Sparer *et al.* (2004) reported similar results with the use of cartridges in 86% of the shops. The main difference is that for Sparer *et al.* (2004) all painters were using dual cartridges (charcoal filter and N95 prefilter) while in Washington State, painters were observed to not always use dual cartridges.

In a negative-pressure respirator, like for APRs, inhalation draws the contaminated air through the purifying filter to the painter. A leak-proof seal between the facepiece and the worker's face is absolutely essential for proper protection. Leaks may be caused by improper fit, the presence of facial hair or foreign substances under the sealing surface, or cracked or damaged seals, valves or cartridges. Because of potential for leaks, negative-pressure respirators provide less protection than all other types. Not surprisingly, supplied air respirators are recommended by NIOSH (2004) for spray painting.

Powered Air Purifying Respirators (PAPR) employ a portable, rechargeable battery pack and blower to force the contaminated air through the cartridge and supply the filtered air to the worker's breathing zone. PAPR are popular because the painter is more mobile since he is not attached to a hose, like in the case of supplied air respirators.

3.4.3. Predictors of PPE Use

Frequency of coverall use was well-described by the number of paint jobs per month. This may indicate that painters with a heavier work load are more aware of exposures. Painters who always used coveralls were more likely to use gloves. The main reasons workers may have worn any dermal PPE were 1) health concerns from their exposure to paints or 2) hygiene. If a painter understands why it is important to wear coveralls, the same reasons may apply to the use of gloves. When adjusted by the number of paint jobs per month the OR increased even higher for coverall and glove use. Users of dermal PPE seem to be more concerned about either health or cleanliness when the exposures were higher.

Smoker status was repeatedly associated with the outcome variables. For example, ever smokers tended to use gloves and coveralls more frequently. In particular, nitrile users were more likely to have ever smoked. Even though these results could be an artifact of the small sample size, it would be interesting to follow up on a larger group of painters to understand these associations further. Ever smokers include those that stopped smoking or those that have respiratory disease due to smoking. So hypothetically, if workers are aware of the respiratory effects that automotive pants have on their health, perhaps workers would be more likely to wear dermal PPE to minimize their exposure. A more plausible explanation may be that smoking is cofounding with a variable that was not investigated in this study.

Although not statistically significany, most painters that changed often their respirator filters (more than every 2 weeks) used thinner gloves, usually disposable. This behavior may come from the belief that disposable means better protection –a frequent concept in marketing. Disposable gloves in a high pace environment such as the collision repair industry also translate in convenience.

Experience may influence dermal PPE choices. Nitrile users have likely painted for more years (not statistically significantly). Further, type of glove and frequency of use were correlated (not statistically significant), which indicated that painters using nitrile gloves were more likely to use gloves frequently. Those who use PPE understand that frequency of use and type of gloves are important factors to ensure protection; considering that nitrile is usually better than latex for spray painting, as recommended by EPA (1999).

BMI as a health determinant of PPE use suggested that heavier painters used thinner gloves and did not wear coveralls as frequently. Even though not statistically significant, these findings appear to suggest that comfort may be an important factor for painter's adoption of PPE use. Comfort has been described as an important factor for users of PPE (Akbar-Khanzadeh 1998). To increase the effectiveness and safety of PPE, the human-factor aspects of PPE design should be emphasized more and quality improvement should cover the wearability of PPE (Akbar-Khanzadeh 1995).

We did not find that age was associated with our outcome variables; however, Geer *et al.* (2007) found that the odds of high exposure increased in younger age group. Older painters may have more experience and therefore may take more shortcuts when it comes to protection, especially if they have never experience problems in the past. Perhaps a larger study would show age as a predictor of dermal PPE use.

3.5. Conclusions

Painters in Washington State collision repair industry are using inadequate dermal protection, such as thin latex gloves. A high percentage of painters used latex gloves, coveralls, and half-face air purifying respirators. No painters used eye protection when using half-face respirators.

Overall, we found that auto painters PPE choices may be determined by smoking status, years spray painting, and frequency of use and type of dermal PPE. We concluded that these determinants affected PPE choices depending on painter's attitudes towards adoption of PPE use. We suggested that users of PPE understand that frequency of use and type of gloves are important factors that affect protection. Further, comfort, convenience, and experience of the painter may also influence their PPE choices. However, given many of the associations are not statistically significant, this study was merely an exploratory approach to generate hypothesis and motivate future research in this area.

There are training and research opportunities with auto painters to improve the use of safety practices, in particular the use of dermal PPE, implementation of respiratory programs, and the use of eye protection. Training has been correlated with use of dermal protection in past studies (McFarlene *et al.* 2008). More data on glove efficacy against isocyanates are needed for painters. Painter should be encouraged to increase their use of full-face respirators. Even though respirators are not traditional dermal PPE, covering the face and/or head can provide more dermal protection. Further, full-face respirators have a higher respiratory protection factor while providing eye protection.

There are possible challenges for future training of painters. There are at least two different groups among auto painters: frequent PPE users versus non-users. The frequent users of PPE (receptive/adopters) may behave and respond differently to those that do not use PPE (not adopters/disinterested/resistant). Barriers for non-adopters are not clear. There are opportunities to train workers to bring them to the same level while not only increasing the use of PPE but also improving work-practices.

In terms of research, there is much to learn about the glove and coverall materials that best protect painters when using isocyanate paint products. This industry would benefit from an intervention to decrease the use of thin latex, which are not protective against solvents or isocyanates (Liu *et al.* 2000, EPA 1999, and Chapter 6), as well as improving work practices to assure the appropriate use of gloves. Published recommendations (NIOSH 2004) can be too general to guide painters satisfactorily. Other publications, such as EPA (1999) and PPG (1997) suggest nitrile but do not make any reference to thickness requirements.

There is also a need to identify more workplace factors and employer and employee preferences that may obstruct or facilitate adoption of efficient dermal PPE. Use of focus groups would be essential to get the information from painters and managers to change behavior (Gates *et al.* 2006). Once these needs are met in the industry, a "social marketing" intervention strategy (SHARP 2005) would be the next ideal step, this approach would use the barriers and benefits to adopting sustainable safe work practices as the foundation of an educational and technical assistance campaign that utilizes the behavior change tools from social science research to promote information, attitudes, values and behaviors. Cowley *et al.*

(2004) also suggests that social marketing is the tool to achieve change in small businesses like autobody shops.

3.6. Notes to Chapter 3

Akbar-Khanzadeh F, Bisesi MS, and Rivas RD (1995): Comfort of personal protective equipment. Appl. Ergon. 26(3):195-8

Akbar-Khanzadeh F (1998): Factors contributing to discomfort or dissatisfaction as a result of wearing personal protective equipment. J. Hum. Ergol. (Tokyo). 27(1-2):70-5

Anna DH. Chemical Protective Clothing, 2nd edition. (2003), 530 pages

Bello D, Sparer J, Redlich CA, *et al.* (2007): Slow curing of aliphatic polyisocyanate paints in automotive refinishing: a potential source for skin exposure. J. Occup. Environ. Hyg. 4(6):406-11.

Cowley S, Else D, and LaMontagne A (2004): Increasing the adoption of OHS risk controls in small business: can social marketing help to achieve change? J. Occup. Health Saf. Aust. Nz. (Cch. Aust.) 20(1):69-77

Creely KS, Hughson GW, Cocker J, *et al.* (2006): Assessing isocyanate exposures in polyurethane industry sectors using biological and air monitoring methods. Ann. Occup. Hyg. 50:609–21

Department of Health, Washington State (2009): Tobacco Prevention and Control Program, Progress Report, March 2009. DOH Pub. 340-130

EPA Nov (1999): Choosing the right gloves for painting cars. U.S. Environmental Protection Agency. Publication EPA/744-F-00-005. Updated June 2000. Available at http://www.epa.gov/dfe/pubs/auto/gloves/gloves.pdf, accessed January 2007

Fent KW, Jayaraj K, Gold A, *et al.* (2008): Quantitative monitoring of dermal and inhalation exposure to 1,6-hexamethylene diisocyanate monomer and oligomers. J. Environ. Monit. 10:500 – 507

Fent KW, Trelles Gaines LG, Thomasen JM,*et al.* (29009) Quantification and Statistical Modeling--Part I: Breathing-Zone Concentrations of Monomeric and Polymeric 1,6-Hexamethylene Diisocyanate. Ann. Occup. Hyg. Submitted

Gates D, Brehm B, Hutton S, *et al.* (2006): Changing the Work Environment to Promote Wellness A Focus Group Study. AAOHN J. 4(12):515-20

Geer LA, Curbow BA, Anna DH, *et al.* (2006): Development of a questionnaire to assess worker knowledge, attitudes and perceptions underlying dermal exposure. Scand. J. Work Environ. Health. 32(3):209-18

Geer LA, Anna D, Curbow B, *et al.* (2007): Survey assessment of worker dermal exposure and underlying behavioral determinants. J. Occup. Environ. Hyg. 4(11):809-20

Jepsen JR, Sparre-Jorgensen A, and Kyst A (1985): Hand protection for car-painters. Contact Derm. 13(5):317-20

Liu YC, Sparer J, Woskie SR, *et al.* (2000): Qualitative Assessment of Isocyanate Skin Exposure in Auto Body Shops: A Pilot Study. Am. J. Ind. Med. 37(3):265-274

The National Institute for Occupational Safety and Health (NIOSH) (2004): A Summary of Health Hazard Evaluations: Issues Related to Occupational Exposure to Isocyanates, 1989 to 2002. Available at http://www.mass.gov/envir/ota/pubs/wbfull.pdf, accessed February 2009

PPG Industries (1997): PPG Two-Component Polyurethane Coating Systems Guidelines for Safe Use. PAM 9379 8/97

Quandt SA, Arcury TA, Austin CK, and Saavedra RM (1998): Farm-worker and farmer perceptions of farmworker agricultural chemical exposure in North Carolina. Hum. Organ. 57(3): 359-68

Safety & Health Assessment & Research for Prevention, (SHARP) Washington State Department of Labor and Industries (2005): Health and Safety in Washington State's Collision Repair Industry: A Needs Assessment. Technical report 69-4-2005. SHARP, Olympia, Washington, December 2005.

Sparer J, Stowe MH, Bello D, *et al.* (2004): Isocyanate exposures in autobody shop work: the SPRAY study. J. Occup. Environ. Hyg. (9):570-81

Vaughan E (1993): Chronic exposure to an environmental hazard: Risk perceptions and self protective behavior. Health Psychol. 12:74-85

Whittaker SG. and Reeb-Whitaker C(2009): Characterizing the Health and Safety Needs of the Collision Repair Industry. J. Occup. Environ. Hyg. 6(5):273-82

Woskie SR, Sparer J, Gore RJ, *et al.* (2004): Determinants of isocyanate exposures in auto body repair and refinishing shops. Ann. Occup. Hyg. 48:393-403

Chapter 4

ISOCYANATE ANALYTICAL METHOD COMPARISON

4.1. Introduction

Isocyanates, in particular aliphatic isocyanates, are essential components of catalyst hardeners in two-part polyurethane coating systems, including clear coats, primers, and sealers in the collision repair industry. Spraying these products can create a significant inhalation hazard for isocyanates and solvents (EPA 2005; Sparer *et al.* 2004; Woskie *et al.* 2004), as well as a dermal hazard (Liu *et al.* 2000; Chang *et al.* 2007). Isocyanates are strong irritants and sensitizers and a leading cause of work-related asthma (Vandenplas *et al.* 1993; Liu and Wisnewski 2003; Redlich *et al.* 2007). The final "clear coat" may result in higher exposures reflecting the high concentrations of isocyanates in the hardener component (Sparer *et al.* 2004).

Clear coats are the clear (non-pigmented) top-coats that are applied over base-coat paints. Clear coats improve the vehicle coating systems' general appearance and durability. Clear coats are typically polyurethane coatings based on a combination of a polyol resin and isocyanate "pre-polymers". The term "polymeric" will be used to denote all higher oligomers and partially polymerized species (resulting from the reaction of an isocyanate with the polyol), containing free isocyanate groups (Liu *et al.* 2007). The most common diisocyanates used in clear coats are 1,6-hexamethylene diisocyanate (HDI) monomer and its oligomers (e.g., uretidone, biuret, and isocyanurate), although some formulations may also contain monomeric and oligomeric isophorone diisocyanate (IPDI). It is typical for hardener formulations to contain only up to 1% of the monomers while the remainder (99%) is composed of polymeric diisocyanates (Sparer *et al.* 2004).

This current study critically compares methods for analyzing the isocyanates present in a common and representative bulk sample of clear coat hardener, as well as comparing the metrics for reporting results. Differences in the results from two air sampling methods sampled side-by-side (LC-MS and ISO-CHEK methods for abreviation) have been reported from the UNC-SHARP field study, and it was not clear if the differences were attributed to the variables associated with air sampling or the analytical chemistry. Further, the EH lab at the Uiversity of Washington had developed a modified OSHA method that had not been validated for the analysis of oligomers. Considering that the NIOSH 5525 was a standard method that measured total isocyanates, it was just reasonable to use this method to compare with the LC-MS, ISO-CHEK, and OSHA methods. Lastly, comparing the different filter systems for the analysis of isocyanate was important for the informed selection of the solid media for the permeation experiments in Chapter 5 and 6.

All methods performed analysis using liquid chromatography (LC) and several detectors, as follows: ultraviolet (UV), fluorescence (FLD), and mass spectrometry (MS). The methods compared were:

- Modified LC/UV-FLD NIOSH 5525 using 1-(9-anthracenylmethyl)piperazine (MAP) as derivatization reagent on a quartz fiber filter system,
- LC-MS using 1-(2- methoxyphenyl)piperazine (MPP) as derivatization reagent on a glass fiber filter system,
- LC/UV-FLD OSHA 42/PV2034 using 1-(2-pyridyl)piperazine (PPZ) as derivatization reagent on a glass fiber filter system,
- Modified LC/UV-FLD Omega Iso-Chek using MPP and 9-(methylaminomethyl)anthracene (MAMA) in a dual filter system (pre-impregnated MAMA glass fiber filter and PTFE filter).

A bulk sample was selected for analysis in order to avoid the variability associated with the sampling of airborne isocyanates, in particular during collection from an air sample. Variations result then from the different methods depending partly on the handling and preparation, which was minimized by doing blinded and randomized spiking by the same person and on the same day. The efficiency of the derivatization reaction may also play a role, which is defined as the percentage of the collected isocyanate species that reacts with the reagent (Streicher *et al.* 2000). Since no polyols are present in this laboratory comparison, there is no competition with the derivatization reagent and therefore, the derivatization kinetics are relatively unimportant (Streicher *et al.* 2000). Other factors that differentiate methods include the separation by HPLC and identification by the different detectors (Streicher *et al.* 2000). In overall, the key issues on which the methods here compared differed from each-other are: 1) derivatization reagent, 2) chromatography and detection, 3) standards used for calibration, and 4) reported units.

Even though this study was not intended to compare derivatization reagents directly, it presents strengths and weaknesses for methods using key derivatization reagent: MAP, 2-MP, PPZ, and MAMA. These amines inherent reactivities with isocyanates typically differ by less than a factor of five (Streicher *et al.* 2000). Streicher *et al.* (2000) commented that this difference is probably not as important as the efficiency of mixing of the collected isocyanates and the derizatizing solution. The mixing is most efficient when using impinger collection of air samples (Streicher *et al.* 2000). In this method comparison however, no method used an impingers, which is reasonable since the use of filters is not only more convenient but also suitable for personal monitoring. All methods used either impregnated filters or filters that were later immerse in a derivatization solution.

The main objective of this study was to compare four analytical methods in order to: 1) determine intra- and inter-method variability; and 2) understand the strengths and weaknesses of the analytical methods. The method comparison protocol (presented in Appendix D.5 and also available on-line at: *www.lni.wa.gov/Safety/Research/Files/InterLab.pdf*) was developed in collaboration with several labs with expertise in isocyanate sampling and analysis (participating labs are listed in protocol). This method comparison study attempts to address the challenges of comparing different methods and metrics by using manufacturer's proprietary information in conjunction with a titration assay to determine total isocyanate content. The titration procedure was similar to that published elsewhere (HSE 1993; Marand 2005). The concentrations chosen for the method comparison study were based on exposure values of industrial hygiene significance, such as the UK-HSE standards for total isocyanates (Bello *et al.* 2004; Liu *et al.* 2006), and expected limits of quantitation (LOQs). The levels chosen were further explained in the protocol (Appendix D.5).

4.2. Methods

4.2.1. Hardener Selection

The hardener selection was based on three criteria: 1) frequency of product usage in the collision repair industry, 2) isocyanate composition, and 3) availability of proprietary data. In return for the proprietary information, the investigators pledged not to divulge the name of the commercial hardener product used in these studies. Survey information from field studies in the WA collision repair industry showed that the selected hardener product was used widely [survey funded by NIOSH, R01 OH 007598 "Dermal Exposure to 1,6-Hexamethylene Diisocyanate", Dr. Nylander-French, PI]. Information from the MSDS and manufacturer's proprietary information revealed that this product contains a mixture of monomeric and oligomeric forms of HDI and IPDI. The expected %NCO mass ranged from 16.0- 17.2. Manufacturer information provided the following composition:

- 0.24% mass HDI monomer,
- 47.9% mass HDI oligomer,
- 0.25% mass IPDI monomer,
- 35.5% mass IPDI oligomer.

4.2.2. Spiking Protocol and Sample Analysis

Participating labs shipped the filters and derivatization solutions specific for their methods to the coordinating lab. Filter handling was minimized by having the participating labs place their filters in individual containers prior to shipment. These containers were ultimately filled with lab's specific derivatization solution. An analyst, who was not a study participant, dissolved the bulk hardener in toluene to load 1, 10, 100, and 400 μg bulk product/filter in triplicate (justification for these levels is provided in Appendix D.5). Each individual filter was treated identically, including those filters from the dual ISO-CHEK filter system. Filters were allowed to dry at room temperature for 2-5 minutes. Each spiked filter was assigned a code to ensure that the participating labs were not aware of the spiking levels on the filters. The loaded filters and the three blanks to which the derivatization solution was added were shipped to the participating labs on ice packs.

Once samples were received by the labs, participants were instructed to remove them from the shipping containers immediately and store them according to the lab's typical methodology. Participants were instructed to analyze the samples as soon as possible and record the date of analysis. Samples were then analyzed for: HDI monomer and HDI oligomers plus IPDI monomer and IPDI oligomers, as the respective analytical methods allowed. Labs were also encouraged to perform an NCO titration of the hardener (in triplicate) in order to determine the %NCO mass in the product. Titration procedure was included in the protocol (Appendix D.5).

The methods used are described in detail in Appendix D.6. A brief description of each method follows:

- Modified NIOSH 5525 method: LC/UV-FLD using MAP as the derivatization reagent. Abbreviation: NIOSH Method;
- 2-MP LC-MS Method: LC/MS-MS method that employed synthesized oligomer standards and 2-MP as the derivatization reagent. Abbreviation: MS Method;
- Modified OSHA 42/PV2034 method: LC/UV-FLD using PPZ as the derivatization reagent. Abbreviation: OSHA Method;
- Modified Omega Iso-Chek Method: LC/UV-FLD analysis that employs a two-filter system. The first filter (PTFE) theoretically captures oligomers in the aerosol phase and is subsequently derivatized with 2-MP. The second filter is pre-impregnated with MAMA and theoretically captures monomers in the vapor phase. Abbreviation: ISO-CHEK Method. The first filter (PTFE) was analyzed for oligomers and the second filter (MAMA) was analyzed for monomers.

Besides the different derivatization reagents and detectors used by each method, there were differences in the standards used, as follow:

- The NIOSH method reported the use of HDI and IPDI monomer standards provided by NIOSH (Sigma purified reported in Bello *et al.* 2002);
- The MS method reported the use of commercial HDI monomer standard and bulk materials for the HDI oligomer standards that were synthesized and prepared like that described in Fent *et al.* 2008;
- The OSHA method used commercially available HDI and IPDI monomer standards;
- The ISO-CHEK method used HDI and IPDI monomer commercial standards as well as bulk materials as standards for the oligomers. The following bulk materials derived from Bayer products are used as standards:
    - HDI Dimer/Uretidone - Desmodur 3400-N
    - Biuret - Desmodur N100
    - Isocyanurate - Desmodur N3300A
    - IPDI Oligomer - Desmodur Z4470-BA

The ISO-CHEK method reported a known bias, recoveries of an average of 159%, for the product N3400.

4.2.3. Data Analysis

Data provided by the different methods were summarized and used to compare analytical results for the levels spiked on the filters. Data analysis was based on the comparison among methods for all the variables (using Microsoft Excel 2003 and SPSS 15.0 for Windows (SPSS Inc. Chicago, IL)). A large fraction of the analytical data reported by the methods was below detection or quantitation limits. Highest fractions were reported by the ISO-CHEK method with 56% below detection for HDI monomer and 50% below detection for IPDI monomer. Labs reported these data in a variety of formats, including "below LOQ", "below limit of detection (LOD)" and occasionally provided a numerical value.

A reference value was defined for each isocyanate-specie as the expected amount loaded on the filter. Proprietary information from the manufacturer was used to estimate reference values for HDI and IPDI monomers and HDI and IPDI oligomer proportions. For example, the mass of HDI reference value was calculated by multiplying the known loaded mass on the filter times the manufacturer percentage of HDI monomer. If a NCO mass reference value was needed, the titration result was used to convert mass of bulk product to total NCO mass. There is no reference value for individual oligomers since the manufacturer did not provide information for these. Mole units cannot be used when analyzing group of oligomers with unknown composition; NCO mass was used instead.

Variables with a reference value, such as monomer and total HDI and IPDI oligomers, were treated as heteroskedastic for the regression analysis, which means that variances are different throughout levels (i.e., the variances for the values below detection and quantitation limits were different from those above limits). A robust regression analysis was required; robust regression is a form of regression analysis designed to circumvent some limitations of traditional parametric and non-parametric methods, specifically in the presence of outliers or heteroskedasticity. The weighted least squares regression in SPSS was used to obtain an equation of the form: Reference Value = Intercept + Slope · Method Reported Value.

In order to ensure consistency, data below LODs and LOQs were assigned the following:

- Values below the LOD were substituted with LOD/2 and
- Values below the LOQ were substituted with the mean value of the LOD and the LOQ

A summary of the values used for substitution of data below LOD and LOQ is presented in Appendix D.7. These substitutions provided a slightly more stable robust regression compared to substituting all data below LODs and LOQs with "zero". Note that all Tables presented in this report reflect the substitutions explained in Appendix D.7.

Each variable was analyzed independently by comparing reported values to a reference value, when a reference value was available. In order to standardize results, all results were converted to mass and to NCO-mass when possible. NCO conversion factors for the different species studied are presented in Appendix D.8. Because reference values for individual HDI oligomer species were not available, the analytical results from each method were compared with each-other, as recommended by Afifi *et al.* (2004).

Robust regression has the advantage that slope and intercept do not change even in the presence of possible outliers. The robust regression would adjust the presence of a possible outlier by increasing the standard error reported. In some instances, the robust regression results reported high standard errors that could be decreased by omitting samples that seemed outside of the expected range. Outlier existence was explored but no data point was excluded from the robust regression for the purpose of this inter-method comparison.

For each analytical method, the results from the robust regression were used to calculate the following five criteria (Fisher and Van Belle, 1993): location shift, scale shift, precision, accuracy, and concordance. Location shift refers to the degree to which the means of the data differ. A scale shift measures the differences in variance. Precision was defined as the coefficient of correlation and accuracy is estimated by the distance that the observations are from the 45 degree line. Concordance is defined as the product of the precision and the accuracy. Denoting two methods by subscripts 1 and 2, we define:

$$Mean\_of\_all\_values = \overline{X}$$

$$S\tan dard\_Deviation = \sigma$$

$$Correlation\_Coefficient = r$$

$$Location\_Shift = u = \frac{\left(\overline{X_1} - \overline{X_2}\right)}{\sqrt{\sigma_1 * \sigma_2}}$$

$$Scale\_Shift = v = \frac{\sigma_1}{\sigma_2}$$

$$\Pr ecision = r$$

$$Accuracy = A = \left(\frac{v + \frac{1}{v} + u^2}{2} \right)^{-1}$$

$$Concordance = r * A$$

The location shift is a standardized estimate of the difference between the two raters. The quantity in the denominator is the geometric mean of the two standard deviations. If there is no location difference between the two raters, this quantity is centered around zero. The scale shift is a ratio, if there is no scale shift this quantity is centered around one. If there is no location or scale shift then accuracy would be one. The concordance is then also bounded by one.

Finally, a t-test was used to compare slope and intercept from the robust regression: the slope from each method was compared to a slope of one and the intercept from each method was compared to an intercept of zero. An ideal slope of one or 45 degrees means that the value reported by the method and the reference value were identical. An intercept of zero ideally reflects no need for background correction.

For those variables that had no reference values (i.e., individual HDI oligomer species), methods were compared with each-other using Fisher and Belle (1993) criteria.

4.3. Results

Results are presented separately for those with a reference value and those without a reference value. Titration results are reported in Table 4.1 together with total NCO reported by HPLC. Although15.3% was the only titration value reported by the different laboratories, this value was chosen as the total hardener %NCO mass because titration assay is more reliable than HPLC.

Table 4.1. Percentage NCO and Content of Different Species in Hardener Sample based on Titration and HPLC Analysis

Method	Species	Modified NIOSH 5525	Modified OSHA 42/PV2034	Manufacturer
HPLC	% HDI	0.06		0.24
	% IPDI			0.25
	% HDI oligomers	64.7		47.9
	% IPDI oligomers	34.7		35.5
	% Total oligomers			
	%NCO	16 in the range15.8-16.2 n=4	15.85	
Titration	%NCO		15.3 n=2	
Unknown method	%NCO			16.0-17.2

4.3.1. Results for Variables with a Reference Value

For those variables with a reference value, reported data versus respective reference values were tabulated and graphed per variable (see Tables 4.1.2-4.1.7 and Figures 4.1.1-4.1.6). The slopes and correlations considered for analysis and comparison were obtained by using a robust regression and are tabulated in Table 4.2 (SPSS output for each robust regression is included n Appendix D.9). To further compare the methods, criteria of the different analytical methods based on the robust regression data were tabulated in Table 4.3. Lastly, results from the robust regression were used to establish how the methods compared using a t-test (Table 4.4).

Table 4.1.2. HDI Monomer Results

		Reference Value	ANALYTICAL RESULTS			
Sample ID	**Mass of product spiked on filter (µg/sample)**	**Calculated Mass of HDI spiked on filter[a] (µg/sample)**	**NIOSH HDI µg/sample**	**MS HDI µg/sample**	**OSHA HDI µg/sample**	**ISO-CHEK HDI µg/sample**
5	0	0	1x10$^{(-3)}$[i]	1.7x10$^{(-6)}$[i]	0.025[i]	0.0575[ii]
11	0	0	1x10$^{(-3)}$[i]	1.7x10$^{(-6)}$[i]	0.025[i]	0.0025[i]
13	0	0	1x10$^{(-3)}$[i]	1.7x10$^{(-6)}$[i]	0.025[i]	0.0575[ii]
4	1.17	0.003	0.0012	1.7x10$^{(-6)}$[i]	0.025[i]	0.0575[ii]
12	1.17	0.003	0.0026	1.7x10$^{(-6)}$[i]	0.025[i]	0.0575[ii]
17	1.17	0.003	0.0226	1.7x10$^{(-6)}$[i]	0.025[i]	0.0575[ii]
1	11.7	0.028	0.0246	0.012	0.025[i]	0.0575[ii]
9	11.7	0.028	0.012	0.012	0.025[i]	0.0575[ii]
18	11.7	0.028	1x10$^{(-3)}$[i]	0.012	0.025[i]	0.0575[ii]
2	93.3	0.224	0.0012	0.096	0.0743	0.0575[ii]
3	93.3	0.224	0.001	0.12	0.112	0.145
8	93.3	0.224	0.0014	0.13	0.0858	0.185
6	117	0.280	*	0.13	0.143	0.305
15	117	0.280	0.163	0.13	0.140	0.205
16	117	0.280	0.163	0.13	0.136	0.245
7	467	1.12	0.605	0.48	0.432	0.595
10	467	1.12	0.735	0.51	0.454	0.845
14	467	1.12	0.711	0.47	0.404	0.685

[a] Reference value derived from manufacturer's proprietary info (HDI content = 0.24% mass monomer/total mass bulk)

[i] Original data below LOD and substituted for LOD/2, as in Appendix D.7

[ii] Original data below LOQ and substituted for (LOD+LOQ)/2, as in Appendix D.7

*Sample spilled during shipping

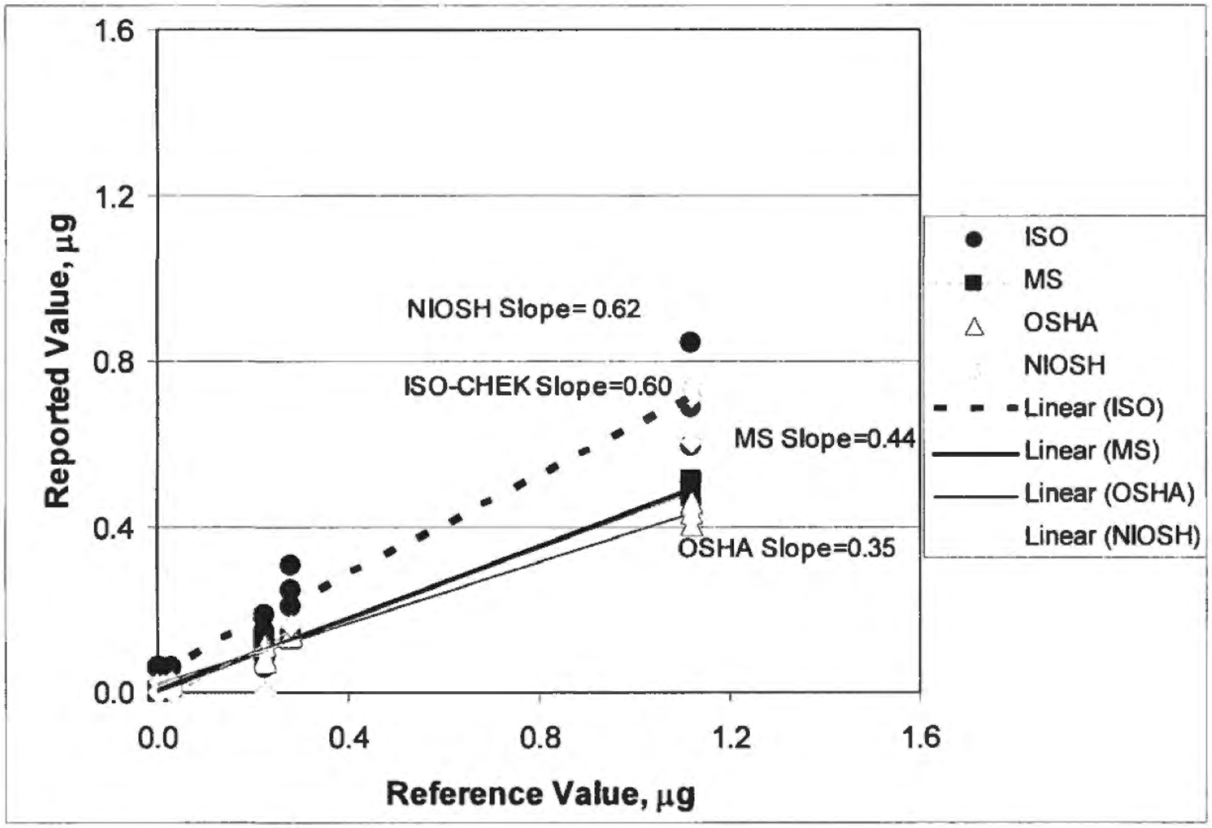


Figure 4.1.1. HDI Monomer Results Compared to Reference Value (Slopes from Robust Regression)

Table 4.1.3. IPDI Monomer Results

		Reference Value	**ANALYTICAL RESULTS**			
Sample ID	**Mass of product spiked on filter (µg/sample)**	**Calculated Mass of IPDI spiked on filter[a] (µg/sample)**	**NIOSH IPDI µg/sample**	**MS IPDI µg/sample**	**OSHA IPDI µg/sample**	**ISO-CHEK IPDI µg/sample**
5	0	0.	N/A	N/A	N/A	0.002[i]
11	0	0	N/A	N/A	N/A	0.067[ii]
13	0	0	N/A	N/A	N/A	0.002[i]
4	1.17	0.00292	N/A	N/A	N/A	0.002[i]
12	1.17	0.00292	N/A	N/A	N/A	0.002[i]
17	1.17	0.00292	N/A	N/A	N/A	0.002[i]
1	11.7	0.0292	N/A	N/A	N/A	0.067[ii]
9	11.7	0.0292	N/A	N/A	N/A	0.067[ii]
18	11.7	0.0292	N/A	N/A	N/A	0.002[i]
2	93.3	0.233	N/A	N/A	N/A	0.170
3	93.3	0.233	N/A	N/A	N/A	0.150
8	93.3	0.233	N/A	N/A	N/A	0.170
6	117	0.292	N/A	N/A	N/A	0.200
15	117	0.292	N/A	N/A	N/A	0.200
16	117	0.292	N/A	N/A	N/A	0.290
7	467	1.17	N/A	N/A	N/A	0.800
10	467	1.17	N/A	N/A	N/A	0.920
14	467	1.17	N/A	N/A	N/A	0.860

[a] Reference value derived from manufacturer's proprietary info (IPDI content = 0.25% mass monomer/total mass bulk)

[i] Original data below LOD and substituted for LOD/2, as in Appendix D.7

[ii] Original data below LOQ and substituted for (LOD+LOQ)/2, as in Appendix D.7

N/A: data were not provided

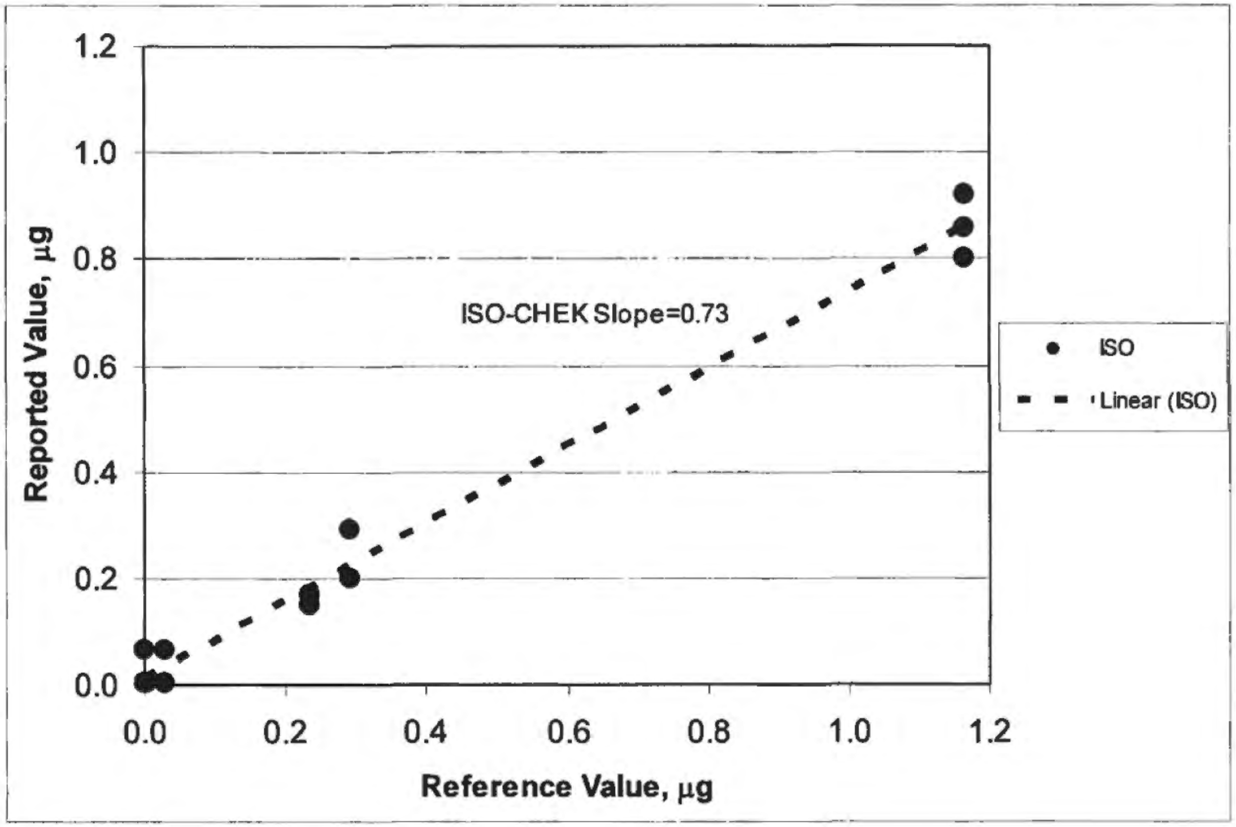


Figure 4.1.2. IPDI Monomer Results Compared to Reference Value (Slopes from Robust Regression)

Table 4.1.4. NCO-HDI Oligomers Results (NCO conversion/sum in D.8)

		Reference Value	**ANALYTICAL RESULTS**			
Sample ID	**NCO Mass of product spiked on filter (µg/sample)**	**Calculated Mass of NCO-HDI oligomers spiked on filter[a] (µg/sample)**	**NIOSH[b] NCO-HDI oligomers µg/sample**	**MS[c] NCO-HDI oligomers µg/sample**	**OSHA NCO-HDI oligomers µg/sample**	**ISO-CHEK[c] NCO-HDI oligomers µg/sample**
5	0	0	0.0025	$1.3\text{x}10^{(-5)}$	N/A	1.03
11	0	0	0.0025	0.0123	N/A	1.03
13	0	0	0.0025	$1.3\text{x}10^{(-5)}$	N/A	1.03
4	0.178	0.085	0.119	0.0361	N/A	1.03
12	0.178	0.085	0.106	0.0298	N/A	1.03
17	0.178	0.085	1.21	0.0283	N/A	1.03
1	1.78	0.855	1.02	0.272	N/A	2.30
9	1.78	0.855	1.11	0.281	N/A	2.46
18	1.78	0.855	0.0760	0.291	N/A	2.67
2	14.3	6.84	0.113	1.73	N/A	14.6
3	14.3	6.84	0.113	2.09	N/A	14.81
8	14.3	6.84	0.115	2.16	N/A	15.3
6	17.8	8.55	*	2.39	N/A	18.5
15	17.8	8.55	12.5	2.47	N/A	22.6
16	17.8	8.55	9.18	2.44	N/A	21.6
7	71.4	34.2	34.3	7.43	N/A	74.7
10	71.4	34.2	34.5	8.45	N/A	83.9
14	71.4	34.2	39.5	7.71	N/A	87.2

[a] Reference value derived from manufacturer's proprietary info (HDI oligomer content = 47.9% mass oligomer/total mass bulk) and titration results (Total NCO Mass = Total Mass * 0.153; overall bulk samples has 15.3% NCO (w/w))
[b] Method quantified all possible oligomers present
[c] Method quantified 3 oligomers: isocyanurate, uretidone, and biuret
*Sample spilled during shipping
N/A: data were not provided

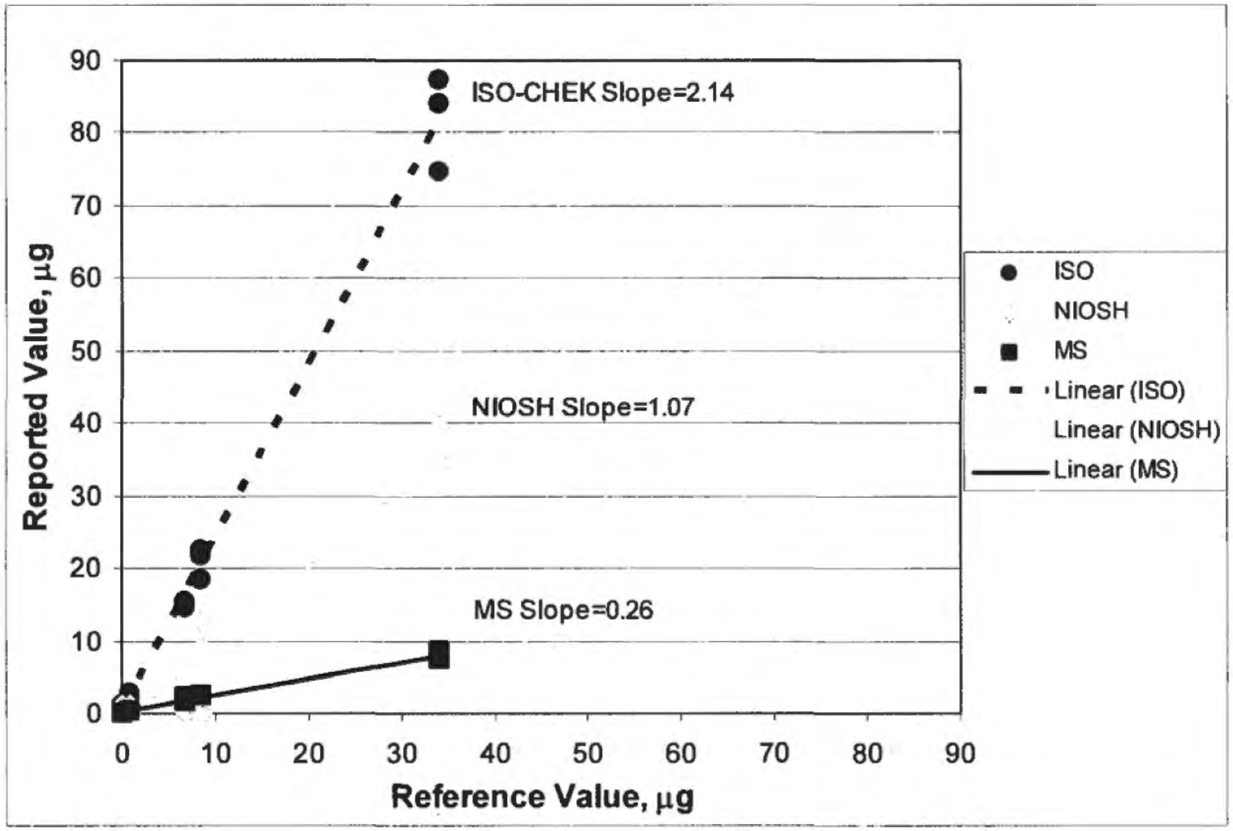


Figure 4.1.3. NCO-HDI Oligomers Results Compared to Reference Value (Slopes from Robust Regression)

Table 4.1.5. NCO-IPDI Oligomer Results (NCO conversion is detailed in Appendix D.8)

		Reference Value	**ANALYTICAL RESULTS**			
Sample ID	**NCO Mass of product spiked on filter (µg/sample)**	**Calculated Mass of NCO-IPDI oligomers spiked on filter[a] (µg/sample)**	**NIOSH NCO-IPDI oligomers µg/sample**	**MS NCO-IPDI oligomers µg/sample**	**OSHA NCO-IPDI oligomers µg/sample**	**ISO-CHEK NCO-IPDI oligomers µg/sample**
5	0	0	0.0025[i]	N/A	N/A	0.147[i]
11	0	0	0.0025[i]	N/A	N/A	0.147[i]
13	0	0	0.0025[i]	N/A	N/A	0.147[i]
4	0.178	0.0633	0.062	N/A	N/A	0.147[i]
12	0.178	0.0633	0.069	N/A	N/A	0.147[i]
17	0.178	0.0633	0.62	N/A	N/A	0.147[i]
1	1.78	0.633	0.572	N/A	N/A	1.50[ii]
9	1.78	0.633	0.58	N/A	N/A	0.70
18	1.78	0.633	0.040	N/A	N/A	0.629
2	14.3	5.07	0.062	N/A	N/A	3.79
3	14.3	5.07	0.050	N/A	N/A	4.05
8	14.3	5.07	0.075	N/A	N/A	4.56
6	17.8	6.33	*	N/A	N/A	4.93
15	17.8	6.33	5.73	N/A	N/A	6.48
16	17.8	6.33	4.89	N/A	N/A	5.79
7	71.4	25.3	17.3	N/A	N/A	19.8
10	71.4	25.3	18.0	N/A	N/A	21.7
14	71.4	25.3	21.1	N/A	N/A	22.4

[a] Reference value derived from manufacturer's proprietary info (IPDI oligomer content = 35.5% mass oligomer/total mass bulk) and titration results (Total NCO Mass = Total Mass * 0.153; overall bulk samples has 15.3% NCO (w/w))

[i] Original data below LOD and substituted for LOD/2, as in Appendix D.7

[ii] Original data below LOQ and substituted for (LOD+LOQ)/2, as in Appendix D.7

*Sample spilled during shipping

N/A: data were not provided

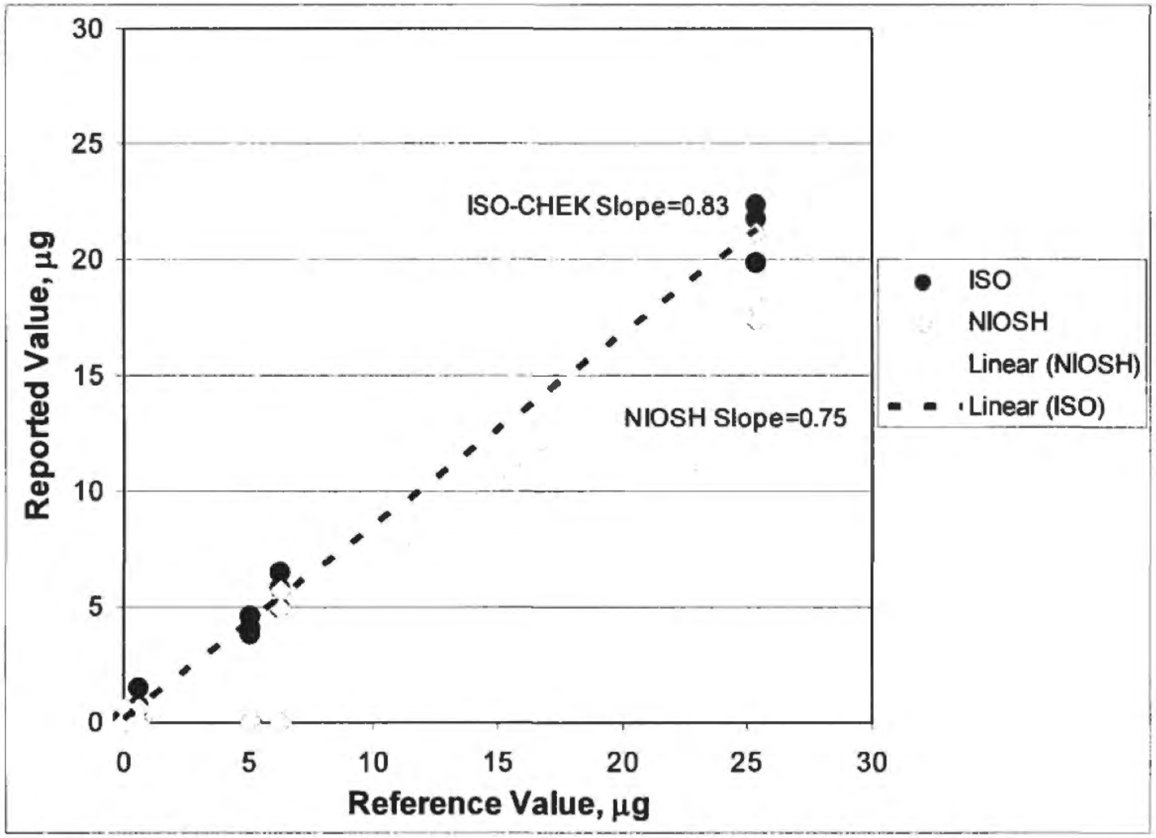


Figure 4.1.4. NCO-IPDI Oligomer Results Compared to Reference Value (Slopes from Robust Regression)

Table 4.1.6. NCO- HDI and IPDI Oligomer Results

		Reference Value	ANALYTICAL RESULTS			
Sample ID	NCO Mass of product spiked on filter (µg/sample)	Calculated Mass of NCO oligomers spiked on filter[a] (µg/sample)	NIOSH[b] Total NCO oligomers µg/sample	MS Total NCO oligomers µg/sample	OSHA[b] Total NCO oligomers µg/sample	ISO[c] Total NCO oligomers µg/sample
5	0	0	0.005	N/A	0.15	1.19
11	0	0	0.005	N/A	0.15	1.19
13	0	0	0.005	N/A	0.15	1.19
4	0.178	0.149	0.181	N/A	0.350	1.19
12	0.178	0.149	0.175	N/A	0.15	1.19
17	0.178	0.149	1.83	N/A	0.15	1.19
1	1.78	1.49	1.59	N/A	1.16	3.82
9	1.78	1.49	1.69	N/A	1.20	3.18
18	1.78	1.49	0.116	N/A	1.22	3.32
2	14.3	11.9	0.175	N/A	4.70	18.5
3	14.3	11.9	0.163	N/A	8.76	18.9
8	14.3	11.9	0.19	N/A	5.87	19.9
6	17.8	14.9	*	N/A	11.69	23.4
15	17.8	14.9	18.2	N/A	13.39	29.0
16	17.8	14.9	14.1	N/A	13.99	27.5
7	71.4	59.5	51.6	N/A	58.8	94.3
10	71.4	59.5	52.5	N/A	57.1	106
14	71.4	59.5	60.6	N/A	57.3	109

[a] Reference value derived from manufacturer's proprietary info (IPDI oligomer content = 35.5% mass oligomer/total mass bulk & HDI oligomer content = 47.9% mass oligomer/total mass bulk; so total oligomer based on manufacturer = 35.5 + 47.9 = 83.4%)

[b] Method quantified all possible HDI and IPDI oligomers present

[c] Method quantified 3 HDI oligomers: isocyanurate, uretidone, and biuret, and IPDI oligomer

*Sample spilled during shipping

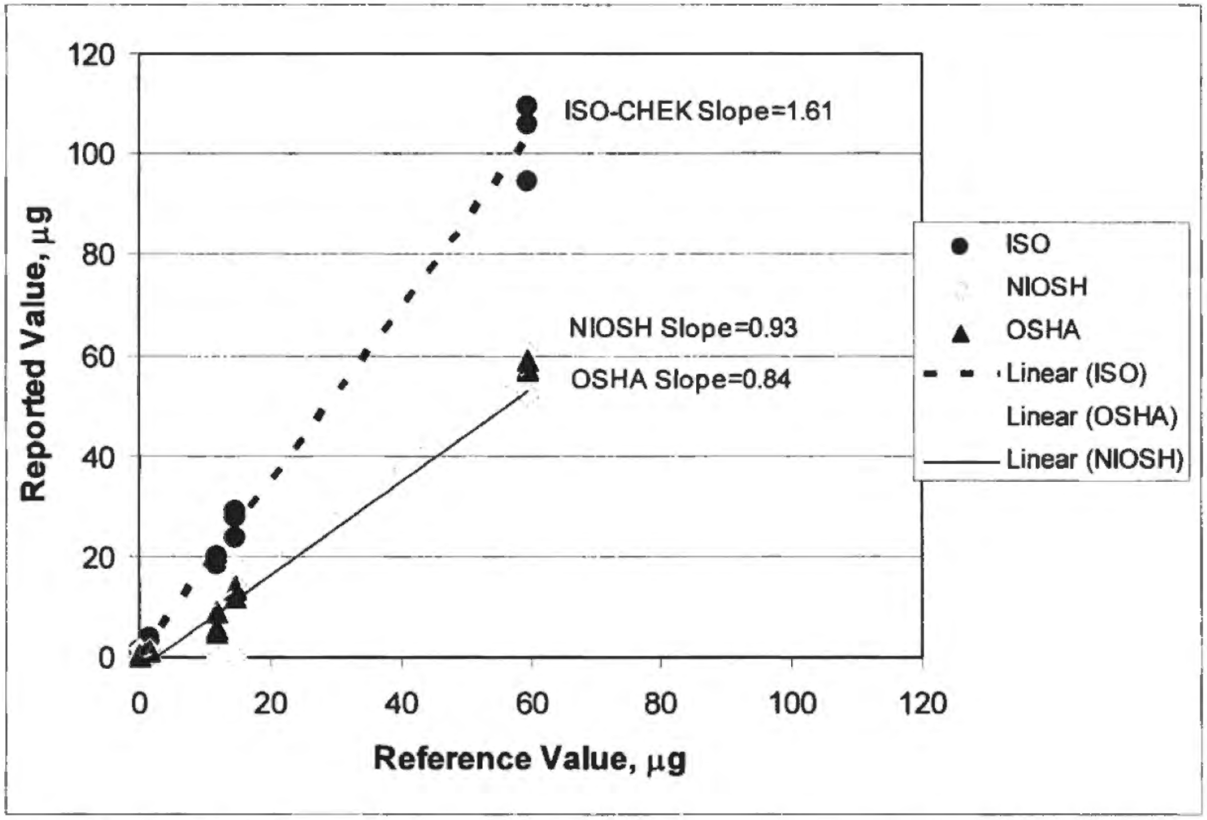


Figure 4.1.5. NCO- HDI and IPDI Oligomers Results Compared to Reference Value (Slopes from Robust Regression)

Table 4.1.7. Total Isocyanate Mass – HDI monomer, HDI oligomers, IPDI monomer, and IPDI oligomers– Results

	Reference Value	**ANALYTICAL RESULTS**			
Sample ID	**Mass of product spiked on filter[a] (µg/sample)**	**NIOSH[b] Total mass µg/sample**	**MS Total mass µg/sample**	**OSHA[b] Total mass µg/sample**	**ISO-CHEK Total mass µg/sample**
5	0	0.0359	N/A	1.06	5.76
11	0	0.0359	N/A	1.06	5.77
13	0	0.0359	N/A	1.06	5.76
4	1.17	1.19	N/A	2.37	5.76
12	1.17	1.15	N/A	1.06	5.76
17	1.17	12.03	N/A	1.06	5.76
1	11.7	10.5	N/A	7.68	19.5
9	11.7	11.1	N/A	7.96	15.6
18	11.7	0.761	N/A	8.09	16.1
2	93.3	1.15	N/A	30.9	89.9
3	93.3	1.07	N/A	57.6	92.3
8	93.3	1.24	N/A	38.6	97.7
6	117	*	N/A	76.8	115
15	117	120	N/A	87.9	142
16	117	92.5	N/A	91.9	134
7	467	339	N/A	386	461
10	467	346	N/A	375	515
14	467	398	N/A	376	534

[a] Reference value directly derived from known spiked levels
[b] Method did not quantify IPDI monomer
*Sample spilled during shipping

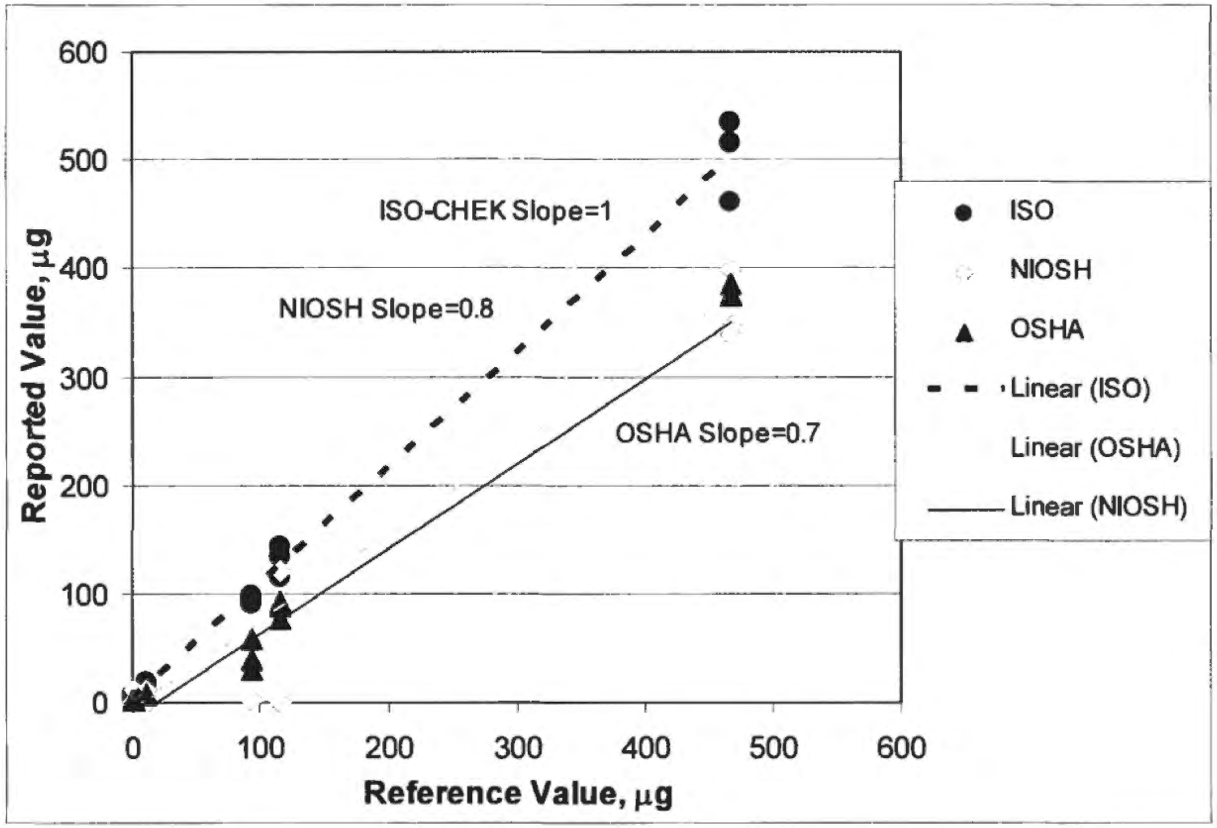


Figure 4.1.6. Total Isocyanate Mass – HDI monomer, HDI oligomers, IPDI monomer, and IPDI oligomers – Results Compared to Reference Value (Slopes from Robust Regression)

Table 4.2. Robust Regression Analysis

		Model Summary		Coefficients			
Analyte	**Method**	**R Square**	**Std. Error**	**Intercept**	**Std. Error**	**Slope**	**Std. Error**
HDI Monomer	NIOSH	0.950	0.061	-0.0260	0.0180	0.6170	0.0360
	MS	0.994	0.022	-0.0006	0.0003	0.4430	0.0088
	OSHA	0.958	0.086	0.0212	0.0018	0.3525	0.0184
	ISO-CHEK	0.918	0.095	0.0301	0.0122	0.5971	0.0445
IPDI Monomer	ISO-CHEK	0.977	0.062	0.0017	0.0051	0.7340	0.0280
NCO-HDI Oligomers	NIOSHa	0.947	3.323	-1.0920	0.9750	1.0670	0.0650
	MS[b]	0.977	0.142	0.0110	0.0015	0.2640	0.0109
	ISO-CHEK[b]	0.980	0.106	0.9350	0.0446	2.1400	0.0761
NCO-IPDI Oligomers	NIOSH	0.946	1.741	-0.6040	0.5110	0.7500	0.0460
	ISO-CHEK	0.976	0.204	0.1250	0.0196	0.8350	0.0327
NCO- HDI and IPDI Oligomers	NIOSH	0.947	5.049	-1.6960	1.4820	0.9320	0.0570
	OSHA	0.971	0.900	0.0590	0.1450	0.8430	0.0520
	ISO-CHEK	0.984	0.096	1.0730	0.0464	1.6070	0.0505
Total Isocyanate Mass: HDI monomer, HDI oligomers, IPDI monomer and IPDI oligomers	NIOSH[c]	0.947	33.171	-11.1710	9.7340	0.7820	0.0480
	OSHA[c]	0.944	2.469	0.4430	0.9820	0.7060	0.0430
	ISO-CHEK	0.983	0.099	5.1650	0.2310	1.0050	0.0330

[a] Method quantified all possible HDI oligomers

[b] Method quantified 3 HDI oligomers: isocyanurate, uretidone, and biuret

[c] Method did not quantify IPDI monomer

Table 4.3. Comparison of Reported Values to Reference Values Based on the Robust Regression Data

		u	v	A	rA	CV	Precision
Analyte	Lab	Location Shift	Scale Shift	Accuracy	Concordance	RMS/Mean Reference Value	r
HDI Monomer	NIOSH	0.403	1.532	0.852	0.831	0.221	0.975
	MS	0.569	2.298	0.654	0.652	0.080	0.997
	OSHA	0.624	2.720	0.575	0.563	0.312	0.979
	ISO-CHEK	0.216	1.631	0.873	0.836	0.345	0.958
IPDI Monomer	ISO-CHEK	0.184	1.370	0.937	0.926	0.216	0.988
NCO-HDI Oligomers	NIOSH[a]	0.041	0.885	0.992	0.965	0.395	0.973
	MS[b]	1.068	4.356	0.349	0.345	0.017	0.988
	ISO-CHEK[b]	-0.628	0.419	0.625	0.619	0.013	0.990
NCO-IPDI Oligomers	NIOSH	0.266	1.258	0.942	0.916	0.279	0.973
	ISO-CHEK	0.100	1.197	0.979	0.967	0.033	0.988
NCO- HDI and IPDI Oligomers	NIOSH	0.127	1.013	0.992	0.965	0.344	0.973
	OSHA	0.072	1.020	0.997	0.983	0.061	0.985
	ISO-CHEK	-0.394	0.580	0.813	0.806	0.007	0.992
Total Isocyanate Mass[c]	NIOSH[d]	0.717	1.462	0.752	0.732	0.071	0.973
	OSHA[d]	0.747	1.937	0.664	0.642	0.005	0.967
	ISO-CHEK	-0.560	0.912	0.861	0.854	0.000	0.991

[a] Method quantified all possible HDI oligomers

[b] Method quantified 3 HDI oligomers: isocyanurate, uretidone, and biuret

[c] Total Isocyanate Mass includes HDI monomer, HDI oligomers, IPDI monomer, and IPDI oligomers

[d] Method did not quantify IPDI monomer

From Table 4.2 it is evident from the high R Square (>0.9) that all methods reported data with small scatter. Note that the standard error reported in the estimate of the R Square was higher in some instances (e.g. NIOSH had high standard error for all analytes except the HDI monomer). The high standard error for the R Square could be minimized by subtracting possible outliers, which could be identified by techniques such as the general F test (Afifi *et al.* 2004), Chauvenet's criterion (Taylor 1982) or the Q-test (Shoemaker *et al.* 1974). In order to understand performance of a particular method compared to the reference values, it is important to consider the intercept and slope in the right side of Table 4.2. The intercept results from the robust regression of the different methods (Table 4.2) revealed that the total isocyanate results have both extremes: NIOSH has a large negative value (-11.2) while ISO-CHEK has a very high value (5.2). Slopes are graphically represented for each analyte in Figures 1.1-1.6.

HDI monomer results presented by the different methods were comparable; NIOSH and ISO-CHEK reported the highest slopes (Table 4.1.2 and Figure 4.1.1 and Table 4.2). IPDI monomer results were only reported by the ISO-CHEK method and were in reasonable agreement (73%) with the reference value (slope of 0.73). When comparing NCO-HDI oligomer data (Table 4.1.3 and Figure 4.1.2 and Table 4.2), the MS method appeared to underestimate oligomer concentrations compared to the reference value (slope of 0.23). The ISO-CHEK method tended to over estimate oligomer concentrations (slope of 2.4), while the NIOSH method predicted the same values as the reference values (slope of 1.07). NCO-IPDI oligomers reported by NIOSH and ISO-CHEK methods were fairly close to the reference values (slope of 0.75 and 0.84 respectively). For total NCO oligomers, the ISO-CHEK method had the highest slope (1.6), MS had the lowest slope (0.15), and NIOSH and OSHA had slopes close to the reference values (0.93 and 0.84 respectively). Finally, total isocyanate mass reported by the ISO-CHEK method was close to the reference values.

Table 4.3 provides performance criteria for the different methods using the robust regression data from Table 4.2. Data accuracy is a reflection of location shift (standardized estimate of difference between means) and scale shift (estimate of the variability). If there is no location or scale shift, accuracy will be 1. The accuracy trends for results submitted by OSHA and ISO-CHEK ranged in accuracy from 0.6 to 1.0 with no significant intra-method trends at either method. Results from NIOSH data did show an intra-method trend of very low accuracy for NIOSH monomer results (0.2) compared to the very high accuracy of NIOSH oligomer results (ranged 0.9 to 1.0). Conversely, the MS intra-method data showed relatively high accuracy for the MS monomer results (0.7) compared to lower accuracy of MS oligomer results (range 0.1 to 0.3). Within the MS data, 3 out of the 4 analytes (75%) had location shifts greater than 1.0 and scale shifts greater than 4.0; no other method had large location and scale shifts this frequently. The high r values and low CV of the spiked levels showed that all methods reported data with high precision.

Table 4.4 provides information on how significantly different the robust regression slope was from 1. P-values higher than 0.05 gave certainty that reported values were close to reference values. For example, slopes for NIOSH and OSHA NCO oligomer were non-significantly different than 1 (0.9 and 0.8 respectively), this is reflected in the not significant numbers ($p>0.05$), which means that these methods reported data that was closest to the reference values. Table 4.4 also presents how significantly different the robust regression intercept was to 0. P-values lower than 0.05 give certainty that background levels are close to zero. For example, the intercept for total isocyanate mass for the ISO-CHEK method is not significant (p-value of 0.77), which means that background was not zero, as shown in Table 4.2.

Table 4.4. Comparing Slopes and Intercepts Among Methods - T-test Versus Slope of One and Intercept of Zero

			T test for Slope versus Slope of 1		T test for Intercept versus Intercept of 0	
		Degrees of freedom		two-tailed		two-tailed
			Slope 1	95% CI	Intercept 0	95% CI
Analyte	**Lab**	**n-2**	**T**	**p-value**	**T**	**p-value**
HDI Monomer	NIOSH	15	-10.6389	0.0000	-1.4444	0.1704
	MS	16	-63.1519	0.0000	-1.9091	0.0744
	OSHA	16	-35.1897	0.0000	11.6066	0.0000
	ISO-CHEK	16	-9.0546	0.0000	2.4644	0.0254
IPDI Monomer	ISO-CHEK	16	-9.5000	0.0000	0.3379	0.7398
NCO-HDI Oligomers	NIOSH	15	1.0308	0.3190	-1.1200	0.2803
	MS	16	-67.8341	0.0000	7.4830	0.0000
	ISO-CHEK	16	14.9803	0.0000	20.9453	0.0000
NCO-IPDI Oligomers	NIOSH	15	-5.4348	0.0001	-1.1820	0.2556
	ISO-CHEK	16	-5.0412	0.0001	6.3906	0.0000
NCO- HDI and IPDI Oligomers	NIOSH	15	-1.1930	0.2518	-1.1444	0.2706
	OSHA	16	-3.0192	0.0082	0.4069	0.6895
	ISO-CHEK	16	12.0150	0.0000	23.1250	0.0000
Total Isocyanate Mass[a]	NIOSH	15	-4.5417	0.0004	-1.1476	0.2693
	OSHA	16	-6.2766	0.0000	0.4575	0.0111
	ISO-CHEK	16	0.0050	0.0118	22.3593	0.7650

[a] Total Isocyanate Mass includes HDI monomer, HDI oligomers, IPDI monomer, and IPDI oligomers

4.3.2. Results for Variables with No Reference Value

For those variables with no reference value (i.e., individual HDI oligomer species), data were tabulated in Table 4.5.1-4.5.4. To further compare the methods, means and standard deviations for each method were tabulated in Table 4.6. Table 4.6 also compiles criteria for the different analytical methods based on Spearman's correlation data among isocyanate analytical methods. High location and scale shifts showed up when method MS was compared to other methods. Inter-method agreement for isocyanurate was consistently high (>0.7) when comparing all reporting methods with each other. However, inter-method accuracies were lowest for uretidone. It was not surprising that the uretidone accuracies for the ISO-CHEK method were low because the method predicts an unexplained bias. Inter-method accuracies were lowest when comparing MS and ISO-CHEK methods; the MS tends to underestimate compared to the NIOSH method and the ISO-CHEK tends to overestimate compared to the NIOSH method.

Table 4.5.1. HDI Isocyanurate Results

Sample	**HDI isocyanurate µg/sample**			
ID	**NIOSH**	**MS**	**OSHA**	**ISO-CHEK**
5	0.0116	2x10$^{(-5)}$[i]	N/A	2.5[ii]
11	0.0025[i]	0.0570	N/A	2.5[ii]
13	0.0116	2x10$^{(-5)}$[i]	N/A	2.5[ii]
4	0.0891	0.099	N/A	2.5[ii]
12	0.108	0.096	N/A	2.5[ii]
17	1.06	0.088	N/A	2.5[ii]
1	0.951	0.93	N/A	2.5[ii]
9	0.997	0.95	N/A	2.4
18	0.0747	0.98	N/A	2.5
2	0.0922	6.3	N/A	10.7
3	0.0933	7.6	N/A	10.4
8	0.102	6.7	N/A	10.7
6	*	8.7	N/A	13.1
15	10.3	8.9	N/A	14.7
16	8.79	8.8	N/A	14.3
7	27.8	26	N/A	52.7
10	31.1	29	N/A	54.4
14	38.7	27	N/A	55.1

[i] Original data below LOD and substituted for LOD/2, as in Appendix D.7

[ii] Original data below LOQ and substituted for (LOD+LOQ)/2, as in Appendix D.7

*Sample spilled during shipping

Table 4.5.2. HDI Uretidone Results

Sample	**HDI uretidone µg/sample**			
ID	**NIOSH**	**MS**	**OSHA**	**ISO-CHEK**
5	0.0116	$1.97x10^{(-5)}$[i]	N/A	1.4[i]
11	0.0116	$1.97x10^{(-5)}$[i]	N/A	1.4[i]
13	0.0116	$1.97x10^{(-5)}$[i]	N/A	1.4[i]
4	0.154	0.068	N/A	1.4[i]
12	0.146	0.042	N/A	1.4[i]
17	1.539	0.043	N/A	1.4[i]
1	2.02	0.26	N/A	7.25
9	1.35	0.28	N/A	8.1
18	0.0116	0.31	N/A	9
2	0.158	1.3	N/A	56.1
3	0.157	1.6	N/A	57.2
8	0.146	2.9	N/A	59.3
6	*	1.8	N/A	71.5
15	1.24	1.9	N/A	87.6
16	17.0	1.9	N/A	83.4
7	55.6	5.9	N/A	291
10	67.4	7.2	N/A	324
14	82.2	6.2	N/A	337

[i] Original data below LOD and substituted for LOD/2, as in Appendix D.7

*Sample spilled during shipping

Table 4.5.3. HDI Biuret Results

Sample	HDI biuret µg/sample			
ID	NIOSH	MS	OSHA	ISO-CHEK
5	0.0114	$2.02\text{x}10^{(-5)}$[i]	N/A	0.85[i]
11	0.0114	$2.02\text{x}10^{(-5)}$[i]	N/A	0.85[i]
13	0.0114	$2.02\text{x}10^{(-5)}$[i]	N/A	0.85[i]
4	0.0114	$2.02\text{x}10^{(-5)}$[i]	N/A	0.85[i]
12	0.0114	$2.02\text{x}10^{(-5)}$[i]	N/A	0.85[i]
17	0.111	$2.02\text{x}10^{(-5)}$[i]	N/A	0.85[i]
1	0.169	0.069	N/A	0.85[i]
9	0.0791	0.069	N/A	0.85[i]
18	0.0114	0.058	N/A	0.85[i]
2	0.0114	0.41	N/A	0.85[i]
3	0.0114	0.51	N/A	0.85[i]
8	0.0114	0.41	N/A	0.85[i]
6	*	0.59	N/A	0.85[i]
15	0.165	0.63	N/A	2
16	1.63	0.62	N/A	2.7
7	6.24	2.5	N/A	1.8[ii]
10	5.91	2.9	N/A	10.2
14	7.69	2.5	N/A	10.8

[i] Original data below LOD and substituted for LOD/2, as in Appendix D.7

[ii] Original data below LOQ and substituted for (LOD+LOQ)/2, as in Appendix D.7

*Sample spilled during shipping

Table 4.5.4. Sum of Isocyanurate, Uretidone, and Biuret HDI Oligomers Results

Sample	Sum HDI Oligomers µg/sample			
ID	**NIOSH**	**MS**	**OSHA**	**ISO-CHEK**
5	0.0345	0.0001	N/A	4.75
11	0.0229	0.0570	N/A	4.75
13	0.0345	0.0001	N/A	4.75
4	0.255	0.167	N/A	4.75
12	0.265	0.138	N/A	4.75
17	2.71	0.131	N/A	4.75
1	3.14	1.26	N/A	10.6
9	2.42	1.30	N/A	11.4
18	0.0976	1.35	N/A	12.4
2	0.262	8.01	N/A	67.7
3	0.261	9.71	N/A	68.5
8	0.260	10.0	N/A	70.9
6	*	11.1	N/A	85.5
15	11.7	11.4	N/A	104
16	27.4	11.3	N/A	100
7	89.7	34.4	N/A	345
10	104	39.1	N/A	388
14	129	35.7	N/A	403

*Sample spilled during shipping

Table 4.6. HDI Oligomers Comparison of Different Analytical Methods

HDI Oligomer	Method 1	Method 2	u Location Shift	v Scale Shift	r Precision	A Accuracy	rA Concordance
Isocyanurate	NIOSH	MS	-0.0238	1.2865	0.7770	0.9688	0.7528
	NIOSH	ISO-CHEK	-0.4709	0.6726	0.6560	0.8399	0.5510
	MS	ISO-CHEK	-0.5146	0.5228	0.8790	0.7407	0.6510
Uretidone	NIOSH	MS	1.4781	11.5384	0.7236	0.1448	0.1048
	NIOSH	ISO-CHEK	-1.1556	0.2347	0.6976	0.3430	0.2393
	MS	ISO-CHEK	-4.6415	0.0203	0.9685	0.0283	0.0274
Biuret	NIOSH	MS	-0.2982	2.6992	0.7094	0.6320	0.4492
	NIOSH	ISO-CHEK	-0.2982	0.8374	0.8282	0.9432	0.7811
	MS	ISO-CHEK	-0.8814	0.3102	0.7875	0.4640	0.3654
Sum HDI Oligomers	NIOSH	MS	0.5163	3.2033	0.9386	0.5288	0.4964
	NIOSH	ISO-CHEK	-0.9572	0.3089	0.9712	0.4482	0.4353
	MS	ISO-CHEK	-2.0002	0.0964	0.9928	0.1383	0.1373

4.4. Discussion

4.4.1. Study Challenges and Limitations

Before comparing methods, it is important to emphasize that estimates (or reference values) of the filter loadings were based on the manufacturer's specifications. Ideally, the manufacturer could have supplied specifications within a specified error, but unfortunately error information was not provided. In addition, manufacturer did not provide reference values for individual oligomers. When MS and ISO-CHEK methods reported HDI oligomers, they only included isocyanurate, uretidone, and biuret whereas NIOSH method reported both individual oligomers and total HDI oligomers. It is important to consider this when evaluating the results from the robust regression in the first result section. A comparison for the HDI oligomers that reflects the individual especie performances was presented in the second section of the results (Tables 4.5.4 and 4.6). However, it was important to still provide a comparison in regards to the reference values, like that presented in the first section.

The comparison of total HDI oligomers was also conducted because the isocyanurate, uretidone, and biuret HDI oligomer have been reported as major constituents in hardeners during the Yale study (Bello *et al.* 2002). Bello *et al.* (2002) reported that many shops surveyed, used many different products. Although products varied in their constituents, these three HDI oligomer compounds appeared to be the major HDI-based components (many products also contained IPDI-based components). For the aliphatic bulk isocyanate products (such as Bayer N100, Bayer 3300, and Bayer 3400) typically used as the basis of the final paints used in the shops, the NIOSH method accounted for the vast majority of isocyanate determined to be present by titration of the product. In the chromatograms, the HDI-biuret and HDI-isocyanurate were the two most common species. The HDI-dimer (uretidone) was also frequently a major constituent (Bello *et al.* 2002).

Some methods reported data as mass of isocyanate species per sample while other methods reported data in NCO-mass. The difference in reporting units can present a challenge, especially when comparing data from different bulk hardener sources, as is the case with field exposure assessments. To compare data in a consistent manner, it was essential to have the %NCO information from the titration of the bulk hardener to allow conversion from mass to NCO-mass, and vice versa. This approach would be increasingly difficult to achieve when comparing samples originating from bulk hardeners with different isocyanate contents. For this report, NCO conversion factors were used (Appendix D.8); however, there were cases in which mass was not associated with particular species. For example, the NIOSH HDI oligomers data reported in NCO-mass were not converted directly to mass because there is no conversion factor for total oligomers. An effective molecular weight of the formulation can form the basis of these conversions, but information on the specific species included in the oligomeric mix would be needed. Further, only 83% of the species in the hardener were reported by the manufacturer as HDI or IPDI-derived, so the remaining 17% isocyanates may not be HDI or IPDI isocyanate forms.

When comparing analytical methods, the derivatization reagent is an important variable that must be considered. However, this study was not designed to try to elucidate specific advantages of a derivatization reagent. The analysis results for a particular derivatization reagent are also influenced by the instrument, chromatography, standards, and many other variables of the method. As an illustration, note that both the MS and ISO-CHEK methods used 2-MP as their derivatization reagent; however, the HDI oligomer results reported were significantly different from each-other. These differences are most likely due to the use of different standards and detectors, rather than the derivatization reagent.

4.4.2. Method Performance

Methods had low scatter (R Square higher than 0.9 in Table 4.2) when compared to reference values by using a robust regression. However, the high standard error of the R Square estimate pointed to the existence of possible outliers, as was the case for NIOSH and OSHA methods. Most methods performed well (accuracy higher than 0.5 in Table 4.3) with the exception of MS method for HDI oligomer (accuracy of 0.3 in Table 4.3). All methods underestimated HDI monomer concentrations compared to the manufacturer's data, although the possibility cannot be excluded that the HDI monomer percentages provided by the manufacturer may be overestimates. Alternatively, the manufacturer's information may be correct, but a fraction of the relatively volatile and reactive monomer may have either evaporated in the dilution of the spikes or reacted with any moisture during storage of the container or transfer of the bulk material. The HDI data derived from the NIOSH and ISO-CHEK methods were the closest to the reference values (slope of 0.61 and 0.6 respectively, Table 4.2).

When comparing data for HDI oligomers, the NIOSH method outperformed other methods. NIOSH slope of 1 in Table 4.2 indicates that NIOSH measured exactly what was expected based on manufacturer data. The MS method appeared to underestimate HDI oligomer concentrations (slope of 0.26, Table 4.2), while the ISO-CHEK method overestimated HDI oligomer concentrations (slope of 2.14, Table 4.2) when compared to the reference values. Manufacturer-provided data suggested that approximately 50% of the sample was a sum of HDI monomer and HDI oligomers. However, it is important to note that the MS and ISO-CHEK methods only measured specifically for three HDI oligomers. Further, the MS method does not use bulk samples to quantitate these oligomers, unlike the ISO-CHEK method, but instead purified standards. It is possible that the bulk materials provided higher responses with the ISO-CHEK method due to intrinsic impurities.

When comparing methods for the particular HDI oligomer species, the MS method is also consistently low compared the other methods for uretidone and biuret (see low accuracy values in Table 4.6). Results for NIOSH and ISO-CHEK method were comparable for biuret and isocyanurate (accuracy above 0.8 in Table 4.6) while results for uretidone are significantly higher for the ISO-CHEK method reflected in the low accuracy (0.3 in Table 4.6). This was not surprising since the ISO-CHEK method anticipated a bias for that particular oligomer based on that reported by the method. The response by the NIOSH and ISO-CHEK methods for biuret and isocyanurate are fairly similar even though the NIOSH method is calculating from monomer calibrations and the ISO-CHEK method from bulk material calibrations.

As for IPDI oligomers, both NIOSH and ISO-CHEK methods performed fairly well (slopes of 0.75 and 0.83 respectively in Table 4.2). The ISO-CHEK method overestimated the sum of HDI and IPDI oligomers (slope of 1.6 in Table 4.2) which is not surprising because HDI oligomers were overestimated. Overall, it seems that among the HDI and IPDI oligomers, the ISO-CHEK is highest for uretidone, which was expected because of the method reported bias. If a correction for the bias was included, the uretidone values would decrease such that the sum of NCO mass for HDI oligomers would also decrease. A robust regression for the corrected NCO HDI oligomers for the ISO-CHEK method would provide a slope of 1.4, wich is considerably lower than the 2.1 slope for the uncorrected data.

The total isocyanate mass was not reported for the MS method since this method only identified HDI monomer and HDI oligomers, unlike the other methods. The closest to the reference value was the ISO-CHEK method (slope of 1 in Table 4.2). It seems that the low slopes on the monomers and IPDI oligomers off set the overall overestimation of the method due to the HDI oligomers.

One possible reason for the MS method's underestimation of HDI oligomers was the presence of prepolymers in the hardener. Use of prepolymers is increasing in the polyurethane industry; they are formed by partially reacting monomers with alcohols. Prepolymers would likely be quantified as oligomers if HPLC-UV or other less specific detectors were used; this error would be less likely when using LC-MS. This problem would not affect the HDI monomer analysis, which explains why MS's monomer results were comparable to the other methods. Another possible explanation for the low response given by the MS method was the presence of ion suppression. Suppression of analyte ionization by co-eluting compounds is a well-known phenomena in LC-MS(-MS) analysis, mainly depending on the sample matrix, sample preparation procedure, quality of chromatographic separation, mobile-phase additives and ionization type (Polettini 2006). Lastly, the use of highly purified standards may play a role in the different response among methods. It would be hard to determine which standards are best because there is no gold standards to which compare them with just yet. It is plausible that what the MS method is measuring is accurate but since we don't have information from the manufacturer specific to the HDI oligomer species in the hardener, it would be difficult to answer this question without further validation of the MS method.

The MS method was extremely sensitive (lowest LOD and LOQ of all methods, see Appendix D.6) and reproducible (high precision). These characteristics make the MS method ideal for trace analysis (Fent el al, 2008) particularly because it is not certain that the differences with the other methods would be the same at the nano-gram to pico-gram level. The advantage of quantification of specific isocyanate species by MS relates to the importance of understanding further the exposure pathways and associated health effects, including asthma. Since mechanism of isocyanate-induced sensitization is unknown, and the physical and chemical properties of isocyanates vary considerably, speciation may be the only way to derive proper control measures.

Overestimation of HDI oligomers by the ISO-CHEK method could be explained by the possible existence of interferences that can be picked up with the UV detection. An alternate explanation is that the ISO-CHEK method uses standards derived from bulk samples for the particular HDI oligomers and the purity of the set of standards may have affected the detector's response. This was different for the NIOSH and OSHA methods that rely on a single-monomer standard calibration. Further, the ISO-CHEK method exhibited consistently high number of below threshold values and high positive intercepts in the robust regression that are mostly attributed to the very high LOQs.

England *et al.* (2000) compared different methods for HDI monomer and oligomers during spray finishing operations, including OSHA 42, NIOSH 5525 (MAP method), and the ISO-CHEK method. The OSHA 42 only measured monomer in this comparison and it agreed fairly well with the other methods, which agrees with our results. The NIOSH 5525 and the ISO-CHEK measured HDI oligomers by using the monomer as standard. NIOSH and ISO-CHEK methods compared favorably but the ISO-CHEK method was higher than the NIOSH 5525 method. Even though England *et al.* (2000) comparison was under air sampling conditions, the elevated results reported by the ISO-CHEK method agree with our findings. What is most interesting is that results are elevated even though the monomer was used as standards and not bulk samples. This may indicate that the bulk samples used as standards are not the only reason why the HDI oligomers are higher than the other methods in our study – even when correcting for the uretidone bias.

The NIOSH data reported a systematic error: an old batch of the derivatization reagent was used mistakenly (Appendix D.6). Therefore, a correction for background was reported (Appendix D.6). The negative intercepts from the robust regression (Table 4.2), however, indicate that there was an overcorrection. Background correction may have been necessary because of the old reagent. The use of a compromised reagent may also be responsible for the precipitation observed in some samples (no other methods reported precipitation) and the existence of potential outliers. It is possible that the accidental use of a compromised batch of derivatization reagent may have degraded the chemical stability of the samples. Other causes for the lack of stability or reproducibility include the possible switch of samples 17 and 18 as well as a possible problem during spiking or analyzing of samples 2, 3, and 8.

The NIOSH results had high accuracy in estimating monomer and oligomer values compared to the reference value (Table 4.3). The MS results had low accuracy in estimating oligomer values, but high accuracy when estimating the monomeric values (0.35 versus 0.65 respectively in Table 4.3). The high location and scale shifts for the MS method HDI oligomers reflect the under prediction discussed previously. Conversely, the OSHA method had low accuracy for HDI monomer compared to estimates of total oligomers (0.58 versus 0.99 respectively in Table 4.3).

Results for variables with no reference values, such as the HDI oligomers isocyanurate, uretidone, and biuret, are better understood from Table 4.6. Inter-method accuracy for isocyanurate was best while it was lowest for uretidone. Inter-method accuracy was lowest when comparing methods MS and ISO-CHEK for biuret and for the sum of HDI oligomers. These results are understandable considering the MS method tends to under-predict oligomers while the ISO-CHEK method tends to over-predict specific oligomers. Further, uretidone was highest for the ISO-CHEK method potentially due to the reported bias.

4.4.3. Method Strengths and Weaknesses

Strengths and weaknesses of the different methods are summarized in Tables 4.7.1 and 4.7.2. Overall, most strengths and weaknesses can be explained by the type of detector used. We acknowledge that the derivatization reagents play a major role in the performance of a method. However, since this method comparison does not allow us to explore the effects of the different derivatization reagents directly, we cannot make strengths or weaknesses' statements based solely on the derivatization reagents.

The most important strength of the MS method was the use of LC/MS, which provided lower detection limits, lower background levels, and enhanced specificity (this method can verify the structure by the mass spectra of the standard). The MS method is best for trace analysis, especially in biological samples. One limitation of the MS method was its current inability to detect monomeric or oligomeric forms of IPDI. A review of the chemical composition of several commercial hardeners revealed the presence of up to 40-50% oligomeric IPDI in the formulation (unpublished data). Method development is necessary to extend the measurement of these species using the 2MP LC-MS system. The MS method specificity is crucial when conducting exposure assessment, risk assessment, or studying the mechanisms of exposure and toxicity for individual isocyanates. Other methods, like the OSHA method, report totals that include unknown compounds, which is not specific enough for such studies.

The most important strength of the ISO-CHEK method was the detection of IPDI monomer (with an accuracy of 0.83 and precision of 0.96), which no other method quantified. However, the greatest weakness of the ISO-CHEK method was that the dual-filter system requires additional sample handling and analysis. In addition, the LOQs are fairly high so it is not the best method for trace analysis.

The Iso-Chek dual system has potential problems during air sampling, which do not apply to our analysis since this method comparison does not have into consideration the sampling of air bornes. The first known problem is that isocyanate species in the aerosol fraction can cure between the times of collection and post-sampling derivatization (Streicher *et al.* 2000), especially for longer samplings. Another potential problem is the misclassification of semi-volatile species, such as monomers, either by adsorption of vapor on the front filter or volatilization of species originally collected as aerosol (Streicher *et al.* 2000).

The greatest advantage of both the OSHA and NIOSH methods was that one standard may be used to quantify all isocyanate compounds. However, the ISO-CHEK method avoided monomer calibration for oligomers because errors were identified during the method development stage. Another advantage of the OSHA method was that the pre-coated filters are commercially available. The main disadvantages of the OSHA method were that it was not able to measure IPDI monomer reliably when analyzing bulk samples and could not discriminate between HDI oligomers from IPDI oligomers.

The OSHA method is usually capable of measuring IPDI monomer using a commercial IPDI standard by running OSHA 42 and OSHA PV2034 simultaneously. Results for IPDI monomer, however, were not presented here because the IPDI monomer results were compromised by the artifactual formation of IPDI-PPZ derivative, presumably from the oligomer. The level of IPDI monomer increased over time in the extracts from the inter-method study. Co-eluting peaks were not present by examining UV/fluorescence ratios so interference was ruled out as a possible explanation. The OSHA 42/ PV2034 method indicated that the IPDI in the form of the derivative on the collection filter is stable for at least seven days. Since the derivative was spiked onto the filters by OSHA analysts, no information was available on stability in the extract of the oligomer. Because the concentration of the oligomer was high relative to the monomer, a small amount of its conversion to the monomer would greatly affect the concentration of the monomer but not the oligomer or the total concentration. In bulk samples the IPDI oligomer derivative can convert to IPDI derivative but we have seen no evidence of this happening in the filter samples or with other derivatives.

The lack of commercial availability of the MAP derivatization reagent is one of the most limiting aspects of the modified NIOSH 5525 method. The second most limiting weakness of the method was its inability to measure IPDI monomer. However, with some development, this method could have the potential to resolve the IPDI monomer peak. One of the greatest advantages of the NIOSH method, considering it uses only one standard (like the OSHA method), is that it can differentiate individual oligomer species.

After interpreting results from the inter-method study, many variables need to be taken into account for choosing the most appropiate method for a particular application. Streicher *et al.* (2002) summarized OSHA and NIOSH isocyanate methods, and provided the following criteria for choosing an air sampling and analysis method: 1) the chemical nature of the isocyanate species, 2) the physical state of the isocyanate species, 3) the cure rate of the product, 4) the required sampling time, 5) whether personal or area sampling is required, and 6) the sensitivity of the detection needed.

Table 4.7.1. Summary of Isocyanate Analysis Methods Strengths

		STRENGTHS			
Comments	**Methods Characteristics**	**2-MP LC/MS**	**Modified NIOSH 5525**	**Modified OSHA 42/PV2034**	**Modified ISO-CHEK**
	Commercially available pre-coated filters are convenient			X	
	Ability to detect individual HDI oligomers	X	X		X
	Ability to detect IPDI				X
	Ability to detect IPDI oligomer individually		X		X
	Ability to report total versus individual oligomers		X		
	Use of one single standard		X	X	
Advantages intrinsic to the use of MS	Method can be used accurately for the measurement of trace analysis of environmental or biological samples	X			
	Lowest detection limits (in the pg range)	X			
	Accurate blank detection	X			
	High precision in replicate samples	X			
Advantages intrinsic to the use of FLD/UV	By using 2 detectors, FLD and UV, results can be compared for validation		X	X	X

Table 4.7.2. Summary of Isocyanate Analysis Methods Weaknesses

		WEAKNESSES			
Comments	**Methods Characteristics**	**2-MP LC/MS**	**Modified NIOSH 5525**	**Modified OSHA 42/PV2034**	**Modified ISO-CHEK**
	Derivatization reagent is not commercially available		X		
	Two filter system implies double sample process and analysis				X
	Current inability to detect IPDI	X	X (IPDI interference with uretidinedione)	X (artifactual formation of IPDI PPZ derivative presumably from the oligomer)	
	Current inability to detect IPDI oligomer individually	X		X	
	Inability to distinguish between HDI oligomers and IPDI oligomers			X	
Disadvantages intrinsic to the use of MS	Only compounds for which analytical standards are available can be quantitated accurately	X			
Disadvantage intrinsic to the use of FLD/UV	Reagent artifacts at very low levels Detection limits in the μg range		X	X	X
	Use of external standards for quantitation		X	X	X
	Absolute identity or structural elucidation of isocyanate species cannot be established		X	X	X

4.5. Conclusions and Recommendations

This study brings to light the challenges faced when comparing different isocyanate analytical methods. Different methods report results in different metrics that make direct comparison sometimes impossible. Further, each method provides a different set of isocyanate species depending on the method's capability. These difficulties were evidenced here even though the analysis of a bulk sample is the simplest approach. In the field, air sampling apparatus and handling of samples adds even more variability to the results. Also, shops can use several hardener products and some of them may not be as well characterized as the one analyzed in this study. The authors suggest caution when comparing results from different isocyanate analytical methods. Using the same metrics and having enough information about the species of isocyanates are the keys for a fair comparison.

Each method showed strengths and weaknesses that seemed to be mostly related to the type of detector used. The differences could also be attributed to sample processing and differences in the methodologies like derivatization reagent, standards used, chromatography, among others. This study was not intended to make conclusions referring to the performance of the different derivatization reagents specifically. Much of the differences when measuring HDI oligomers by the different methods come from the lack of commercially available oligomer standards.

The next step in method development points to a method that uses UV/FLD coupled with MS (or MS-MS). This powerful combination would bring the advantages associated with both detectors: UV/FLD would be able to measure total NCO-mass of isocyanates, monomers and oligomers and the MS detector can then check for specificity of the different species. The MS would also provide lower detection limits. Several derivatization reagents should be tested to ensure that the method works equally well for both detector types. The refinement of standards would also be essential in developing an UV-MS method, which would ideally measure not only currently measured HDI monomer and oligomers but also IPDI monomer and oligomers.

4.6. Notes to Chapter 4

Afifi A, Clark V; and May S: Computer-aided Multivariate Analysis. Contributor Virginia Clark, Susanne May. Published by CRC Press, (2004). 489 pages

Bello D, Streicher RP, and Woskie SR (2002): Evaluation of the NIOSH draft method 5525 for determination of the total reactive isocyanate group (TRIG) for aliphatic isocyanates in autobody repair shops. National Institute for Occupational Safety and Health. J. Environ. Monit. 4(3):351-360

Bello D, Woskie SR, Streicher RP, *et al.* (2004): Polyisocyanates in occupational environments: a critical review of exposure limits and metrics. Am. J. Ind. Med. 46(5):480-91

Chang FK, Chen ML, Cheng SF, Shih TS, Mao IF (2007): Dermal absorption of solvents as a major source of exposure among shipyard spray painters. J. Occup. Environ. Med. 49(4):430-6

England E, Key-Schwartz R, Lesage J, *et al.* (2000): Comparison of sampling methods for monomer and polyisocyanates of 1,6-hexamethylene diisocyanate during spray finishing operations. Appl. Occup. Environ. Hyg.15(6):472-8

U.S. Environmental Protection Agency (EPA) (2005): Revised Automotive Refinishing Industry Isocyanate Profile. U.S. Environmental Protection Agency. January 2005. Available at www.epa.gov/opptintr/dfe/pubs/auto/profile/index.htm, accessed October 2005

Fent KW, Jayaraj K, Gold A, *et al.* (2008): Quantitative monitoring of dermal and inhalation exposure to 1,6-hexamethylene diisocyanate monomer and oligomers. J. Environ. Monit. 10:500-507

Fisher LD and Van Belle G. Biostatistics: A methodology for the health sciences. Wiley interscience. US. (1993). page 900. total 991 pages

Health Safety Laboratory (HSL) (1993): Preparation of samples for the HSE diisocyanate AQUA scheme. Report # IR/L/SP/93/01. UK: Health and Safety Executive.

Liu Y, Sparer J, Woskie SR *et al.* (2000): Qualitative assessment of isocyanate skin exposure in auto body shops: a pilot study. Am. J. Ind. Med. 37: 265-74

Liu Q and Wisnewski AV (2003). Recent developments in diisocyanate asthma. Ann. Allergy Asthma Immun. 90:35-41

Liu Y, Stowe M, Bello D, *et al.* (2006): Respiratory Protection from Isocyanate Exposure in the Autobody Repair and Refinishing Industry. J. Occup. Environ. Hyg. 3(5): 234-249

Liu Y, Bello D, Sparer JA, *et al.* (2007): Skin Exposure to Aliphatic Polyisocyanates in the Auto Body Repair and Refinishing Industry: A Qualitative Assessment. Ann. Occup. Hyg. 51:429-439

Marand A, Karlsson D, Dalene M, and Skarping G (2005): Solvent-free sampling with di-n-butylamine for monitoring of isocyanates in air. J. Environ. Monit. 7:335-343

Polettini A: Applications of LC-MS in Toxicology, Pharmaceutical Press, (2006), pp. 275

Shoemaker JP, Garland CW, and Steinfeld JI: Experiments in Physical Chemistry, McGraw-Hill, Inc., (1974), pp. 34-39

Sparer J, Stowe MH, Bello D, *et al.* (2004) Isocyanate exposures in autobody shop work: the SPRAY study. J. Occup. Environ. Hyg. 1(9):570-81

Streicher RP, Reh CM, Key-Schwartz RJ, *et al.* (2000). Determination of airborne isocyanate exposure: considerations in method selection. AIHA J. 61(4):544-56. Review

Streicher R, Reh CM, Key-Schwartz RK, *et al.* (2002). Selecting Isocyanate Sampling and Analytical Methods. Appl. Occup. Environ. Hyg. 17(3):157-162

Taylor J: An Introduction to Error Analysis, University Science Books, Mill Valley CA, (1982)

Vandenplas O, Cartier A, Lesage J *et al.* (1993) prepolymers of hexamethylene diisocyanate as a cause of occupational asthma. J. Allergy Clin. Immunol. 91: 850-61

Woskie SR, Sparer J. Gore RJ *et al.* (2004). Determinants of isocyanate exposures in auto body repair and refinishing shops. Ann. Occup. Hyg. 48: 393-403.

Chapter 5

PERMEATION PANEL DEVELOPMENT

5.1. Introduction

Selecting the appropriate protective clothing is essential, but only the first step towards an effective worker protection program; training and good work practices are equally important (Boman *et al.* 2004). Dermal protective clothing remains a primary means of preventing skin exposures in some work places, followed by administrative and engineering controls (Bello *et al.* 2007). Substitution of hazardous materials and robotics are ideal ways to minimize exposure but are frequently not feasible solutions (Boman *et al.* 2004). Consequently, measuring permeation and breakthrough time for the chemical of interest is necessary; these parameters help the worker choose the appropriate protective clothing and institutionalize good work practices and effective training.

Permeation is defined as the dissolution and molecular diffusion of chemicals through a material. Gloves usually are selected based on laboratory permeation testing following ASTM Method F739-99a "standard method for resistance of protective clothing materials to permeation by liquids or gases under conditions of continuous contact." The purpose of this method is to determine the relative resistance of a material to permeation of selected chemicals. This method does not consider the toxicity of chemicals or other material-related performance factors. The lack of glove material recommendations for many chemicals reflects the lack of a standard method for testing breakthrough and permeation of chemicals with low vapor pressures or water solubility, such as isocyanates. Another challenge of the ASTM Method F 739 is that the studied chemical must be soluble in a fluid and that fluid cannot permeate the tested material (Klingner and Boeniger, 2002).

No study to date has systematically quantified permeation of a complex chemical mixture like polymerizing materials. Most permeation studies are performed with pure compounds or a binary mixture (Evans *et al.* 2001 and Mickelsen *et al.* 1986). Mickelsen *et al.* (1986) determined that binary mixtures of solvents permeate differently than the pure components. These authors recommended that protective clothing permeation studies should be performed using mixtures that reflect actual working conditions. Evans *et al.* (2001) is emphatic that permeation tests should be performed at temperatures that approximate real conditions. However, the ASTM standard method (ASTM F739-99a) is not adequate to test polymerizing materials because the apparatus could not be reused after the polymerizing materials cured.

The standard permeation method also is not adequate for low volatility, low water solubility agents (Ehntholt *et al.* 1990; Klingner and Boeniger 2002; Anna 2003). No fluid would collect permeants with these properties and at the same time be impermeable to the test material. Chemicals of low volatility and water solubility generally include higher molecular weight chemicals such as polynuclear aromatics, polychlorinated diphenyls (PCBs), isocyanates, and some pesticides (Anna 2003). One approach for conducting permeation tests with these chemicals has been to use solid collection media (Ehntholt *et al.* 1990). This technique involves placing a solid, highly absorbent film directly against the material specimen. Ehntholt *et al.* (1990) designed a special test cell, successfully using a silicone rubber material for collection of pesticides. Other approaches include the use of a liquid splash collection and permeation testing with halogenated pyridines (Anna 2003).

We developed a novel field approach for testing efficacy of gloves and coveralls against polymerizing materials using a permeation panel. Each panel is comprised of eight permeation units that quantify permeation through the protective materials, and several loading ports that assess homogeneity of the clear coat loading across the panel. The permeation units essentially are modified standard permeation cells (ASTM F 739). Permeation is measured by placing a solid medium behind the test material. Media are treated with derivatization reagent to assure accurate quantification of the very reactive chemicals.

The choice of solid media and loading media depends on the polymerizing material and permeant of interest. In this case, we were studying isocyanate permeation of gloves from clear coats used in the collision repair industry (Chapter 1). SWYPE colorimetric pads for aliphatic isocyanates are used as solid media as well as filters coated with 1-(2-pyridyl)-piperazine (PPZ). SWYPEs provide an estimate of breakthrough time by visual scoring, or semi-quantitative permeation using RGB analysis (Chapter 2). The PPZ-coated filters are analyzed by HPLC-UV according to modified OSHA 42/PV2034 (described in Chapter 4). Loading is measured on pre-weighed PTFE filters mounted in aluminum foil with 1 inch diameter openings; these filters then are taped to the outside of the panel, interspersed between the permeation cells.

The main advantage of the permeation panel compared to a conventional permeation cell is that the layer of sprayed polymerizing material is representative of workplace conditions. The panel can be used to test materials in a time course or several glove materials simultaneously under actual spray painting operations.

The main goals of this project are to design, construct, and characterize a permeation test panel to evaluate dermal protective clothing for resistance to polymerizing materials. In this study, we are specifically using the permeation panel to test permeation of aliphatic isocyanates present in clear coat formulations. Potential applications extend to other isocyanate compounds present in different sprayed coatings, including liners, foam, and glues. Other low volatility/low water solubility permeants or solvents also could be tested.

5.2. Permeation Panel Prototype

A permeation panel prototype was constructed with the assistance of Marc Beaudreau (Field Research and Consultation Group, UW). Essentially, air sampling cassettes (SKC 225-9002) were adapted for use as permeation cells. Cassettes were mounted on a plastic case with 12 holes designed to fit the cassettes snugly. The plastic case was closed to protect the back of the cassettes from overspray. Test materials were cut in 37 mm diameter circles, placed on top of the solid media, and then placed inside the air sampling cassettes. A backing pad was used to ensure contact of the solid media with the test material. The panel was then sprayed inside a spray booth under conditions typical of clear coat applications.

Permeation was evaluated in four ports with colorimetric SWYPEs (CLI lab, part No. 1023 described in Chapter 2) and in four ports with 1-(2-pyridyl)-piperazine (PPZ) coated filters (SKC 225-9002, SKC Inc., Eighty Four, PA). The SWYPEs provided an immediate visual qualitative response, while the PPZ-coated filters yield a quantitative permeation result. The remaining four ports contained pre-weighed glass fiber filters to assess surface loading and determine the homogeneity of the clear coat layer (by post-weighing the filters). The prototype was then spray-painted as if it were a car part. Following spray-application, the prototype was left inside the spray booth for a prescribed period of time and then disassembled for processing of the cells.

To measure the thickness of the clear coat, a metal strip of known thickness was placed on top of the panel. Following spray-application, the thickness of the metal strip was measured for a second time. Clear coat thickness was then calculated by subtracting the pre-coating thickness from the post-thickness. All thicknesses were measured using a micrometer.

To evaluate surface loading for the applied clear coat mixture, the total mass applied to the surface was calculated based on the residual non-volatile fraction of the clear coat mixture on the filters (dry clear coat mass). The non-volatile fraction was estimated by measuring the clear coat density and dry weight of an aliquot of the clear coat. The density was determined by weighing a known volume of freshly prepared mixture in a closed glass vial. Three quartz filters were desiccated in a vacuum oven for 1 h (75 °C, 15 psi) and pre-weighed in a microbalance. Clear coat (100 µL) was then added to each filter. Filters were baked on watch glasses for 2 h in a vacuum oven and post-weighed. The percentage of solids in the coating was compared to the value provided by the manufacturer.

The first experiment with the prototype was to determine reproducibility of the permeation and loading measurements. Testing used thin latex glove material (Shamrock 6100, 5mil; description found at http://www.smcgloves.com/products/61kseriesC.pdf). The panel was sprayed with approximately 60 ml of product (4 part clear coat, 1 part hardener, and 1 part reducer) in two coats, with the first spraying for 13 s and a second for 17 s. The clear coat was left in contact with the glove material for 19 minutes, which is the typical duration of a spray application (painters are more likely to change gloves at the end of a spray job). The clear coat density was 0.7 mg/µL. The percentage of solids in the coating determined by measuring the residual non-volatile fraction, was 67%, which is greater than the calculated value (46.6%) based on the solids percentage for each of the components of the clear coat provided by the manufacturer.

Coating thickness, as measured using the 0.51-mm metal strip, was fairly consistent (mean = 0.06 mm, CV = 24% n = 20). Permeation of reactive isocyanates was indicated by the immediate color change of the SWYPE medium placed beneath thin latex, and further verified by the measured average of 0.6 µg HDI monomer in the PPZ-coated filters (Table 5.1). Loading of the clear coat was fairly homogeneous (21% CV), as measured by the mass of the dry product on glass fiber filters. The average mass gain in the loading filters was 48.5 mg.

Another round of testing was performed to examine different materials in the permeation panel prototype:

- Coverall: SAS coverall polyester fabric

- Thick latex: Thickster latex 14mil
- Thin latex gloves: M Safe latex 5mil
- Thin nitrile gloves: Supreno SE nitrile 5.5mil

Materials were sprayed as described previously, but with a different product (5 part clear coat, 1.7 part activator, 3 part reducer, and 0.3 part enhancer). Permeation was evaluated after a 90 min contact time, reflecting an upper-end duration that a painter would wear gloves in the field (results shown in Table 5.2). Thin latex was observed to have the greatest permeation; SWYPE permeation was observed in the following rank order: thin latex > coverall = thick latex > Supreno SE nitrile. Permeation, as measured by the quantitative filters and analyzed by OSHA 42 method, was ranked as follows: thin latex> coverall> Supreno SE nitrile = thick latex.

Table 5.1. Permeation (19 min) Prototype Reproducibility

Material	Media	Latex Thickness (mil)	SWYPE Color Scale	HDI (µg)	Oligomers (µg)[2]
Thin latex	PPZ Filter	5		0.7	<0.1
Thin latex	PPZ Filter	4.9		0.6	<0.1
Thin latex	PPZ Filter	5		0.3	<0.1
Thin latex	PPZ Filter	5		0.8	<0.1
Thin latex	PPZ Filter	5		0.5	<0.1
Thin latex	SWYPE	4.5	0-1		
Thin latex	SWYPE	5	0-1		
Thin latex	SWYPE	5	0-1		
Average (%CV)		4.9 (4%)		0.6 (15%)	

[1] Immediate color change;
[2] Modified OSHA 42/PV2034 method calibration R^2=0.998; reporting limit 0.05 µg/sample.

The use of this prototype demonstrated that chemical permeation could be measured using solid media analyzed with standard methods. In addition, several ports allowed different materials to be tested simultaneously, ensuring consistency in experiment conditions. There were, however, several challenges:

- The air sampling cassettes were fragile. When placing the materials inside the cassette, the cassette material would break occasionally and could not be used.
- The manufacturing tolerances of the dimensions of the air sampling cassettes were too great. Reproducible intimate contact of the test material and solid media was not always possible.
- There was evidence of clear coat penetration in several of the samples: intense red spots were observed on the borders of some SWYPEs. This was not surprising because it was difficult to assure a seal with the fragile filter cassette material.
- The top surface was not completely flat because the filter cassettes did not allow for flush mounting on the case. Homogenous loading throughout the panel may not be achieved when a flat surface cannot be guaranteed.
- The cassettes could not be reused because they could not be cleaned with chemicals that remove clear coat.
- The loading and unloading of samples was difficult and time consuming.

Table 5.2. Permeation (90min) Prototype Results for Different Protective Clothing Materials

Test Material	Back Material	Thickness (mil)	SWYPE Color Scale	HDI (μg)[1]	Oligomers (μg)[1]
Coverall SAS	PPZ Filter	11.2		0.2	<0.8
Thickster latex	PPZ Filter	10.2		<0.05	3.4
M Safe latex	PPZ Filter	4.5		0.8	<0.8
Supreno SE nitrile	PPZ Filter	4.6		<0.05	<0.8
Coverall SAS	SWYPE[2]	10	0-0.5[3]		
Thickster latex	SWYPE[3]	10.2	0-0.5		
M Safe latex	SWYPE	4.2	1		
Supreno SE nitrile	SWYPE	4.6	1		

[1] Modified OSHA 42/PV2034 method.calibration R^2=0.994; reporting limit 0.05 μg/sample. [2] An aliquot of the activator was used as a positive control for the SWYPE. [3] Few red spots denoted possible penetration of the clear coat to the back material.

5.3. Permeation Panel

5.3.1. Selection of Clear Coat Formulations

Two clear coats with different formulations (named A and B for confidentiality purposes) were chosen because they are commonly used in the collision repair industry (confidential communication with the manufacturer). Both formulations' technical data sheets reported they were composed of 46.8 percent solids. The clear coat was prepared using the ratios suggested by the manufacturer (4 part clear, 1 part hardener, and 1 part reducer), which resulted in 13.9% total isocyanates in the mixture (hardener bulk analysis presented in Chapter 4). These formulations contained the same hardener, which was extensively characterized by chemical bulk analysis (Chapter 3). The final mixture for both formulations resulted in the same isocyanate content, with some differences in the solvent content. Solvent content was determined from the products' MSDSs and the mixing ratios. These data were verified by conducting bulk chemical analysis for all unmixed components.

5.3.2. Permeation Cells Construction

Applying lessons learned from the prototype experiments, an improved design of the permeation cell parts was drawn in AutoCad (version 12.0, Autodesk, Inc., San Rafael, CA, USA). The original drawings were then imported by Jeff Brandon (Brandon Company, Inc. 12708 Alexander Road. Everett, WA 98204-5427, phone 425-290-5427 fax 425-513-5606) to a SolidWorks application (Solidworks Corp., Concord, Mass., USA). Two different model permeation cells were machined in aluminum by Brandon Company, Inc. After testing the models and making several improvements, the final modified permeation cells were produced. Seventeen cells were shaped with a lathe using 6061-T6 Al (Lytle Machining in Mukilteo, WA phone 425-290-3538). Final drawings of the cell parts: bezel, body, and base are presented in Appendix E.1, including the accessories used. Cells were then coated with a hard anodize type III class 2 black and PTFE coating, also known as a Teflon seal – bake (Production Plating, Inc. 4412 Russell Road, Mukilteo, WA 98275, phone 425-347-4635, www.productionplating.com). The components of the cell are shown in Figure 5.1.

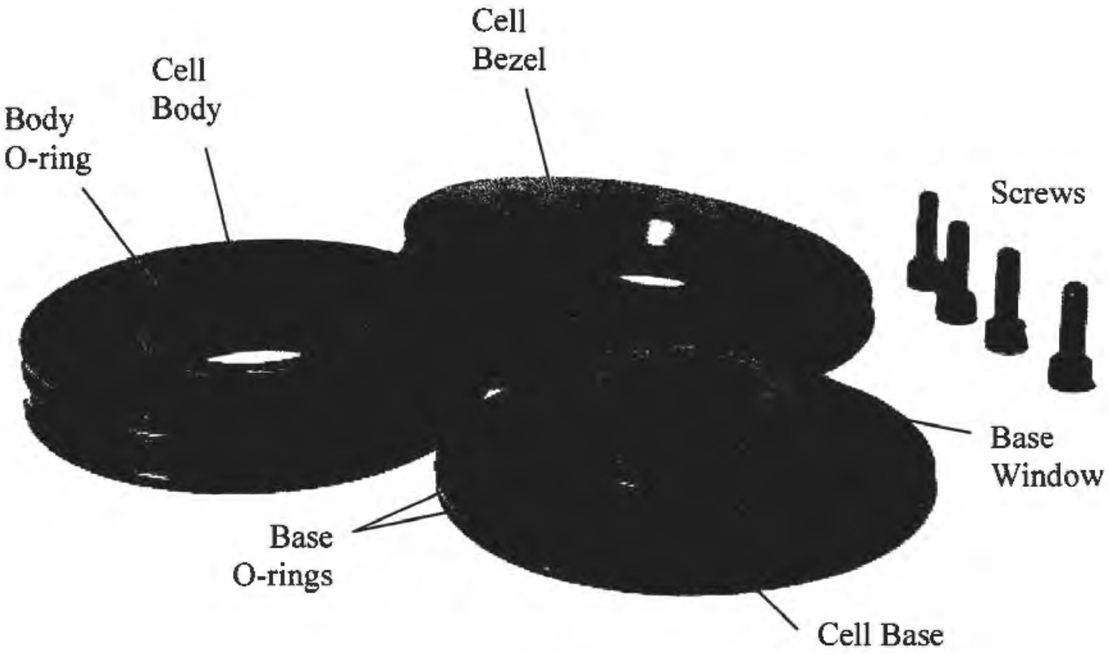


Figure 5.1. Permeation Cell Components. Prior to assembly, solid media are placed on top of the base window and test material is held in place between the body and bezel. The cell is then assembled using four screws, providing close contact between the solid media and test material and a leak-proof seal. A 1 inch diameter test surface is exposed to clear coat.

Note that if cells were ever recoated (stripped and coated again), this process removes approximately 0.001 inch on the overall dimensions of the material surface. Cells were stripped and recoated (March 2009) because the coating was compromised after the inadvertent use of a harsh soap when washing the cells. After recoating, the O-rings of the base were replaced to ensure that the cells still sealed properly[i].

---

[i] The new Top base O-ring was a McMaster# 9452K78, BUNA-N O-ring, AS568A dash number 024. The new bottom base)-ring was a McMaster# 9262K648, metric BUNA-N O-ring, 1.5mm width, 28mm id.

5.3.3. Permeation Cell Assembly Instructions

Assembly of the cells takes place from top to bottom: bezel to body to base. A picture of a complete cell is shown in Figure 5.2. Approximately 3 inch diameter glove material samples from the palm of the glove is first cut and measured for thickness. Four holes of 3/16 inch diameter are made in the test materials that were aligned with the screw holes. The test material is placed between the bezel and body, ensuring that that the normal outside surface of the glove is the side in contact with the clear coat. Screws are used to connect the bezel to the body.

Once the bezel and body are connected, the top-body O-ring guaranteed a good seal. Solid media was pre-cut into 1 inch diameter circles with a clean circular paper cutter. Media are then placed on the base window and connected to the body inside a clean ventilation hood to avoid contamination of the media. The base O-rings ensured that there was a seal between the base and the body. Screws are tightened to assure seal of the test material. A seal is essential to ensure that any isocyanate getting in contact with the solid media resulted from permeation only.

Figure 5.2. Assembled Permeation Cell (without test material)

5.3.4. Permeation Panel Construction

Improved permeation panels (Figure 5.3) were constructed in order to overcome potential shortcomings of the preliminary design described in the prototype section. Permeation panel frames were made of large durable Pelican 1700 cases (Pelican Products, Inc. Torrance, CA). Cases were chosen because of their size, light weight, and sturdiness. Further, the cases were easy to transport because they had strong polyurethane side wheels with stainless steel bearings. Holes to flush mount the permeation cells were machined in the top of the cases by Brandon Company Inc. A drawing of a permeation panel is presented in Appendix E.2.

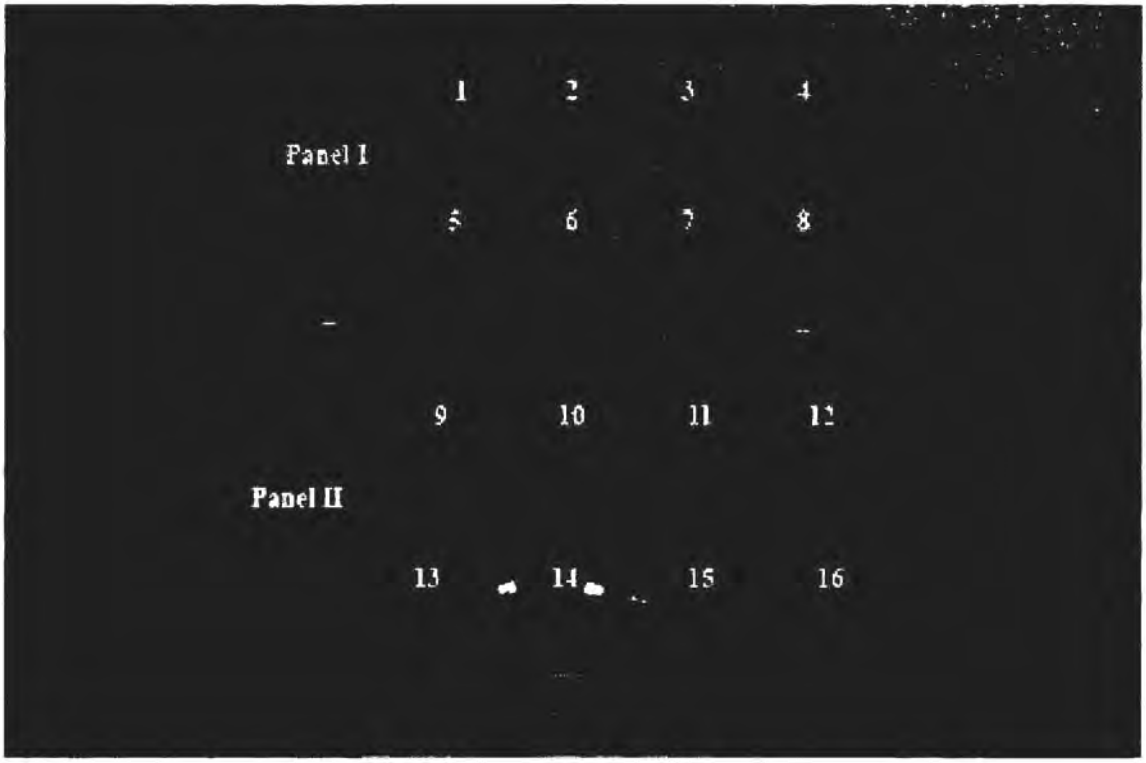


Figure 5.3. Permeation Panels (note the 8 permeation cells per panel)

5.3.5. Permeation Panel Assembly Instructions

Each labeled permeation cell was placed in the permeation panel cases. The panel tops between the permeation cell openings were masked with tape. This was accomplished by either masking around the cell openings or masking over and cutting a 1 inch circle of tape at the opening. Then, loading ports were built: pre-weighed PTFE filters (Zefluor 47mm 0.5µm

Supported PTFE P/N P5PQ047 Pall – Life Sciences) were mounted in 50x50 mm^2 thick aluminum foil with 1 inch diameter openings. These loading ports were then taped to the outside of the panel – interspersed between the permeation cells. A photograph of a section of the panel prepared for spray application is shown in Figures 5.4 and 5.5.

Figure 5.4. Permeation Panel Prepared for Spray-Application Inside the Spray Booth. PTFE loading media are held with aluminum foil and taped to the exterior surface of the panel. Note the addition of masking tape and paper to protect the panel surface from clear coat. All cells and ports are 1 inch in diameter.

This new design had the following advantages over the prototype described previously:

- Tight seals around the test material to prevent seepage of coatings on to the filter media;
- Allows for simultaneous testing of several materials;
- A flat panel surface to ensure homogeneous loading;
- Allows for rapid change-out of media;

- Provides a base window to facilitate media loading and inspection;
- Media are held in close contact with the test material;
- Cells are reusable;
- Teflon-coated anodized aluminum surfaces facilitate cleaning;
- Robust loading port media using PTFE filters.

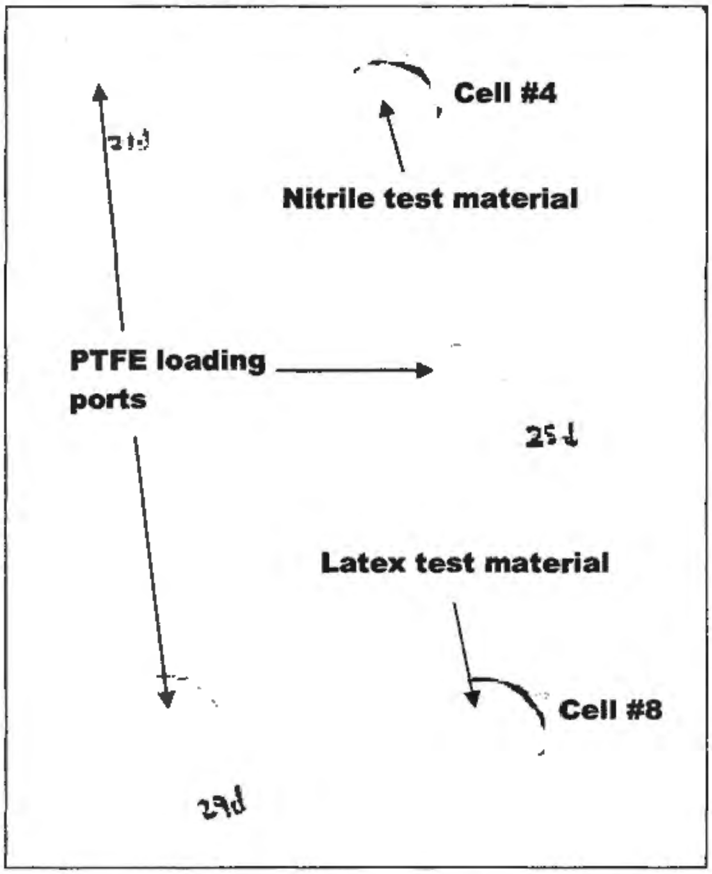


Figure 5.5. Close-Up of a Section of The Permeation Panel Prepared for Spray-Application.

Temperature was monitored using wireless HOBO External Data Loggers (Model H08-004-02; Onset Computer Corporation, Pocasset, MA) placed inside each panel before closing and masking the sides of the panels. Distribution of the loading ports is shown in Figure 5.6 and 5.7. Detailed standard operating procedures (SOPs) for field testing with the permeation panels are presented in Appendix E.4.

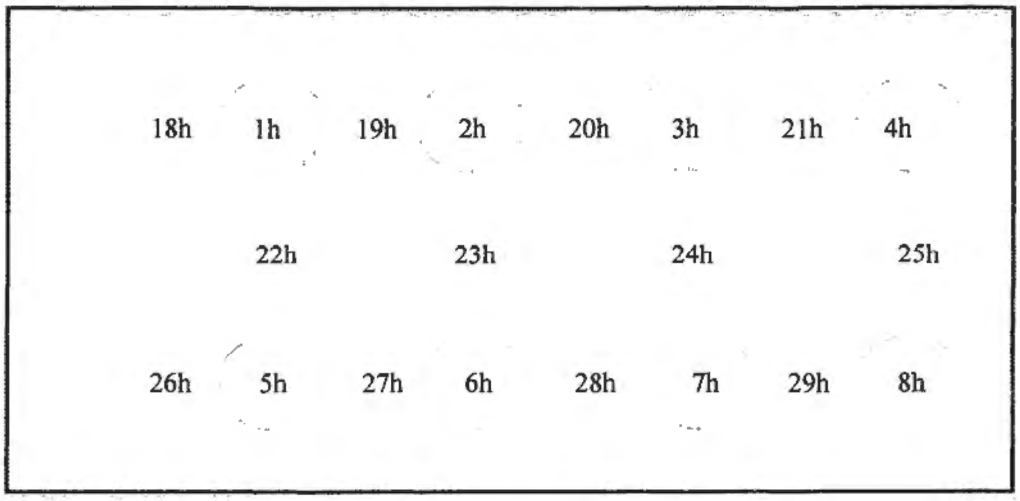


Figure 5.6. Distribution of Loading Ports 18h-29h Relative to Permeation Cells 1h-8h for Panel I During a Day's Experiment Labeled h.

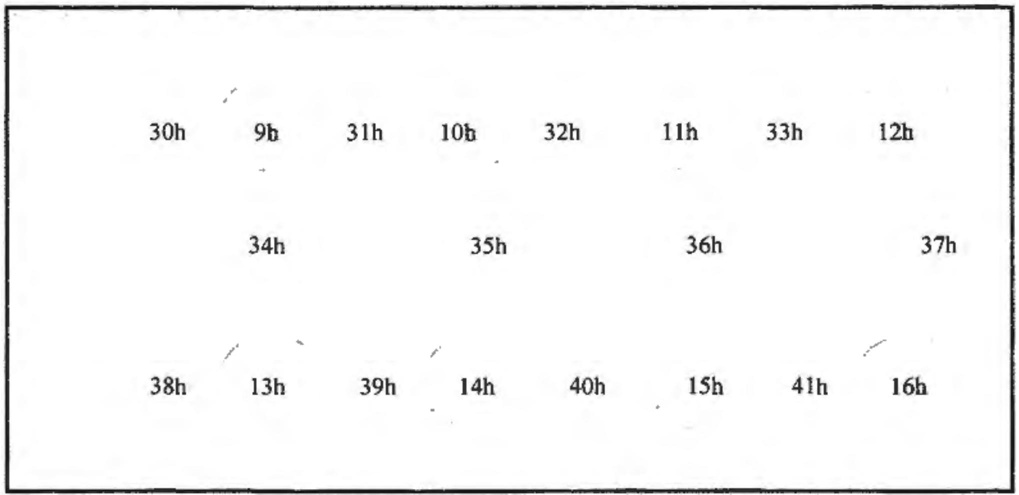


Figure 5.7. Distribution of Loading Ports 30h-41h Relative to Permeation Cells 9h-16h for Panel II During a Day's Experiment Labeled h.

5.3.6. Spray Painting the Permeation Panel

The paint booth (downdraft DeVilbiss spray booth) was maintained at a temperature of approximately 70°F. Temperature conditions were chosen to reflect typical spray-application conditions. The target temperature conformed to the specifications for the clear coat formulation applied.

Booth air-flow was measured in the temperature-conditioned booth with a Spatial Anemometer ALNOR model RVA501 (ALNOR a TSHI Company, Huntington Beach, CA). Linear velocity was measured 1 to 2 inches from the floor vents in feet per minute (ft/min or LFM). Several velocity measurements were made throughout the two floor vents. Booth dimensions are presented in Appendix E.4. An example of the distribution of flow measurements among both sides of the booth is presented in Appendix E.5. Velocity measurement locations are presented in Appendix E.6. Volumetric flow in cubic feet per minute (ft^3/min or CFM) was calculated by multiplying the average velocity and area per floor vent (each with an area of 46.44 ft^2). Flow rate values for the vents were summed to calculate total flow rate.

Panels were placed inside the booth for temperature and relative humidity (RH) conditioning. A commercial clear coat formulation was applied by the same painter and using the same spray gun (IWATA LPH400, with a 1.3 mm nozzle and operated at 20 psi). Temperature and relative humidity (RH) were monitored every 10 seconds both inside the permeation panels and at the interior perimeter of the spray booth using wireless HOBO External Data Loggers. Instrument's temperature accuracy reported by the manufacturer was ±1.27°F (±0.7°C) at +70°F and RH accuracy: ±5%. Spraying the panels was equivalent to painting a car part. Panels were sprayed for few seconds (approximately 18 sec) in two separate applications, with approximately 7 minutes between applications. During each spray-application, the painter applied clear coat using six passes of the spray gun for the whole panel. Spraying times were recorded both with a timer and video recorder. The panel was left inside the temperature-controlled booth for the duration of the experiment. Permeation times were recorded starting at the end of the second (final) spraying application. Panels were removed from the booth, to be disassembled for sample collection. During permeation rate experiments, cells were removed from the booth at specific time points.

5.3.7. Permeation Measurement Methods

Following spray application, solid media were collected for later analysis. The solid media were chosen according to the analysis methods available for the measurement of the permeant of interest. In this case, we wanted to measure aliphatic isocyanates in clear coat formulations. We chose current techniques for the sampling and analysis of isocyanates, such as air sampling modified OSHA 42/PV2034 method (described in Chapter 4) and SWYPE surface sampling technique (described in Chapter 2). Colorimetric SWYPEs for aliphatic isocyanates (CLI lab, part No. 1023) and glass fiber filters coated with 1-(2-pyridyl)-piperazine (PPZ) were used.

The SWYPEs were intended to provide an immediate visual response and a semi-quantitative estimate of permeation. Breakthrough time was the time at which a color change appeared on the SWYPE when observing the glove during the experiments. Thin latex gloves were sufficiently thin that the SWYPE color change was visible through the glove. At the end of the experiment, SWYPEs were analyzed using RGB analysis to provide semi-quantitative permeation data, as described in Chapter 2 and Ceballos *et al.* (2009) (with some modifications). The SWYPEs were used without developing solution (mineral oil) because we determined that this solution is incompatible with latex, which degraded. Sampled SWYPE pads in plastic wrap were digitized on a calibrated portable flatbed scanner and red-green-blue (RGB) histograms of SWYPE images were created, as described in Chapter 2. A calibration curve was created from a series of reference images derived from SWYPEs, which were loaded with known amounts of an isocyanate-containing product. The SWYPE method used was different from that described in Chapter 2 because the developing solution was not used. Reference loadings were spiked onto aluminum foil. Without using developing solution, SWYPEs were used to wipe the surface in a circular motion immediately after the spiking and without waiting for the toluene to dry. Wiping immediately after spiking was different from the method described in Chapter 2, but was necessary to ensure reproducibility. Recoveries with the SWYPE were enhanced using the solvent, rather than the developing solution.

PPZ-coated filters were analyzed by modified OSHA 42/ PV2034 (HPLC-UV described in Chapter 4). Filters provided a quantitative permeation result for both monomers and oligomers.

5.3.8. Loading Measurements

PTFE filters used to determine the loading of the panel were pre- and post-weighed to account for the mass of dry clear coat deposited during the spray application. The %CV of the Post-Pre weighed loading filters was used to determine the homogeneity of spray application and to normalize permeation measurements (all panels showed <13%CV). The loading of PTFE filters throughout the panel was averaged. The mass of total isocyanate detected on the SWYPE or PPZ-coated filter was normalized by dividing by the average loading of dry clear coat in the specifc panel.

Several loading ports were tried to identify the optimal method (detailed data in Appendix E.7):

a) Thick aluminum circle: pre-weighed thick aluminum was covered with masking tape with a 1 inch circle opening. Masking tape was removed before the clear coat had dried fully. Post-weighed aluminum was used to assess the dry clear coat mass.

b) Thick aluminum square: thick aluminum was half-covered with masking tape, which was removed after the spray event. One 1-inch circle was cut from the painted area and from the non-painted area. Both circles were weighed and compared.

c) PTFE: Teflon filter held with aluminum and masking tape with a 1inch circle opening.

d) PC: polycarbonate (plastic) filter held with aluminum and masking tape with a 1-inch circle opening.

e) Metal tape: pre-weighed metal tape without the glue being exposed was covered with masking tape that had a 1-inch circle opening. Masking tape was removed before the clear coat had dried fully. Metal tape was post-weighed to measure the mass of loaded dry clear coat.

f) Aluminum foil: Pre weighed commercial heavy duty aluminum foil was covered with masking tape that had a 1-inch circle opening. Masking tape was removed before the clear coat had dried fully. Aluminum was post-weighed to assess the dry clear coat mass.

The preferred method to measure loading was PTFE filters. This type of filter was superior to quartz (used in panel prototypes) because it was reproducible and maintained its integrity. PTFE filters were lighter, so the measured clear coat mass was more precise. The painted area on the PTFE filter was a perfectly-defined circle (Figure 5.8). The second-best loading method was option b, but the tare weight of the thick aluminum was very high. Other methods had problems such as ripped material or clear coat layer. Lastly, PC filters dissolved in the presence the clear coat.

Standardized loading measurements, as mentioned previously, were performed by using 12 interspaced PTFE pre-weighed filters, distributed around the panel, as shown in Figure 5.6 and 5.7.

Figure 5.8. PTFE Loading Filter with 1 inch Diameter Circle of Dry Clear Coat.

5.3.9. Collection of Permeation and Loading Samples

Filters were removed in a timely fashion while avoiding cross-contamination. PPZ-coated filters were placed in their original cassettes, sealed with paraffin, and placed in a cooler with blue ice for transportation to the lab, where they were stored frozen. SWYPEs were immediately wrapped in plastic wrap and scanned for later RGB analysis (as described previously).

The pre-weighed PTFE loading media were also removed from the exterior surface of the panel and placed inside their labeled filter holders. After temperature conditioning in the weighing room, loading media were post-weighed using an anti-static device. Waiting a week to post-weigh allowed for the clear coat to off-gas and ensured a stable weight reading. When necessary, loading media were dried under vacuum to ensure that the clear coat was completely dry.

5.3.10. Permeation Panel Transport, Clean Up, and Storage

When sample collection was completed, all the remaining masking tape was removed. Cells were disassembled and wiped with acetone or alcohol to remove clear coat residue. Individual cells were stored temporarily in small transparent plastic bags (sealed with tape) inside a box to prevent cells breaking during transport. The box was covered with a large plastic bag to prevent it from opening. Back at the lab, the cells were cleaned thoroughly (with acetone, N-Methylpyrrolidone or NMP, and water/lab detergent sonication bath) before being reused. The cleaning procedure SOP is presented in Appendix E.8. Clean cells were stored in a secured acrylic holder built by Brandon Company Inc.

To verify that the cleaning procedure was successful at removing traces of isocyanates, daily cleaning blanks were prepared the morning of the permeation experiments (i.e., before leaving the lab to conduct the field work). Every day for four days, a random cell was loaded with a filter and left in place for approximately one hour. This filter was later analyzed along with all the other samples from the day's experiment. the goal was to determine whether there was any carry-over contamination from the previous experiment. No contamination was found above the limits of detection of the method (LOD of 0.5 μg).

5.4. Permeation Panel Characterization

Thin latex glove material (powder free Gloveworks Industrial Latex Ammex~5mil, TLF46100, lot#0070807-072-120, Shipmt#RS11084) was tested to evaluate performance, reproducibility, and handling of the panels (Table 5.3). All procedures were performed following the SOP presented in Appendix E.3. Each panel was prepared with eight identical glove patches of measured thickness (Baker dial thickness gauge type E142/1B).

The panel experiment was replicated during the same day to evaluate variability due to variables such as clear coat loading and temperature. We wanted to characterize the in-between, within, and day-to-day variability of permeation by the SWYPE and OSHA filter methods. Permeation time was measured from the completion of the second spray application.

SWYPEs (detection limit 6 μg/sample) and PPZ-coated filters (detection limit of 0.05 – 0.10 μg HDI/sample) were used to evaluate permeation at 30 minutes. The first sign of color change of the SWYPE was used to estimate breakthrough time. Calibration curves were developed for PPZ-coated filter and SWYPE RGB analysis for the specific hardener used (PPZ-coated filter calibration with R^2=0.99 and SWYPE calibration with R^2=0.87).

Table 5.3. Permeation Panel Characterization Experiments

Date	Experiment	Factors	Response variable	Measurements**
May 27, 2008	Between- and within- panel characterization	Glove type (1): thin latex Clear coats A (1): Clear A, Reducer I	Breakthrough time* (SWYPE)	Time at color change (time)
			Permeation at 30 minutes after second spray (SWYPE & OSHA filter)	Mass permeated in area and time
May 28, 2008	Day-to-day characterization	Glove type (1): thin latex Clear coats A & B (2): Clear A, Reducer I & Clear B, Reducer I	Breakthrough time* (SWYPE)	Time at color change (time)
			Permeation at 30 minutes after second spray (SWYPE & OSHA filter)	Mass permeated in area and time

*Breakthrough time observed on the permeation cells when color is visible through the glove material.

**Loading was measured as mass of clear coat dry solids/area.

Permeation cells using SWYPEs were positive (red) within 2 minutes of the start of the experiments, indicating immediate permeation of isocyanates through thin latex gloves (detailed data in Appendix E.9). The histogram in Figure 5.9 illustrates the variability in total isocyanates permeation detected by the SWYPE through latex per panel and per day. In parallel, the histogram in Figure 5.10 illustrates the variability in total isocyanate permeation through latex per panel and per day obtained by using PPZ-coated filters (detailed data in Appendix E.10). The total mass of isocyanates was equivalent to the sum of HDI and IPDI monomer. For those samples below detection limits, a zero permeation was assigned. No oligomer species (LOD of 0.1 µg) were detected by the PPZ-coated filters analyzed by modified OSHA42/PV2034.

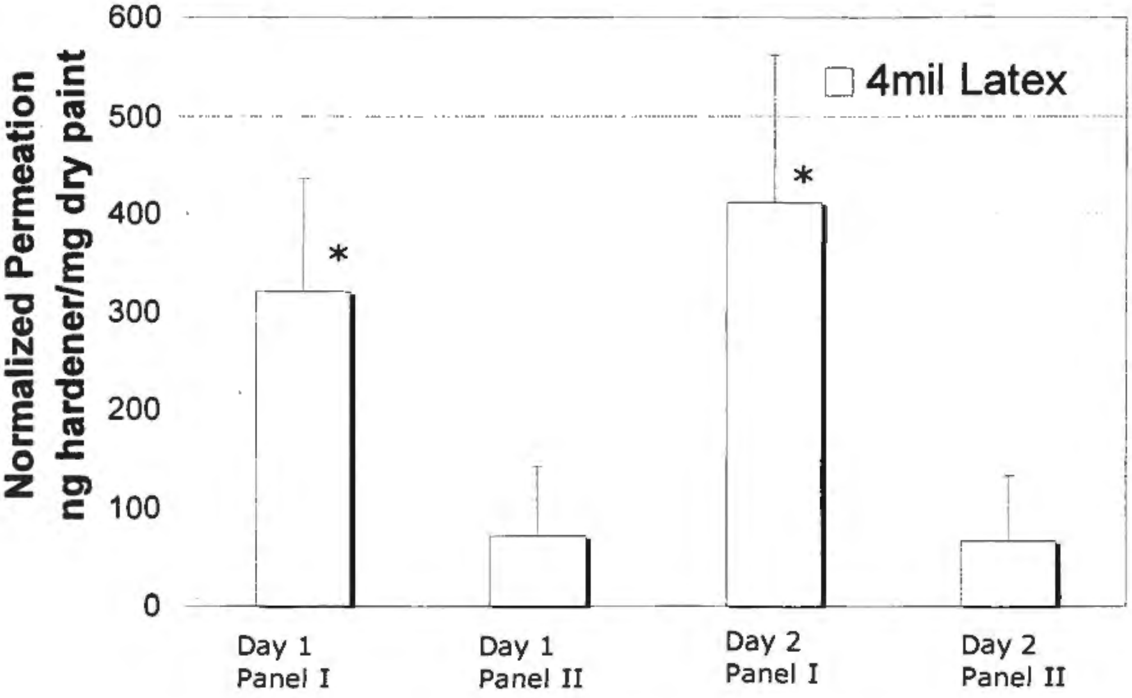


Figure 5.9. Isocyanate Permeation (30 min post-spraying) Using SWYPE RGB Analysis for Thin Latex (4mil). Permeation normalized by the mass of dry clear coat loaded. *At least one sample below detection limit, <3 µg hardener.

Permeation variability was assessed by one-way ANOVA for factors such as day, clear coat, and panel; with only panel having a significant difference in permeation for both PPZ-coated filter (F = 8.1 p-value = 0.013) and SWYPE (F = 14.4 p-value = 0.002). Some of the variation for both SWYPEs and PPZ-coated filters could be attributed to the different clear coat formulations, but there was no significant difference among clear coats A and B. Day 1 displays similar differences between Panel I and Panel II than day 2 panels even though different clear coats were used. Temperature did not appear to contribute to the variability of the experiment. The temperature measured on both days were fairly stable and similar: approximately 72F (+/-1F) and 50%RH (+/-1%RH). Some of the variability, at least for the SWYPEs, may be attributed to partial color transfer from the SWYPE to the glove material being tested. This was evident after inspecting the test materials while disassembling the cells.

Coating thickness on a metal strip showed that the clear coat application was fairly consistent, with a thickness of 0.06 mm (CV=24%, n=20). The average dry coating loaded per 1-inch diameter surface was 34mg (5.5%CV from panel to panel and up to 13% within panel). This mass of dry coating was equivalent to 72.6 mg of wet coating (by using the information on percent of solids). Since the percentage of isocyanates in wet coating for both formulations was 13.9%, approximately 10 mg of isocyanates were loaded on each permeation cell.

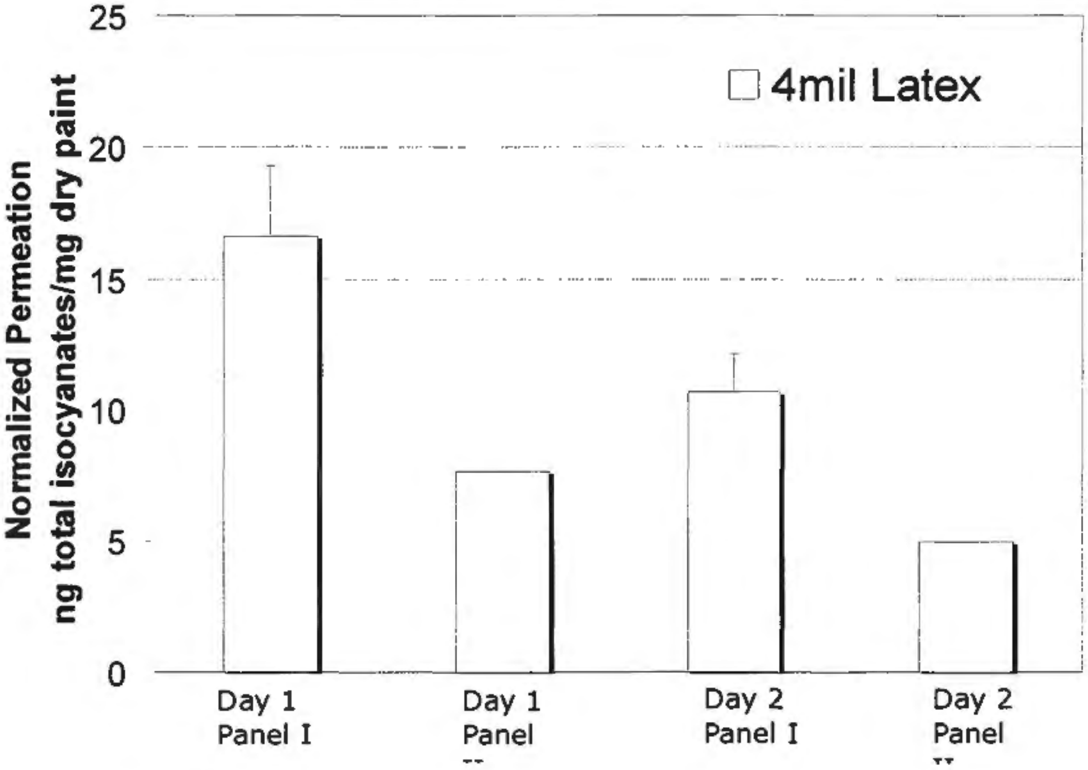


Figure 5.10. Isocyanate Permeation (30 min post-spraying) Using PPZ-coated Filters and Analyzed by Modified OSHA 42/PV2034 Method for Thin Latex (4mil). Permeation normalized by the mass of dry coating loaded.

5.5. Discussion

The improved permeation panel represents a viable method to evaluate the permeation of dermal protective materials. Permeation of reactive aliphatic diisocyanates was evidenced by the immediate color change of the SWYPEs, and further verified by the measured mass of isocyanates on the PPZ-coated filters . Loading on filters of the clear coat had acceptable uniformity (~20% variation for prototype and <13% for final design). The permeation panel performed as expected under spray conditions and reuse. The design of the panel and permeation cells was successful in that it was easy to use, samples were easily loaded and unloaded, and we did not see any interferences or contamination problems. Temperature was controled under typical work conditions.

Results from the permeation panel prototype showed reasonable levels of permeation measured with PPZ-coated filters when compared with the improved permeation panel (prototype average thin latex permeation was 0.6 μg HDI for the prototype characterization and 0.3 μg HDI for the improved permeation panel characterization). The highest permeation for both SWYPEs and PPZ-coated filters for the prototype experiments was with thin latex. The improved permeation panel also showed detectable permeation of thin latex material. During the prototype experiments, one sample exhibited oligomer permeation. We suspect that this was due to penetration of the clear coat mixture or contamination while unloading the media, for the following reasons: 1) the test material was a thick latex and thus unlikely to have more permeation than thin latex and 2) we did not detect any oligomer permeation with the improved permeation panel. Lastly, permeation measurements from the panel prototype provided valuable information with which to design our experiments.

The preferred method to measure loading was PTFE filters. Standardized loading measurements provided uniform loading (approximately 13%). Loading measurements provided the means for normalization in-between panels due to differences on clear coat sprayed. Normalization was performed by dividing the mass of permeated isocyanates by the mass of dry paint loaded. To facilitate normalization, the area exposed to the clear coat was the same for both the test material and the PTFE filter. Normalization could alternatively be presented by describing the total mass of isocyanates (or NCO mass) contained in the mass of dry clear coat.

Calibration with the RGB analysis was performed per mass of hardener loaded on the SWYPE. Note that the units are in ng of hardener per mg of dry clear coat. Only a fraction of this mass would represent the amount of isocyanates that permeated. When comparing Figure 5.9 and 5.10, SWYPE permeation results were 20 times higher compared with PPZ-coated filters. This difference in permeation is significant and is mostly due to the differences in units used for the calibrations. The RGB analysis measures mass of hardener without being specific to the isocyanates studied, whereas PPZ-coated filters measure specific species of isocyanates. PPZ-coated filter data are presented as total isocyanates, which includes the sum of all detected species. Permeation results provided only detectable HDI and IPDI monomer but no oligomer species. More specifically, the permeated mass of total isocyanates reported in the histograms relates to the total mass of molecules containing isocyanate (NCO) groups.

Modifications on the SWYPE calibration from Chapter 2 using the RGB analysis, were necessary because the interaction with the test materials with mineral oil constrained the use of developing solution. The calibration of the SWYPE was performed by wiping freshly spiked surfaces so that standards were as homogeneoulsy loaded as possible. Direct spike of the SWYPE would have been an easier calibration, but it would not necessarely mimic the homogeneous color exhibited by the SWYPE typical of the permeation experiments.

If the average of all PPZ-coated filters data points is divided by the average of all SWYPE data points, we obtain 0.043. This means that the mass on PPZ-coated filters is approximately 4.3% of that found by the SWYPE. We know that the coating formulations contained 13.9% isocyanates with less than 1% as monomers. The SWYPE seem to be detecting more than that contributed by the monomer which may indicate the SWYPE is detecting some polymeric isocyanates.

It is encouraging that both SWYPEs and PPZ-coated filters showed the same pattern of permeation throughout the panels and days. Permeation variability assessed by one-way ANOVA determined that only panel had a significant difference in permeation for both PPZ-coated filters (F = 8.1 p-value = 0.013) and SWYPE (F = 14.4 p=value = 0.002). This means that there were some differences between panels that were greater than within panels, and this variance was higher than that attributed to clear coat and day. Further standarization could include decreasing the variability within spray application by controlling the exact number of passes of the spray gun and the time interval between applications. These factors can be controlled and this was shown in later experiments (included in Chapter 6). Standardization of experiments will be crucial to diminish the variability between panels so data from different panels can be pooled.

Variation within a panel can be mainly attributed to small variations in time, quality of the test material, and loading homogeneity. Variations between panels can be mainly attributed to temperature (which is related to day), loading, and clear coat. To reduce differences in test material quality, we used gloves from the same box. As for time, permeation cells from a panel were dissasambled simulatenously. Exact disasembling time was noted to account for differences. Small variations in the stretching of the test materials when loaded into the permeation cells may contriute to panel variability. Stretching of the test material makes testing more realistic since a glove is stretched when use, however its possible that stretching is different from glove to glove.

Small variations should be expected from mixing of different batches of clear coat. To minimize this uncertainty, an aliquot of the clear coat mixture could be collected in the field for subsequent analysis. These results could be then compared with bulk analysis of the unmixed components.

We concluded that using PPZ-coated filters were the prefered media to measure permeation; color transfer from the SWYPEs onto the dermal protective material makes quantification unreliable. SWYPEs would still be useful for immediate screening in the field of different materials tested simultaneously. Even though SWYPEs provided comparable permeation results to PPZ-coated filters, there are different ways of improving further the use of SWYPEs as solid media for the permeation panel experiments. Color change could also be measured on the back of the test materials so that there are no color losses. To do so, calibration would need to be done with the color background of each particular glove studied.

Considering that there was color transfer of the derivatization reagent used for the SWYPEs onto the test materials, it is reasonable to postulate that the same can happen with the PPZ-coated filters. Some of the PPZ excess from the filter may transfer onto the test material. In the case of the SWYPE, the color change was easy to observe but more tests would need to be performed to verify the extent to which this may be happening on PPZ-coated filters. This could be tested by surface spectroscopic analysis of the glove.

SWYPEs provided an estimate of breakthrough time that was below 2 minutes. Gloves were fairly translucent, so the color change was visible from the top surface. No color change was ever persived from the bottom of the SWYPE, which could be viewed from the base window of the permeation cell base. When using test materials that are darker and thicker, the SWYPE color change may not be recognized until the permeation cells are opened. To compare these results with quantitative estimates of breakthrough using PPZ-coated filters, more experiments would need to be performed. Permeation measurements could be repeated at different time points, so that a permeation rate and breakthrough times are calculated. To verify the SWYPE's breakthrough time of <2 min, we also suggest evaluating permeation at different time points using the SWYPE RGB analysis.

Considering that isocyanates in the total wet mixture comprised approximately 13.9%, we can conclude that the mass of isocyanates that the permeation cells were loaded to was approximately 10 mg of the 34mg of dry coating. Using PPZ-coated filter permeation results, the average thin latex permeation at 30 minutes was 336 ng of total isocyanates. This indicates that only a very small percentage of loaded isocyanate permeates through thin latex (0.003%). However, since isocyanates are known sensitizer the dose-response for asthma may not be linear.

A thirty minute time point was chosen to measure permeation because it reflects a typical clear coat application. We wanted to determine whether gloves would be protective in case the painter did not change gloves throughout the whole clear coat application. The permeation time was measured after the completion of the 2nd spraying. Permeation results using thin latex (30 min after spray application) provide evidence that these gloves are inappropriate for such lengthy spraying applications. Further, the immediate color change of the SWYPE suggests that thin latex gloves may not be appropriate for shorter duration spray applications. Verification of the breakthrough time for thin latex gloves using the PPZ-coated filters would provide further information to inform how long gloves should be used by painters (Chapter 6).

The SWYPE RGB method in Chapter 2 described how the SWYPE response is color stable for up to 20 minutes after sampling. We assumed that within the 30 minute time-frame in the characterization experiments, the color of the SWYPE was stable because the cell was sealed, thereby reducing the potential for color degradation. However, more experiments may be needed to assess color stability for longer duration permeation experiments.

A disadvantage of the permeation panel experiments is that the permeation panel is a field-testing device, so results could depend highly on the quality and standardization of the work performed in the field. Even though results have been fairly reproducible (no significant day-to-day variability found), further improvements are possible so that panel to panel variability is also not significant (as shown in later experiments in Chapter 6). These improvements were only possible because we worked with the same painter. The standardization process ultimately would involve automating by a robotic hand for the spraying of the panel. Ideally, the automated spraying would be inside a controlled booth designed specifically for permeation panel experiments. This would allow numerous tests to be completed fairly rapidly. There is a commercial robotic option which is used for research and development of paints (Spraymation, Fort Lauderdale, Florida) that can be considered for future experiments.

We acknowledge that a possible disadvantage of using solid media to collect permeants, besides being time intensive, is that swelling of the test material may prevent uniform contact of the specimen with the solid collection medium (Anna 2003). We did not observe considerable swelling of the test materials during the times studied. Another potential disadvantage of the current permeation system is that it measures permeation at work temperature conditions but not at painter's hand temperature conditions. This could be easily fixed by adding a temperature controlled case that would keep the permeation cells during the experiment at body temperature.

An advantage of the permeation panel is that it provides information that is more relevant to the work conditions of painters. Traditional standard measures of permeation usually resemble conditions of immersion, which are fairly unlikely during spray application. With the permeation panel, the test material is challenged with a layer of clear coat that mimics a gloved hand being sprayed over or spilled upon. Although this is a worst-case scenario, we have observed small spills while in mixing rooms and workers wearing thin latex gloves while spraying his hand directly when holding a small car part. Besides permeation from clear coat formulations, the permeation panel would allow study of many other polymerizing materials, including foams, liners, adhesives, and resins.

There is much to learn about the mass transfer mechanisms behind the polymerization process and all the variables that would need to be measured to be able to model such processes. Some examples include understanding the influence of loading, temperature, and solvent composition in the mass transfer. We encourage future studies in this area but it may be challenging because much information about product formulation remains proprietary. We suspect that polymerization may be stratified while drying, thereby impacting the mechanisms of transport of the permeants from the polymerizing material to the glove. The process is dynamic in time and there is transfer in different directions, some from the polymerizing material to the air and some to the test material.

Within a permeation panel several test materials under the same conditions could be compared (as demosntrated in Chapter 6). Further, not only chemicals with low volatility or low water solubility can be tested. We are already working on measuring solvent permeation using the permeation panel. A charcoal cloth or colorimetric pad that changes color with the presence of solvent (such as permea tec by CLI labs) are used as solid media. There are also many other chemicals that could be tested using an especific and appropiate solid media.

5.6. Conclusions

Dermal protective clothing still remains the most practical means of protecting skin in many workplaces. Yet for compounds that have low volatility and water solubility, like isocyanates, there is not enough information to be able to select a product based on protection. No method to measure permeation is available for complex mixtures that polymerize. There is a need, therefore, for manufacturers and standard-setters to consider new methods for the generation of permeation data for such chemicals, especially when tests are performed under realistic work conditions, like with the permeation panel. Ideally, product substitution or process change would be prefered rather than using dermal protective clothing, but unfortunately this is not always possible.

The permeation panel succeded in providing permeation data under spray application conditions. Standardization of experiments is crucial to minimize the variability among panels and within panels. Variations among panels can be attributed mainly to differences in temperature, loading, and clear coat - when the same painter applies the coating. Spraying standarization, including controlling the exact number of passes of the spray gun and the time interval between applications also represent potential improvements. Variation within a panel can be attributed mainly to small variations in sampling time, quality of the test material, and loading homogeneity. Most of these variables can be controlled with a systematic field approach and normalizing for differences in loading in between panels. Prior to using the permeation panel, tests could be performed to ensure quality and homogeneity of representative test material and clear coat samples. The standardization process would ultimately involve automating using a robotic hand for the panel spraying.

In conclusion, the permeation panel is a practical device that can provide reliable measures of permeation for several test materials under typical working conditions. Loading assessment determined that the clear coat was uniformily sprayed throughout the panel and provided means for normalization of the data. Further, reproducing the permeation panel should be cost effective, especially if many permeation cells are machined at the same time. The panel has no moving parts, is easy to clean, reusable, and its coating is chemically resistant. There is great potential for the use of the permeation panel with different polymerizing formulations and to measure different permeants. Results from the permeation panel can inform recommendations to workers to improve work practices and reduce illnesses linked to dermal exposures, such as dermatitis and work-related asthma (like that described in Chapter 6).

5.7. Notes to Chapter 5

Anna D. H. Chemical Protective Clothing, 2nd edition. (2003), 530 pages

ASTM F739-07 Standard Test Method for Permeation of Liquids and Gases through Protective Clothing. Materials under Conditions of Continuous Contact. Annual book of ASTM standards by American Society for Testing and Materials. Philadelphia, Pa: ASTM, 1970-2001. 7 Edition. Vol. 11.03

Bello D, Herrick CA, Smith TJ, *et al.*(2007): Skin Exposure to Isocyanates: Reasons for Concern. Environ. Health Perspect. 115(3):328-335

Boman A, Estlander T, and Wahlberg JE. Protective Gloves for Occupational Use. 2nd Ed. CRD Press. Published by Informa Health Care, (2004). 343 pgs.

Ceballos DM, Yost MG, Whittaker SG, *et al.* (2009): Objective Color Scale for the SWYPE Surface Sampling Technique Using Computerized Image Analysis Tools. J. Occup. Environ. Hyg. (in press)

Ehntholt DJ, Cerandolo DL, Bodek I, *et al.* (1990): A test method for the evaluation of protective glove materials used in agricultural pesticide operations. AIHA J. 51:462-468

Evans PG, McAlinden JJ, Griffin P (2001): Personal protective equipment and dermal exposure. Appl. Occup. Environ. Hyg. 16(2):334-7

Klingner TD and Boeniger MF (2002): A critique of assumptions about selecting chemical resistant gloves: a case for workplace evaluation of glove efficacy. AOEHJ 17(5):360-367. See file on-line at: http://www.clilabs.com/clidownloads.htm (file: GLOVEPAP1-final.pdf)

Mickelsen RL, Roder MM, Berardinelli SP (1986): Permeation of chemical protective clothing by three binary solvent mixtures. AIHA J. 47(4):236-40

Chapter 6

PERMEATION PANEL EXPERIMENTS

6.1. Introduction

Gloves are used to protect one of our most valuable tools – our hands (Boman *et al.* 2004). Our hands can do marvelous things and perform many tasks. These tasks may require the use of gloves for protection against exposure to hazardous physical, chemical, and biological agents during the normal workday. Gloves are barriers between our skin and the hazard encountered (Boman *et al.* 2004). Finding the most appropriate glove then is essential. This study centers on testing the chemical protective gloves used in the collision repair industry.

Paint spraying and mixing processes present an opportunity for an inhalation and dermal exposure hazard. While the majority of painters wear respirators while spray-painting, they do not necessarily wear gloves. About 50% of autobody shop owners in Washington State reported that their painters used latex gloves, 40% used nitrile gloves, and 5% did not use gloves (Whittaker and Reeb-Whitaker, 2009). Observations from the field study "Evaluating Isocyanate Exposures in Collision Repair Workers" in Washington State, a collaboration between UNC, SHARP and UW, suggest that painters commonly used inadequate protective clothing. Fifty percent of shops use latex gloves. Some painters preferred thin gloves because of desired dexterity; however we observed that >30% of painters used thicker latex, nitrile, or neoprene gloves (6mil – 14mil). More on the use of dermal protective clothing and the need for testing protective clothings' efficacy is described in Chapter 1 and 3.

Berardinelli (1988) recommended the use of butyl rubber gloves for with irritant contact dermatitis who spray-painted at an automobile dealership. However, the use of butyl rubber gloves in autobody shops has not been reported elsewhere (Whittaker and Reeb-Whitaker, 2009; Sparer *et al.* 2004). Nitrile rubber gloves are fairly comfortable and have been recommended over latex rubber (EPA 1999, PPG 1997, OSHA 1999). However, none of these documents address thickness in their recommendations. Further, no systematic study of the permeation of gloves against isocyanates has ever been conducted and there is no permeation and breakthrough time information for aliphatic isocyanates and gloves used in the collision repair industry. A novel field testing device or permeation panel was therefore developed

(Chapter 5) to use under spray conditions and to measure permeation of low volatile and water soluble agents like isocyanates in clear coat formulations.

The main goal of this project was to standardize the use of a permeation test panel. We evaluated the chemical protective gloves commonly used in the collision repair industry for their resistance to isocyanates. Our specific aims were to: 1) perform screening experiments to evaluate glove protection based on glove type and thickness with SWYPE and PPZ-coated filters; 2) validate screening experiments by using a modified ISO-CHEK method; 3) measure the permeation rate of the most commonly used gloves (thin latex and thin nitrile); and 4) summarize the findings with best-practice recommendations for glove usage in auto body painting. The testing included the following glove types: thin latex (~4mil), thick latex (~14mil), thin nitrile (~5mil), and thick nitrile (~8mil). Three different clear coat formulations were chosen for representativeness, although our study did not attempt to determine the effect of solvents on isocyanate permeation.

6.2. Methods

6.2.1. Protective Gloves Tested

Gloves were selected based upon their usage in the collision repair industry, as described in Chapter 3. Latex and nitrile were chosen as priorities for testing because of their common use in the field. Thickness of the gloves was measured using a Baker dial thickness gauge type E142/1B. To minimize variability in the quality of gloves, all glove types were drawn from the same box. More specifically, the following gloves were tested:

- Thin latex (powder free Gloveworks Industrial Latex Ammex~5mil, TLF46100, lot#0070807-072-120, Shipmt#RS11084),
- Thin nitrile (Xtreme Nitrile Industrial Gloves, powder free, Ammex 5mil, XNPF46100, Lot#200712, Shipmt#RS11333),
- Thick nitrile (8mil M-Safe 3277, powdered free, industrial grade, Lot#32779707),
- Thick latex (15mil M-Safe 3418, examination glove, powdered free).

6.2.2. Selection of Isocyanate Clear Coat Formulations

Aliphatic isocyanate-containing clear coats were chosen for the permeation panel experiments. Mixtures of diisocyanate monomers and polyisocyanates are used as catalyst hardeners in two-part polyurethane paint systems, primers, sealers, and basecoats. However, the final "clear coat" usually contains the highest isocyanate concentrations (Sparer *et al.* 2004) and may result in higher exposures. Clear coats are the clear (non-pigmented) top-coats that are applied over base-coat paints. In the auto body shop, painters typically combine three constituents to yield the final clear-coat spray mixture. The first constituent is the "clear", which contributes the polyols (plus other solids and organic solvents). The second constituent is the "hardener", which contains the isocyanates. The final constituent is the "reducer" or "thinner", which lowers the viscosity of the mixture for spray application.

Within the solvent groups present in clear coat formulations, those affecting the integrity of a painter's gloves were the most important to study. Glove protection generally is compromised by degradation of glove materials. The main solvent groups considered when choosing the clear coat mixtures were ketones, acetates, and aromatics. A database of clear coat components, mixing ratios, and ingredients for the most commonly used clear coats was used to select potential clear coat formulations for the permeation experiments (survey data from the UNC-SHARP-UW field study in Washington State). Most commonly-used clear coats and were selected first, in particular, those using a well characterized hardener (same hardener used in Chapter 3 inter-method study). The solvent content of a combination of the selected hardener with 6 clears and 6 different reducers was studied. Ingredients listed on manufacturer's MSDSs were grouped into chemical functional groups, such as aliphatic hydrocarbons, aromatic hydrocarbons, ketones, acetates, alcohols, isocyanates, and others. Mixing ratio information was used to determine the final average solvent content in the clear coat mixtures.

Three clear coat formulations using two different clears (named A and B for confidentiality purposes) and two different reducers (named I and II for confidentiality purposes) were chosen based solely on MSDS base calculations, as follows: Clear A / Reducer I, Clear A / Reducer II, and Clear B / Reducer II. These formulations were chosen based on the solvent content that specifically affect the glove materials studied and the frequency of use (confidential information provided by the manufacturer). Bulk samples were taken to the lab on the day of the permeation experiments for solvents analysis.

Clear coats were mixed at the ratios suggested by the manufacturer (4 part clear coat, 1 part hardener, and 1 part reducer). These formulations contained the same hardener that was characterized extensively by chemical bulk analysis (Chapter 3). These formulations used different clear or reducer components but contained the same isocyanate content with slightly different solvent content. Prediction of the solvent content was based on the MSDS and mixing ratio information of the product and corroborated with bulk chemical analysis for all unmixed parts.

6.2.3. Permeation Panel

Description, handling, and procedures were described in Chapter 5. Booth flow measurement procedures were also described in Chapter 5. Temperature and relative humidity (RH) data collection was also collected as described in Chapter 5. Experimental procedures followed the SOPs presented in Appendix E.3 and E.7. Modifications in the methods section compared to chapter 5 are as follows:

6.2.4. Permeation Measurement Methods

Isocyanates that permeated the test materials were collected in several solid media for later analysis, as described in Chapter 5. In brief, colorimetric SWYPEs for aliphatic isocyanates (CLI lab, part No. 1023 described in Chapter 2) were used to provide an immediate estimate of breakthrough and to provide semi-quantitative permeation estimates by RGB analysis (Chapter 2 and Ceballos *et al.* 2009). Glass fiber filters coated with 1-(2-pyridyl)-piperazine (PPZ) were used for analysis by modified OSHA 42/ PV2034 (HPLC-UV described in Chapter 4), which measures HDI, IPDI, and total oligomers. In Chapter 4 we suggested that when doing bulk analysis the IPDI monomer cannot be measured because artifactual monomer can be detected. Fortunately, for the samples analyzed here, artifact generation was not a problem and we obtained data for IPDI monomer using the modified OSHA 42/PV2034 method. As a validation step (beyond what was described in Chapter 5), we also performed experiments using filters analyzed by the modified ISO-CHEK method: 9-(methylaminomethyl)anthracene or MAMA impregnated fiber glass filters and PTFE filters that were placed in glass vials after sampling with 1-(2- methoxyphenyl)piperazine or 2-MP derivatization solution (described in more detail in Chapter 4). These filters provided a quantitative permeation result. PPZ-coated filters were analyzed for both monomers and oligomers, while MAMA-impregnated fiber glass filters were analyzed for monomers, and PTFE filters were analyzed for oligomers (more details on analysis is provided in Chapter 4).

6.2.5. Loading Measurements

Loading was assessed as described in Chapter 5. The mass of total isocyanates detected on the solid media was normalized by dividing by the average mass loading of dry clear coat in the panel. This normalization was used to account for the differences in clear coat applied between panels.

Homogeneity of the clear coat application was evaluated by assessing the spatial variation of the loading of mass of dry clear coat throughout the panel. Spatial variability was studied by calculating coefficients of variations within sections of the panel. Horizontal %CV loading was compared with vertical %CV loading and total average %CV to understand homogeneity of the panel sprayed surface. Each panel was comprised of three horizontal and four vertical sections (refer to Figure 5.7 and 5.8 in Chapter 5). Taking Panel 1 as an example, the top horizontal section included loading ports 18-21, the bottom horizontal section included loading ports 26-29, and the middle horizontal section included loading ports 22-25. Also for Panel 1, the far left vertical section included loading ports 18, 22, and 26 while the far right included loading ports 21, 25, and 29.

6.2.6. Percent Solids of Clear coat

To assess surface loading for the applied clear coat mixture, the total mass applied to the surface was calculated based on the residual non-volatile fraction (percentage of solids) on the filters. This procedure is similar to that described in the prototype (Chapter 5), with the difference that PTFE filters were used in these later experiments. The dry weight of clear coat formulation found on PTFE filters was converted into a volume of wet clear coat using the fraction of solids and the clear coat density. The non-volatile fraction of the clear coat was estimated in a separate spiking experiment. First, the clear coat density was determined by weighing a known volume in a closed glass vial. Three PTFE filters were desiccated in a vacuum oven for 1 h (25 °C, 15 psi) and pre-weighed in a microbalance with an anti-static device. Clear coat (40 μL) was then added to each filter. Filters were dried on watch glasses for 1 h in a vacuum oven and post-weighed. The clear coat density and the percentage of solids in the coating were calculated and compared to data reported on the manufacturer's technical sheets. The percentage of solids reported by the manufacturer for each product component was averaged based on the mixing ratios of the product.

6.2.7. Thickness of Clear coat

Clear coat thickness was determined by spraying metal sticks immediately before the panels were sprayed. One side of the stick was taped; the thickness of the clear coat was equal to the thickness of both the stick and the clear coat minus the thickness of the stick. Using a digital caliper, the thickness of the clear coat film was measured for each panel, for each coat layer, and for each clear coat formulation.

6.3. Permeation Panel Experiments

6.3.1. Permeation Panel Screening of Gloves Experiments

SWYPEs, OSHA PPZ-coated filters, and ISO-CHEK filters were used to study the permeation of different glove materials, as described in Table 6.1. Thirty minutes of permeation time was chosen because this was an approximate average of how long gloves were used before they were discarded in the field (Chapter 3). Breakthrough time and permeation at fixed time intervals (30 minutes) were measured following the procedures outlined in Chapter 5. The panels were prepared with duplicate swatches of glove materials in randomized locations. Two types of clear coat were tested in random order throughout the first tests (Clear A / Reducer I & Clear B / Reducer I, May 29 & 30, 2008). Two other types of clear coats were tested during Oct 29 & 30, 2008 (Clear A / Reducer I & Clear B / Reducer II). Comparison of the filters and SWYPEs were made to assess differences in permeation at 30 minutes for the different gloves and different clear coats. Comparison with the ISO-CHEK method was made to validate findings with the PPZ-coated filters.

Table 6.1. Permeation Panel Screening of Gloves Experiments

Date	Permeation Solid Media	Factors	Response variable	Measurements**
May 29 & 30, 2008	SWYPE & PPZ-coated filters (OSHA Method)	Glove type (2): thin latex & thin nitrile Clear coats (2): Clear A / Reducer I & Clear B / Reducer I	Breakthrough time* (SWYPE)	Time at color change
			Permeation at 30 minutes after second spray (SWYPE & OSHA filter)	Mass permeated in area and time
Oct 29, 2008	MAMA coated filters and PTFE filters (ISO-CHEK Method)	Glove type (2): thin latex & thin nitrile Clear coats (2): Clear A / Reducer I & Clear B / Reducer II	Permeation at 30 minutes after second spray	Mass permeated in area and time
Oct 30, 2008	PPZ-coated filters (OSHA Method)	Glove type (4): thin latex & thin nitrile & thick latex & thick nitrile Clear coats (2): Clear A / Reducer I & Clear B / Reducer II	Permeation at 30 minutes after second spray	Mass permeated in area and time

*Breakthrough time measured from the top when color is visible through the glove material.
**Loading will also be measured as mass of clear coat dry solids/area to be used as a covariate by various methods.

6.3.2. Permeation Panel Permeation Rate Experiments

Experiments to determine permeation rate for both thin latex and thin nitrile are described in Table 6.2. Four identical swatches for each glove test material (thin latex and thin nitrile) were mounted in random locations with PPZ-coated filters on the back surface to measure permeation at different time points. Four time measures per glove and two different gloves yield eight sampling ports per permeation panel. Two types of clear coat were randomly tested throughout the first permeation rate experiment (Clear A / Reducer I & Clear B / Reducer II, Oct 13 & 28, 2008). One type of clear coat was tested in second permeation rate experiment (Hardener with Clear A / Reducer I, March 20, 2009). A filter from each test material was removed at different time intervals after the end of the second (final) spraying application. Permeation estimates combined with loading data were used to calculate permeation rates standardized by surface loading or the slope of the linear fit. Breakthrough was calculated by observing the time point at which permeation first started.

Table 6.2. Permeation Panel Permeation Rate Experiments

Date	Permeation Solid Media	Factors	Response variable	Measurements
Oct 13 & 28, 2008	PPZ-coated filters (OSHA Method)	Glove type (2): thin latex & thin nitrile Clear coats (2): Clear A / Reducer I & Clear B / Reducer II	Permeation at 5, 10, 20, 30 minutes	Slope of curve and extrapolated breakthrough time
March 20, 2009	PPZ-coated filters (OSHA Method)	Glove type (2): thin latex & thin nitrile Clear coats (2): Clear A / Reducer I	Permeation at 40, 50, 60, 90 minutes after second spray	Slope of curve and extrapolated breakthrough time

6.4. Results

6.4.1. Protective Gloves Thickness

The gauge-measured thickness of the different type of gloves was: thin latex with 4mil (1.6% CV), thin nitrile with 4.8mil (4.4% CV), thick nitrile with 7.8 mil (3%CV), and thick latex with 13.9mil (2.1% CV). The gauge instrument had a precision of +/- 1 mil in the range of 0-100 mil. Lower precision would have been possible if the dial for 0-1 mil resolution had been been functioning.

6.4.2. Composition of Clear Coat Formulations

The MSDS for the hardener used reported a content of 0.1-10% for HDI monomer, 0.1-10% for IPDI monomer, 40-70% for HDI polymer, and 15-40% for IPDI polymer. Hardener information from the MSDS versus the manufacturer (from Chapter 4) is presented in Table 6.3. Prediction of the solvent content was based on the MSDS values and mixing ratio information of the product from manufacturer technical sheets (as shown in Table 6.4). Bulk analysis by NIOSH 1500, GC-FID for all unmixed parts (as shown in Appendix E.11) was combined into the different solvent groups in Table 6.5.

Table 6.3. MSDS Versus Manufacturer Hardener Information

			Hardener in clear coat formulation, dilution 4:1:1	
Compound	**MSDS**	**Manufacturer Value**	**MSDS**	**Manufacturer Value**
	%w/w	**%w/w**	**%w/w**	**%w/w**
	(40-70)		(6.7-11.7)	
HDI polymer	55	47.9	9.17	7.9
	(0.1-1.0)		(0.02-0.17)	
HDI	0.5	0.24	0.09	0.04
	(15-40)		(2.5-6.7)	
IPDI polymer	27.5	35.5	4.58	5.9
	(0.1-1.0)		(0.02-0.17)	
IPDI	0.5	0.24	0.09	0.04
	(55.2-112)		(9.2-18.7)	
Total	83.6	83.9	13.9	13.9

Table 6.4. Clear coat Formulation Range and Average Composition (%w/w) Based on MSDS

Component	**Total Aromatic Hydrocarbon**	**Total Acetates**	**Total Ketones**	**Total Isocyanates**
	(11.7-33.2)	(1.68-5.17)	(8.83-16)	(9.2-18.7)
Hardener / Clear A / Reducer I	22.03%	3.43%	12.42%	13.93%
	(2.4-9)	(1.7-5.2)	(4.2-11.7)	(9.2-18.7)
Hardener / Clear B / Reducer I	5.70%	3.43%	7.92%	13.93%
	(2.4-7.5)	(2.9-7.3)	(3.8-11.2)	(9.2-18.7)
Hardener / Clear B / Reducer II	4.96%	5.09%	7.50%	13.93%

Table 6.5. Clear coat Formulation Average Composition (%w/w) Based on Bulk Analysis

Component	**Total Aromatic Hydrocarbon %w/w**	**Total Acetates %w/w**	**Total Ketones %w/w**
Clear A	28.2	0.90	0.09
Clear B	31.5	<0.04	9.2
Reducer I	21.1	<0.01	31.6
Reducer II	15.6	11	17
Hardener	0.02	<0.01	<0.01
Hardener / Clear A / Reducer I*	22.3	0.6	5.3
Hardener / Clear B / Reducer I*	21	<0.01	11.4
Hardener / Clear B / Reducer II*	23.6	1.8	9

*Weighed average based on component mixing ratios

6.4.3. Percent Solids of Clear Coat

The measured clear coat density was 0.93 mg/μL for Clear A / Reducer I and 1 mg/μL for Clear B / Reducer I (0.03-0.05% CV). The percentage of solids experimentally found in the coating was 50.5% for a clear coat formulation with Clear A / Reducer I and 47.5% for Clear B / Reducer I. These are similar values to the weighed averages per clear coat formulation based on the MSDS values provided by the manufacturer in Table 6.6. PTFE filters were not very absorbent; we observed that for Clear A / Reducer I formulation the aliquot of clear coat formed a bubble and did not dry uniformly. This problem could have contributed to the slightly higher estimate of solid percentage compare to that provided by the manufacturer (50.5% versus 46.8%). Overall, this experiment verified that the information provided by the manufacturer was accurate. Therefore, we only performed this experiment for the first two formulations and subsequently relied on information reported by the manufacturer.

Table 6.6. Percent Solids of Clear Coat Formulation Based on MSDS

Clear coat Component	Specific Gravity	Percent Solids
Clear A	0.9	49.2
Clear B	0.9	48.9
Hardener	1.1	83.9
Reducer I	0.8	0
Reducer II	0.8	0
Hardener / Clear A / Reducer I*		46.8
Hardener / Clear B / Reducer I*		46.6
Hardener / Clear B / Reducer II*		46.6

*Weighed average based on component mixing ratios

6.4.4. Spray Painting and Booth Conditions

Air flow measurements were reasonably consistent from day to day, varying 8.5% with an average of 9423 CFM (Table 6.7). The booth was maintained in good condition: cleaned and filters changed regularly. An example of individual flow measurements and locations in the floor vents for a sampling day are shown in Appendix E.5. Booth air flow data for all experiments are presented in Appendix E.6. Temperature and RH inside the panel and in the spray booth, including experiments from May 2008 to March 2009, are presented in Appendix E.12 (for conciseness, data per every 10 seconds were not presented. Rather, averages per minute or per 5 minutes were tabulated).

For each experiment, clear coat was applied in two separate applications, each lasting an average of 18 seconds. Each application was composed of an average of 6 spray passes per application and an average of 7.7 minutes between applications (to mimic actual product usage when spray-painting). A summary description of spraying conditions for each panel experiment is presented in Table 6.8.

Table 6.7. Summary of Booth Flows on the Day of the Permeation Experiments

Date	Average Left LFM	Average Right LFM	total CFM
27-May-08	87	88	8111
28-May-08	107	104	9805
29-May-08	91	92	8504
13-Oct-08	94	102	9102
28-Oct-08	116	94	9731
29-Oct-08	111	107	10135
30-Oct-08	112	113	10453
20-Mar-09	103	102	9539
Average	103	100	9423
Standard Deviation	11	8	801
%CV	10	8	8

Temperature and RH data are summarized in Table 6.9 for the time periods of the permeation experiments. This includes observations from the beginning of the first spray application to when cells were removed from the booth to be disassembled. The temperature was maintained by by turning the heater on and off, as needed. The actual average booth temperature was 73 °F (+/-8 °F variation within a sampling period and +/-3 °F within day to day) while the actual temperature inside the permeation panel was 71°F (+/-3 °F variation within a sampling period and +/-3 °F within day to day). Actual average booth RH% was 42% (+/-13% variation within the sampling period and +/-16% within day to day) while the RH inside the permeation panel was also 42% (+/-9 °F variation within a sampling period and +/-17 °F within day to day). Both the right and left side of the booth reported similar average temperatures (73 and 74 °F respectively) and RH (42% for both).

Temperature and RH% for the sampling period in a typical panel experiment are shown in Figures 6.1-6.2. Figure 6.1 shows how temperature was stable inside the panel and Figure 6.2 shows typical fluctuations outside the panel. Overall, all experiments showed the same trend, with temperature variability higher outside the panel than inside the panel and left of the booth similar to the right of the booth.

Table 6.8. Summary of Spraying Conditions for Permeation Experiments

Date	Panel	Time First Spray	Clear	Reducer	Duration 1st spray sec	No. Passes 1st spray	Duration 2nd spray sec	No. Passes 2nd spray	Time Between Sprays min	Time from end of 2nd spray min
5/27/2008	I	11:11	A	I	21	6	22	6	8	33
	II	12:40	A	I	23	6	25	6	7	27
5/28/2008	I	10:36	A	I	19	5	20	5	3	27
	II	11:51	B	I	18	6	17	6	11	27
5/29/2008	I	10:47	A	I	20	6	16	6	8	30
	II	11:47	B	I	22	6	18	6	10	30
5/30/2008	I	11:10	A	I	24	6	32	6	7	30
	II	12:08	B	I	21	5	20	5	7	30
10/13/2008	I	10:30	A	I	16	6	15	6	9.0	time course*
	II	11:20	B	II	15	6	16	6	7.6	time course*
10/28/2008	I	10:36	A	I	19	6	16	6	8.0	time course*
	II	11:56	B	II	16	6	16	6	7.0	time course*
10/29/2008	I	10:41	B	II	17	6	13	6	7.6	32
	II	12:10	A	I	17	6	14	6	8.0	35
10/30/2008	I	10:17	B	II	17	6	16	6	7.0	33
	II	11:13	A	I	14	6	15	6	9.0	31
3/20/2009	I	10:42	A	I	18	6	15	6	7	time course*
	II	10:50	A	I	16	6	17	6	8	time course*
Average (SD)					19 (2.8)	6 (0.32)	18 (4.6)	6 (0.32)	7.7 (1.6)	30.4 (2.6)**

*Time course defined as: permeation time was different for the different cells. This was used in the permeation rate experiments.

**Time course data excluded from average, not appropriate.

Table 6.9. Summary of Temperature and RH% for Permeation Experiments

		Inside Panel	
Day	Panel	avg T (SD)	avg RH (SD)
		F	%
5/27/2008	I	72.2 (0.57)	47.9 (0.50)
	II	*	*
5/28/2008	I	71.5 (0.40)	51.5 (0.47)
	II	70.3 (0.49)	53.8 (0.57)
5/29/2008	I	71.96(0.42)	39.6 (0.44)
	II	72.74(0.34)	38.8 (0.24)
5/30/2008	I	74.6 (0.40)	32.8 (0.28)
	II	74.1 (0.33)	32.8 (0.27)
10/13/2008	I	68.2 (0.53)	52.8 (4.0)
	II	69.2 (0.82)	49.7 (4.8)
10/28/2008	I	71.3 (1.6)	38.1 (1.8)
	II	*	*
10/29/2008	I	70.7 (0.6)	44.6 (1.2)
	II	*	*
10/30/2008	I	70.9 (0.32)	42.9 (0.36)
	II	*	*
3/20/2009	I	70.6 (0.96)	46.2 (3.5)
	II	71.3 (1.1)	44.7 (2.9)
Average (SD)		71.4 (1.6)	41.7 (8.6)

*Instrument failed to record information

Continued on next page

		Right of the Booth		Left of the Booth		Average Booth	
Day	**Panel**	**avg T (SD)**	**avg RH (SD)**	**avg T (SD)**	**avg RH (SD)**	**avg T**	**avg RH**
		F	**%**	**F**	**%**	**F**	**%**
5/27/2008	I	71.3 (1.5)	49.4 (2.1)	72.1 (1.6)	48.2 (2.3)	71.7	48.8
	II	71.9 (1.6)	51.6 (1.3)	72.4 (1.9)	50.5 (1.7)	72.2	51.0
5/28/2008	I	71.9 (2.0)	51.0 (2.3)	72.3 (2.6)	49.7 (3.3)	72.1	50.3
	II	72.1 (1.8)	52.3 (2.1)	72.4 (2.2)	51.0 (3.6)	72.3	51.7
5/29/2008	I	74.7 (0.32)	30.6 (0.21)	75.0 (0.32)	30.1 (0.26)	74.9	30.4
	II	75.2 (0)	30.4 (0.12)	75.6 (0.35)	29.8 (0.16)	75.4	30.1
5/30/2008	I	76.1 (1.5)	30.1 (0.84)	76.7 (1.5)	29.5 (0.82)	76.4	29.8
	II	75.6 (1.8)	29.6 (1.8)	75.9 (1.7)	29.3 (1.7)	75.8	29.5
10/13/2008	I	72.4 (1.9)	52.0 (2.3)	71.3 (2.0)	52.8 (3.1)	70.7	52.5
	II	70.6 (0.41)	53.7 (1.3)	69.5 (0.3)	55.0 (1.4)	69.8	52.8
10/28/2008	I	71.8 (0.36)	41.7 (0.27)	72.2 (0.6)	40.1 (0.48)	71.8	39.9
	II	*	*	*	*		
10/29/2008	I	72.8 (3.3)	43.3 (6.5)	75.3 (4.1)	40.0 (6.7)	72.9	42.7
	II	*	*	*	*		
10/30/2008	I	74.1 (0.46)	42.2 (0.4)	75.3 (0.54)	40.0 (0.47)	73.4	41.7
	II	*	*	*	*		
3/20/2009	I	73.2 (1.9)	45.3 (3.4)	73.1 (1.8)	44.2 (2.8)	73.2	44.8
	II	73.3 (2.0)	45.0 (3.5)	73.2 (1.9)	43.9 (2.9)	73.2	44.5
Average (SD)		73.1 (1.6)	42.2 (8.5)	73.5 (1.9)	42.3 (8.8)	73.0 (1.8)	41.6 (8.3)

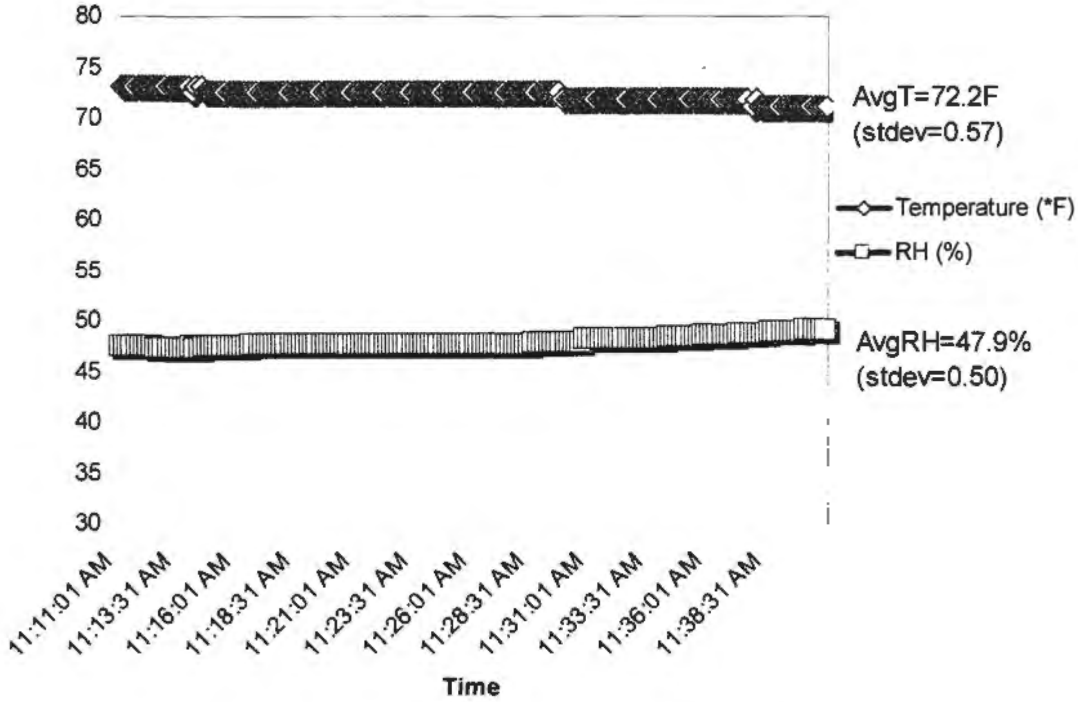


Figure 6.1. Temperature Profile inside the Panel May, 27, 2008 Panel I

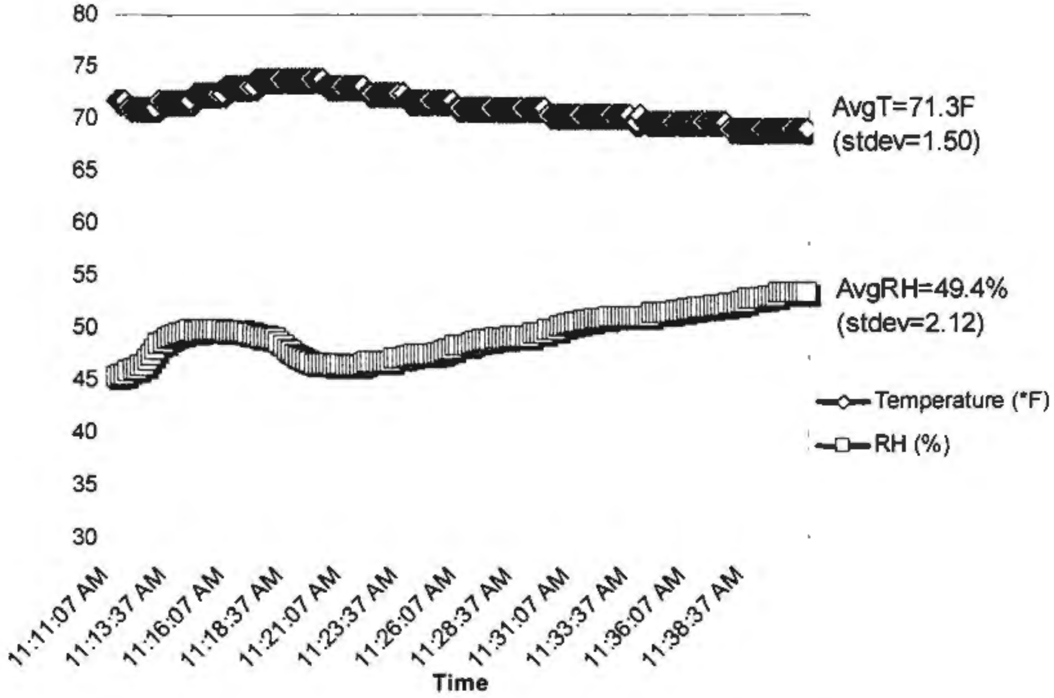


Figure 6.2. Temperature Profile Right of the Booth, May 28, 2008 Panel I

6.4.5. Loading Measurements

Average loading was 34 mg with 13%CV in the range of 29.8-42.6mg (see summary Table 6.10 for loading of dry clear coat for all experiments). Variability of the loading was fairly consistent from day-to-day, regardless of the clear coat formulation, time, or season (average 12.5%CV). Detailed data is found in Appendix E.7 and E.13. Variability within-panel showed that loading of horizontal and vertical sections in the panel had similar variability (for all October experiments, the average horizontal variability was 9.2% while the average vertical variability was 12.7%).

Table 6.10. Summary Loading Dry Clear coat

Date	Clear	Reducer	Panel	Average Mass mg	%CV
5/27/2008	A	I	I	33.68	11.98
5/27/2008	A	I	II	35.83	8.83
5/28/2008	A	I	I	31.46	9.02
5/28/2008	B	I	II	34.80	12.85
5/29/2008	A	I	I	29.35	16.17
5/29/2008	B	I	II	42.57	8.54
5/30/2008	A	I	I	29.51	11.42
5/30/2008	B	I	II	32.97	10.13
10/13/2008	A	I	I	28.16	12.43
10/13/2008	B	II	II	26.79	11.83
10/28/2008	A	I	I	34.14	13.45
10/28/2008	B	II	II	34.47	9.34
10/29/2008	B	II	I	38.60	16.70
10/29/2008	A	I	II	38.52	17.85
10/30/2008	B	II	I	31.88	12.54
10/30/2008	A	I	II	29.36	14.90
3/20/2009	A	I	I	38.08	12.91
3/20/2009	A	I	II	39.76	14.87
Average				33.88	12.54
Standard Deviation				4.41	
%CV				13.01	

6.4.6. Thickness of Clear coat

The thickness of the clear coat film was measured for each panel with a thickness gauge. Summary of results are shown in Table 6.11. At least 2 different readers recorded the measurement of thickness during the first trials to establish the variation of the method based on handling of the caliper. Average thickness for Clear A / Reducer I was: 1 coat 0.03mm (26%CV) and for 2 coats 0.06mm (26%CV). Average thickness for Clear B / Reducer I was: 1 coat 0.03mm (33%CV) and for 2 coats 0.06mm (1.5%CV). Thickness for Clear B / Reducer II was 0.06mm for 2 coats.

Table 6.11. Summary of Clear coat Thickness Measures

Date	Panel	Coats	Clear	Reducer	Reader 1 mm	Reader 2 mm	Reader 3 mm	Reader 4 mm	Average mm	%CV
5/27/2008	I	1	A	I	0.03	0.03	0.045		0.04	
5/27/2008	I	2	A	I	0.05	0.07	0.05		**0.06**	
5/27/2008	II	1	A	I	0.05	0.03	0.03		0.04	
5/27/2008	II	2	A	I	0.07	0.05	0.05		**0.06**	
5/28/2008	I	1	A	I	0.02	0.03	0.02		0.02	
5/28/2008	I	2	A	I	0.07	0.07	0.09		**0.08**	
5/29/2008	I	1	A	I		0.02		0.02	0.02	
5/29/2008	I	2	A	I		0.08		0.08	**0.08**	
5/30/2008	I	1	A	I		0.03		0.02	0.03	
5/30/2008	I	2	A	I		0.05		0.03	**0.04**	
10/13/2008	I	2	A	I	0.05				**0.05**	
Average		1	A	I					0.03	26
		2	A	I					**0.06**	26
5/28/2008	II	1	B	I	0.04	0.03	0.05		0.04	
5/28/2008	II	2	B	I	0.07	0.04	0.08		**0.06**	
5/29/2008	II	1	B	I		0.02		0.02	0.02	
5/29/2008	II	2	B	I		0.07		0.06	**0.07**	
5/30/2008	II	1	B	I		0.04		0.03	0.04	
5/30/2008	II	2	B	I		0.07		0.06	**0.07**	
Average		1	B	I					0.03	33
		2	B						**0.06**	1.5
10/13/2008	II	2	B	II	0.06				**0.06**	

6.4.7. Permeation Panel Screening Experiments

Isocyanates Permeation Using Colorimetric (SWYPE RGB Analysis) and Quantitative Analytical (OSHA) Method

For both latex and nitrile gloves, permeation cells using SWYPEs for permeation measurements were positive (orange to red) within 2 minutes of the start of the experiments. SWYPE used under thin latex gloves were consistently redder in color than those used under thin nitrile glove material. Hardener calibration using the RGB analysis had a correlation of 0.87 (calibration RGB data in Appendix E.14). The histogram in Figure 6.4 illustrates the SWYPE difference in permeation between nitrile and latex gloves (detailed data in Appendix E.15). Some of the variation could be atributed to the different clear coat formulations, although there was no discernable difference between Clears A and B. One-way ANOVA tested different factors including clear coat, day, panel, and glove with none of the variables having a significant difference between groups. However, the SWYPE method was able to distinguish between thin latex and thin nitrile, with higher permeation for thin latex as observed with PPZ-coated filters in Figure 6.5.

Permeation of isocyanates using PPZ-coated filters, described in Figure 6.5 (detailed data in Appendix 16), illustrates that thin latex gloves exhibited greater permeation than thin nitrile ($t = 4.8$, $df = 14$, and p-value=0.0003). Data in the histogram below limits of detection were substituted as zero permeation (LOD of 0.05 μg HDI/IPDI and 0.5 μg oligomers). One-way ANOVA tested different factors, including clear coat, day, panel, and glove. Only glove showed significant variance ($F = 22.9$ p-value = 0.0003). Note that when comparing Figure 6.4 and 6.5, colorimetric permeation results indicate total isocyanates up to 600 ng per mg of dry clear coat, while PPZ-coated filters indicated permeation on the order of 20 ng per mg of dry clear coat. These differences are explained further in Chapter 5.

During the permeation experiments, cleaning blanks were used to assess effectiveness of the cell clean up procedure. Blanks were sampled every day for four days. No traces of isocyanate contamination were detected; permeation cells were cleaned successfully between experiments.

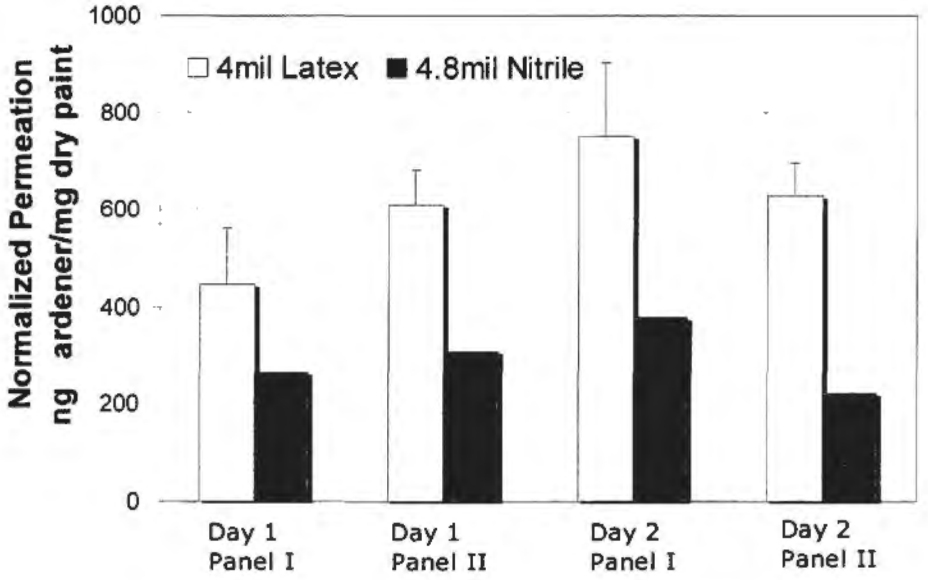


Figure 6.4. Isocyanate Permeation (30 min post-spraying) Using SWYPEs and Analyzed by RGB Method. Permeation normalized by the mass of dry clear coat loaded.

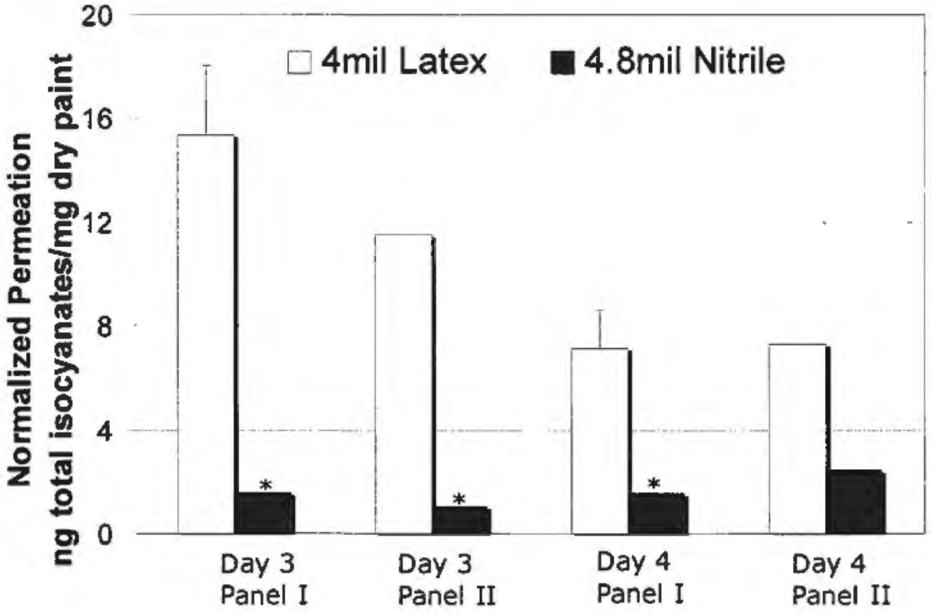


Figure 6.5. Isocyanate Permeation (30 min post-spraying) Using PPZ-coated Filters and Analyzed by Modified OSHA 42/PV2034 Method. Permeation normalized by the mass of dry clear coat loaded. *Below detection limit, <0.05 μg HDI/IPDI and <0.5 μg oligomers.

Isocyanates Permeation Using Quantitative Analytical OSHA and ISO-CHEK Methods

Experiments using ISO-CHEK filters (detailed data presented in Appendix E.17) showed evidence of HDI and IPDI monomer permeation but no oligomer permeation, as was observed previously using the modified OSHA 42/PV2-34 with PPZ-coated filters. Only one sample (nitrile glove) exhibited traces amounts (1.78 μg) of HDI oligomer (isocyanurate), but it was present at levels between the LOQ (5 μg) and the LOD (1.2 μg). HDI, IPDI, and total permeation results in Figure 6.6 show pooled data for both panels. Total permeation represents the sum of HDI and IPDI monomers. Although each panel used a different clear coat formulation (Clear A / Reducer I & Clear B / Reducer II), there was not a significant difference so data were presented together. One-way ANOVA was performed to determine whether panel and glove-type had an effect on the variance. Only glove-type had a significant effect, with thin latex showing more permeation than thin nitrile at a statistically significant level for all species (HDI F = 5.8 p-value = 0.05; IPDI F = 11 p-value = 0.016; and Total F 6.3 p-value = 0.046).

Figure 6.6 and 6.7 show that MAMA filters had a very similar performance to PPZ-coated filters. Monomers of both HDI and IPDI permeated through gloves, with HDI monomer permeation representing the majority for both MAMA- and PPZ-coated filters. Figure 6.7 was created with data from May 29 and 30, 2008 where thin latex and thin nitrile were compared using PPZ-coated filters. Both days used two different clears in the clear coat mixture (Clear A and B) but data were pooled because there were no significant differences based on clear coat formulation.

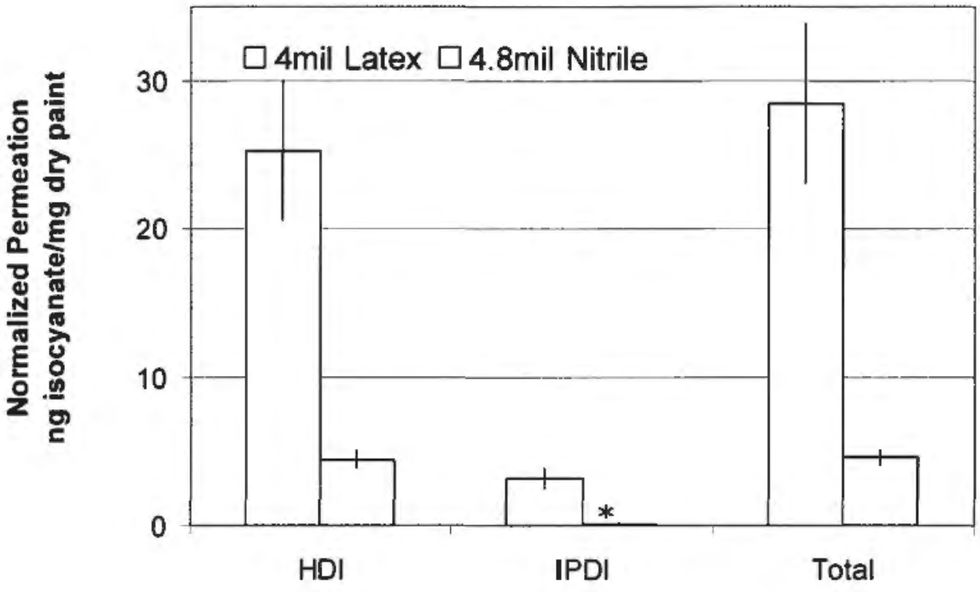


Figure 6.6. Isocyanate Permeation (30 min post-spraying) Using MAMA-treated Filters and analyzed by Modified ISO-CHEK Method. Permeation normalized by the mass of dry clear coat loaded (October 29, 2008, two panels). Only HDI and IPDI monomer were reported; no oligomers were detected. *Below detection limit, <0.001 μg HDI/IPDI.

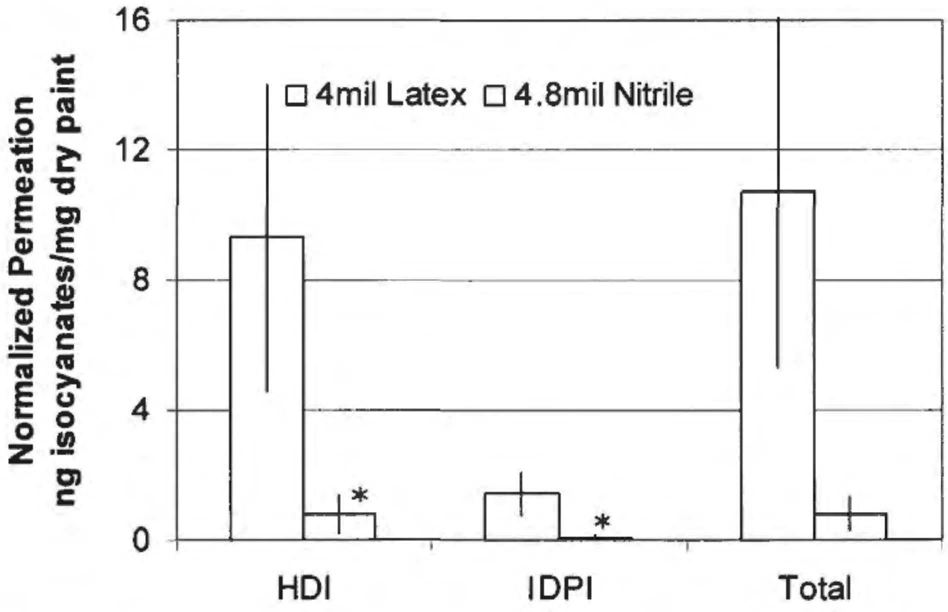


Figure 6.7. Isocyanate Permeation (30 min post-spraying) Using PPZ-coated Filters and analyzed by Modified OSHA 42/PV2034 Method. Permeation normalized by the mass of dry clear coat loaded (May 29 and 30, 2008, four panels). Only HDI and IPDI monomer were reported, no oligomers were detected above quantitation limits. *Below detection limit, <0.05 μg HDI/IPDI and <0.5 μg oligomers.

Isocyanates Permeation - Comparing Thin versus Thick Latex and Nitrile

Experiments evaluating permeation of different glove thickness indicated that thicker gloves were more protective than thinner gloves for both latex and nitrile. Figure 6.8 (detailed data in Appendix E.16) show no permeation after 30 minutes post-spray above detection limit for both thick gloves. Permeation results in Figure 6.8 show data for both panels. Although each panel used a different clear coat formulation (Clear A / Reducer I & Clear B / Reducer II), there was no significant difference so data was presented together.

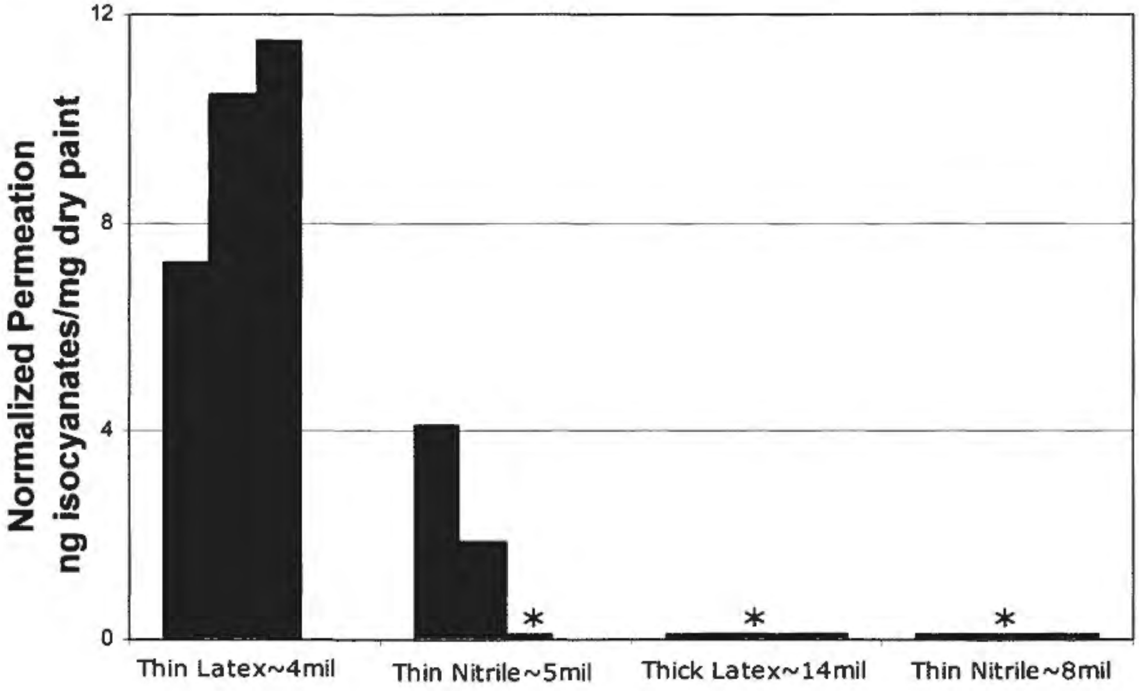


Figure 6.8. Isocyanate Permeation (30 min post-spraying) Using PPZ-coated Filters, for Different Glove Material And Thickness. Permeation normalized by the mass of dry clear coat loaded. (October 30, 2008, two panels). *Below LOD, <0.05 μg HDI/IPDI and <0.5 μg oligomers.

6.4.8. Permeation Panel Permeation Rate Experiments

Permeation between 0 to 30 minutes (October 13 and 28, 2008) provided information for thin latex only - all nitrile samples were below the LOQ. The second experiment was performed

(March 20, 2009) to extend the timeline to 90 minutes, in particular for nitrile. Permeation data for the permeation rate experiments are presented in Appendix E.18.

An example for thin latex permeation rate data for total isocyanates from 0 to 30 minutes is presented in Figure 6.9. The permeation rate is described by the slope or 0.55 ng isocyanates/mg of dry clear coat-min ($R^2 = 0.95$). Note that the intercept of zero permeation at zero minutes is included. The value zero was assigned to samples below the LOD. Figure 6.10 shows pooled data from two panels using different clear coats. Data including both 0-30 minutes and 40-90 minutes were also pooled (Figure 6.11). Note that the permeation rate and correlation did not change significantly. Since the average loading of dry clear coat for all panels was 33.9 mg in an area of 5 cm^2, the permeation rate was equivalent to the slope (0.43 ng isocyanates/mg of dry clear coat-min) times 33.9mg and divided by 5 cm^2, which is equal to 2.9 ng/cm^2-min. This means that 2.9 ng of isocyanates permeated per square centimeter of glove, per minute. Figure 6.12 shows pooled permeation rate data for thin latex for individual permeants: HDI and IPDI monomers. HDI monomer drives the rate (HDI has the same slope as when HDI was added to IPDI), most of IPDI is non-detect.

An example of permeation rate data for thin nitrile from 40 to 90 minutes is presented in Figure 6.13 (for one of the panels) and Figure 6.14 (for both panels). Permeation results at approximately 40 and 90 minutes were consistently above the LOQ. To better understand the behavior of thin nitrile over time, data from 0-30 and 40-90 minutes were pooled (Figure 6.15). There was no permeation until 40 minutes. Figure 6.16 shows the permeation rate data for thin nitrile for individual permeants: monomers of HDI and IPDI. IPDI is consistently below detection limits for nitrile.

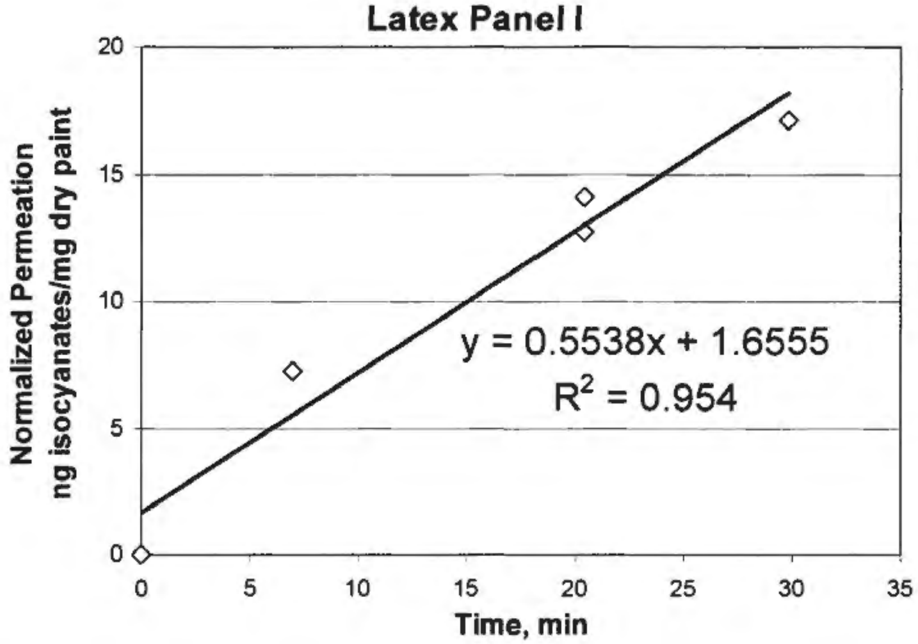


Figure 6.9. Isocyanate Permeation over Time for Thin Latex (4mil) For One Panel. Time was measured after the second spray application (October 28, 2008 Panel I). Data were normalized by the mass of dry clear coat loaded. Permeation was evident 5 minutes after spraying of clear coat.

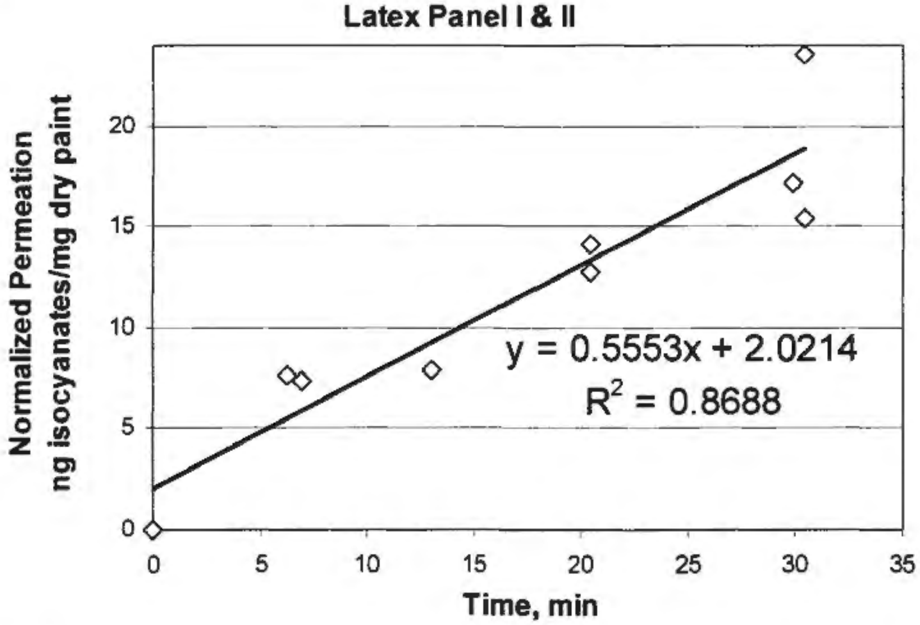


Figure 6.10. Isocyanate Permeation over Time for Thin Latex (4mil) For Two Panels. Time was measured after the second spray application (October 28, 2008 Panel I and II). Data were normalized by the mass of dry clear coat loaded. Permeation was evident 5 minutes after spraying of clear coat.

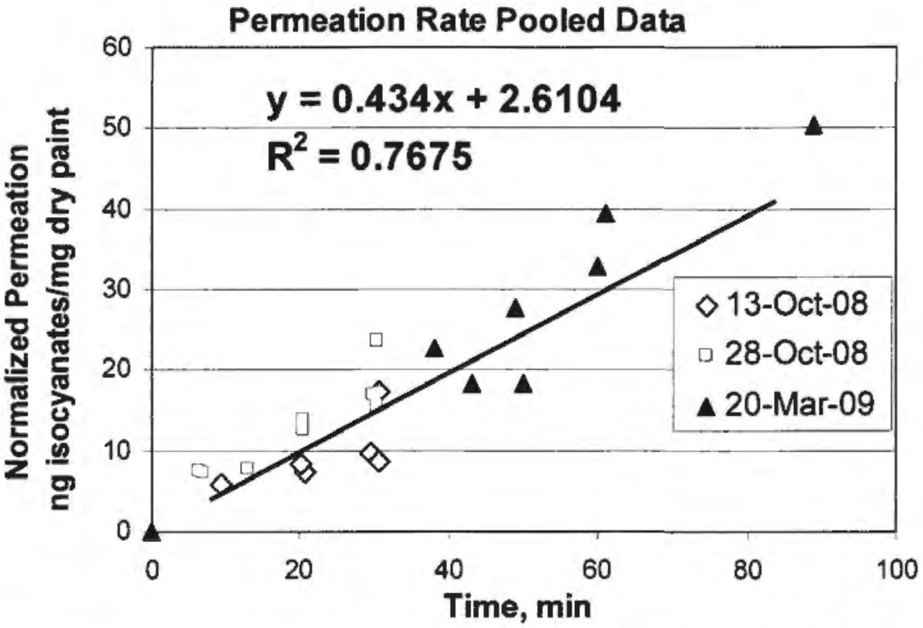


Figure 6.11. Isocyanate Permeation over Time for Thin Latex (4mil) For Pooled Data. Time was measured after the second spray application (October 13 and 28, 2008 and March 20, 2009). Data were normalized by the mass of dry clear coat loaded. Permeation was evident 5 minutes after spraying of clear coat.

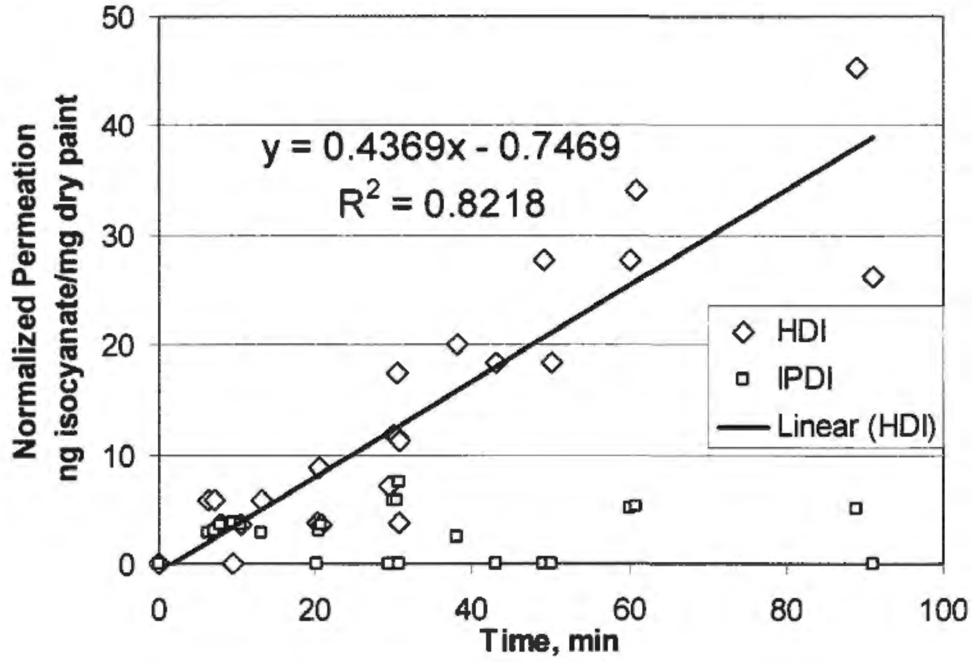


Figure 6.12. HDI and IPDI Monomers Permeation over Time for Thin Latex (4mil) For Pooled Data. Time was measured after the second spray application (October 13 and 28, 2008 and March 20, 2009). Data were normalized by the mass of dry clear coat loaded. Permeation was evident 5 minutes after spraying of clear coat.

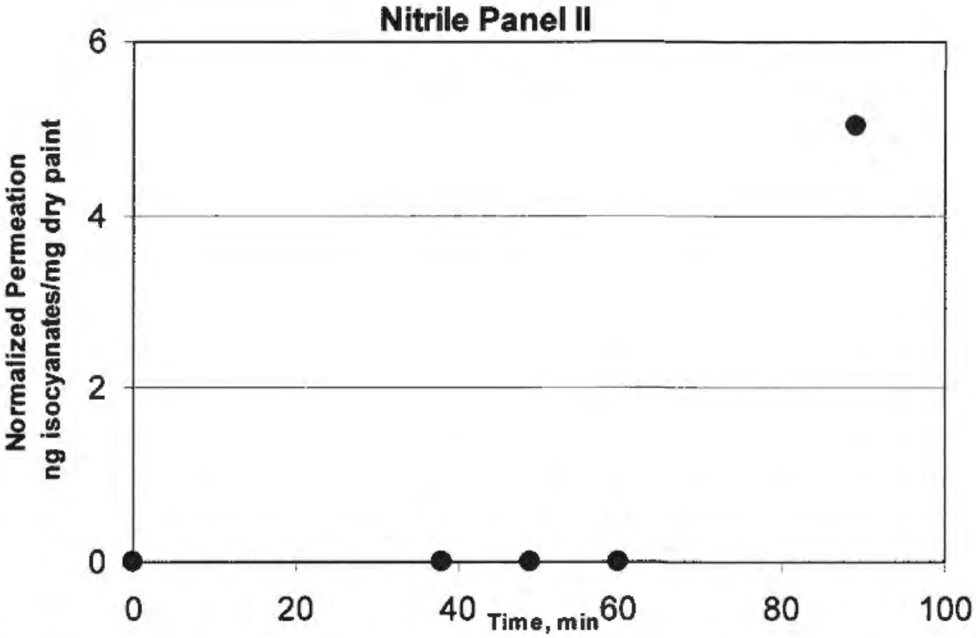


Figure 6.13. Isocyanate Permeation over Time for Thin Nitrile (4.8mil) For One Panel. Time was measured after the second spray application (March 20, Panel II). Data were normalized by the mass of dry clear coat loaded. Permeation was evident 90 minutes after spraying of clear coat.

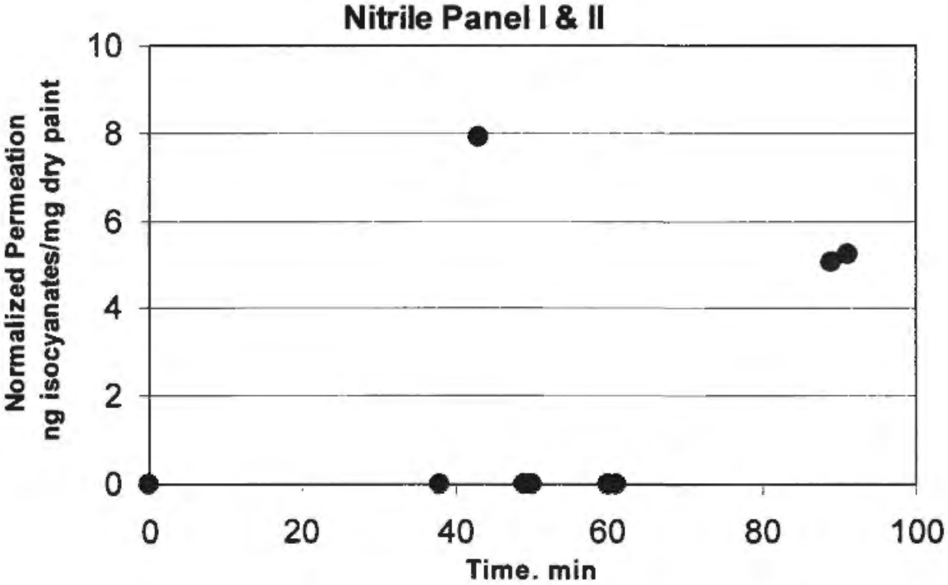


Figure 6.14. Isocyanate Permeation over Time for Thin Nitrile (4.8mil) For Two Panels. Time was measured after the second spray application (March 20, Panel I and II). Data were normalized by the mass of dry clear coat loaded. Permeation was evident 40 minutes after spraying of clear coat.

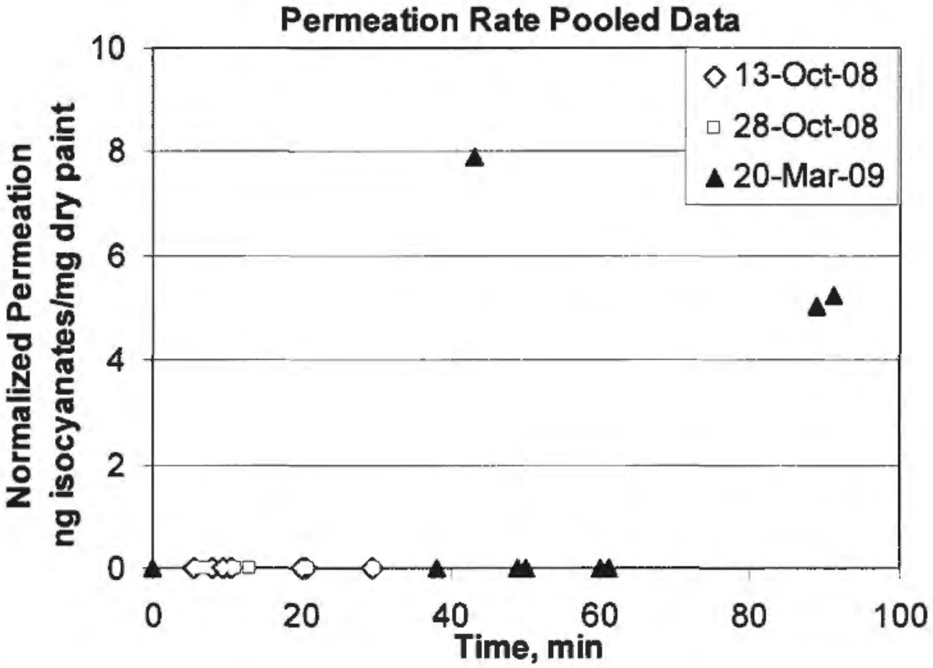


Figure 6.15. Isocyanate Permeation over Time for Thin Nitrile (4.8mil) For Pooled Data. Time was measured after the second spray application (October 13 and 28, 2008 and March 20, 2009). Data were normalized by the mass of dry clear coat loaded. Permeation was evident 40 minutes after spraying of clear coat.

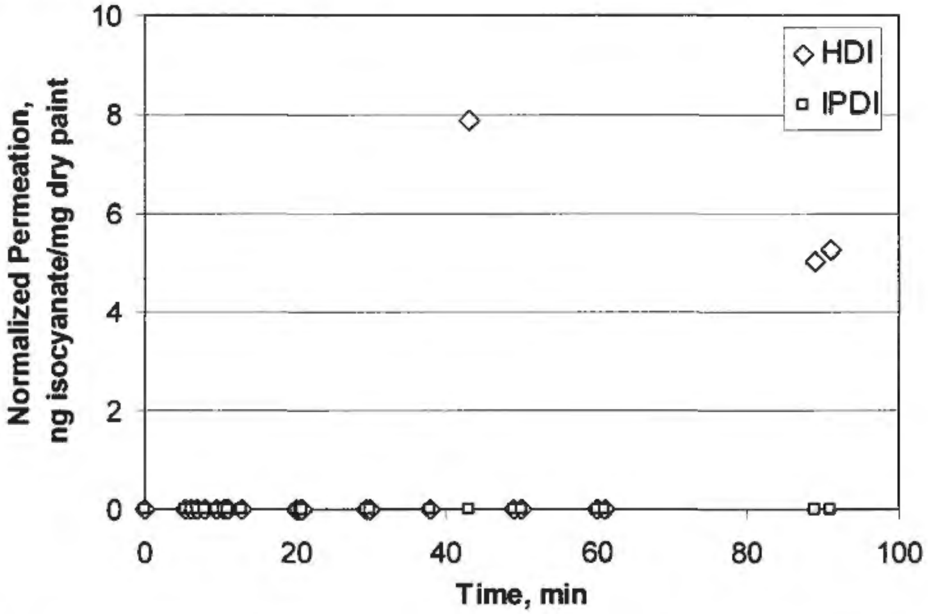


Figure 6.16. HDI and IPDI Monomers Permeation over Time for Thin Nitrile (4.8mil) For Pooled Data. Time was measured after the second spray application (October 13 and 28, 2008 and March 20, 2009). Data were normalized by the mass of dry clear coat loaded. Permeation was evident 40 minutes after spraying of clear coat.

6.5. Discussion

The improved permeation panel represents a viable method to evaluate the permeation of dermal protective material like gloves. The gloves most frequently used by painters (thin latex and thin nitrile as described in Chapter 3) allowed permeation of isocyanates. Using different solid media, including the SWYPE and PPZ- and MAMA-coated filters, thin latex consistently allowed greater permeation than thin nitrile. Thin latex gloves showed breakthrough within the first few minutes of spraying clear coat, whereas thin nitrile gloves showed evidence of permeation after 30 minutes of contact.

The spraying of the permeation panel was successful in that the layer of clear coat was homogenous (within 13%CV). Measurements of surface loading using PTFE filters resulted in an average of 34 mg loading of dry clear coat mass. The solids percentage in the clear coat formulation was 47%; therefore the mass of dry clear coat found on the PTFE filters was equivalent to 73 mg of clear coat formulation (weight of wet clear coat) and within a range of 72.8-80.9 μL clear coat formulation (calculated with a range of clear coat formulation density of 0.9-1.0 mg/μL). Further, 10.1-11.2 mg of total isocyanates loaded per 1 inch diameter area, considering that the total isocyanates percentage based on MSDS and bulk analysis in the clear coat formulations was 13.9%.

The type of clear coat formulation and date did not appear to affect the thickness of the clear coat layers; both clears and reducers had a thickness of 0.03mm for 1 coat and 0.06mm for 2 coats. This was more evidence of the consistency of spraying performed by the same painter.

Characterization experiments determined that standardization of the field experiments was very important for reproducibility of the data. After the first field season (May 2008), we better assessed the characteristics of the spraying event and the variability associated with same painter. We observed an average of 6 passes of clear coat and approximately 7 minutes between sprayings. All other experiments were performed by replicating this timing to make spraying as consistent as possible. Pooled data showed that experiments were reproducible. Many factors that were controlled to standardize experiments in the field included having the same painter and similar conditions, such as spraying, booth, booth flows, temperature, and relative humidity. Finally, as mentioned in Chapter 5, the ultimate potential for standardization of the permeation panel would be done by automated spraying using a robot arm, or similar.

SWYPEs showed more variability that PPZ-coated filters. Some of the SWYPE variability may be atributed to partial color transfer from the SWYPE to the glove material being tested (discussed in Chapter 5). This was evident after inspecting the test materials while disassambling the cells.

Temperature and relative humidity averages among all panel experiments were 71.4 +/- 3F and 41.7+/-17%, respectively. Overall, temperature variability was higher outside the panel than inside the panel. The panel case may have kept the temperature more stable while the air flow inside the booth may have caused temperature fluctuations. The greatest temperature fluctuations occured days with particularly cold outside temperatures, likely because the booth drew in outside unheated air. Weather also influenced the relative humidity, particularly during rainfall. Relative humidity was more variable than temperature. However, temperature is the most important variable because of its influence on chemical diffusivity.

Screening experiments showed that permeation of latex was greater than for thin nitrile for both SWYPEs and PPZ-coated filters. Data using PPZ-coated filters showed that thicker gloves (8-14 mil) performed better than thinner gloves, with thin latex performing the worst. Breakthrough times indicated by the SWYPEs were the same for both latex and nitrile (positive in less than 2 minutes).

The main advantage of using the SWYPE method to determine permeation is that it provided a visual immediate response in the field. SWYPE permeation results indicated permeation up to 600 ng hardener per mg of dry clear coat, while PPZ-coated filters indicated permeation on the order of 20 ng total isocyanate per mg of dry clear coat. This difference in permeation scale was explained in Chapter 5. In brief, the methods provide results in different units: the SWYPE RGB analysis measures mass of hardener, whereas OSHA 42/PV2034 PPZ-coated filters measures particular isocyanate species.

Some of the advantages of using the PPZ- or MAMA-coated filters to measure permeation include the low detection limits and speciation of the permeants. Note that when comparing results from PPZ and MAMA coated filters, MAMA filters gave consistently higher levels of permeation. This was the case even though both PPZ- and MAMA-coated filters reported only permeation of monomers. This was not surprising considering that the ISO-CHEK method reported higher than the OSHA method, specifically for HDI monomer (Chapter 4).

Since we found traces of oligomers in one of the permeation samples (even though it was between the LOD and LOQ) it is important to do more work in this area. To know if there is oligomer breakthrough we need more sensitive analysis, such as mass spectrometry (refer to Chapter 4). Another viable approach would be to do permeation experiments for much longer times so that mass on the filters are larger. These longer times are not as relevant in the work place with disposable gloves but it would help understand if oligomers can actually permeate these gloves.

During the UNC-SHARP field studies, tape-stripping of painters before and after spray-tasks showed the presence of oligomers on the skin of workers even when they wore gloves (Fent et al 2009). There are several possibilities: 1) permeation through the glove material, 2) penetration through a hole or seem, 3) direct deposition on the skin because of a spill or overspray before the glove was worn, or 4) incorrect doffing and donning of the gloves.

Permeation rate experiments indicated that the breakthrough time for thin latex is immediate because there was a positive Y intercept (intercept of 0.8 minutes, $R^2 = 0.5$). Thus, permeation occurred within the first few seconds of application. Thin latex allowed permeation at a rate of 2.9 ng/min-cm^2. Thin nitrile (5 mil) allowed permeation after 30 minutes. More experiments are necessary to evaluate breakthrough time and permeation rate for thin nitrile gloves and thicker gloves. During permeation rate experiments with thin nitrile, there was no permeation until 40 minutes. This was not surprising since in the past we had observed occasional permeation of nitrile after 30 minutes. No permeation rate was calculated because of the few data points in the time studied. However, permeation after 40 and 90 minutes may indicate that a fraction of the gloves started to fail before the others.

Data from different permeation rate experiments were pooled successfully. For latex, the slope lowered slightly when all the permeation rate experiments were pooled. This may indicate that permeation starts to reach saturation (suggested by the lower right data point at 90 minutes). Note that Figure 6.11 shows alignment of data from experiments performed at different dates. This indicates that the normalization and systematic field-approach in between days were optimal. Figure 6.12 shows HDI monomer as the driver of the permeation through thin latex because the slope of HDI permeation (Figure 6.12) is equal to that of the slope of total isocyanate permeation (Figure 6.11). IPDI monomer was never detected when testing nitrile, which suggests that HDI monomer behaves differently than IPDI. More experiments are needed to sort out these differences.

SWYPEs indicated immediate signs of breakthrough for thin latex, which coincides with the results from using PPZ-coated filters. SWYPEs also indicated that thin nitrile exhibited the first signs of breakthrough within the first few minutes. However, the permeation rate experiments for nitrile exhibited the first signs of breakthrough after 40 minutes. This discrepancy may reflect the fact that the clear coats interact with the gloves differently in the presence of a SWYPE compared to PPZ. This finding requires further evaluation.

Although the isocyanate ranges provided on MSDSs compared reasonably well with information reported by the manufacturer, there were differences between the MSDS estimates and the bulk analyses for the solvent groups, including: MSDS calculations predicted formulations using Clear B with much lower and distinct hydrocarbon content. Further, MSDS calculations predicted a greater amount of acetates than was measured by bulk analysis. No studies have been conducted to characterize the main solvent groups and content in different hardeners and clear coat formulations. In future experiments, investigators should rely on both bulk analysis and MSDS information before selecting clear coats.

We recommend that workers do not use thin (4-5ml) latex gloves for mixing or spray painting because there is ample evidence of breakthrough within typical usage times. Thin nitrile gloves provide better protection than thin latex only if they are changed frequently. Although the permeation for thin nitrile was first detected at 30 minutes, we recommend frequency of change of gloves to be 20 minutes to ensure no breakthrough, which is as long as a typical clear coat application.

Further permeation experiments with a wide selection of clear coats are needed. Ultimately, selecting clear coats that permeate to a lesser extent through gloves could potentially help reduce dermal exposures. We demonstrated that substitutions in the clear or reducer was not sufficient to affect permeation. To observe a solvent effect, investigators may need to selet clear coat formulations that are drastically different from each-other, which would imply not only having different solvent content but also different isocyanate content. Normalization or cofactor analysis with the amount of isocyanate may be necessary to evaluate the effect on permeation. We hypothesize that ranking of gloves based on solvent compatibility would correlate with isocyanate permeation panel results.

Gloves with longer breakthrough times and reduced isocyanate permeation will likely be more protective. Consequently, nitrile gloves are likely more protective than latex. Our finding of possible dual permeation behavior in nitrile gloves may point to inconsistencies in glove manufacturing (Mickelsen and Hall 1987; Perkins and Pool 1997; Oppl 2001a). Imperfections during manufacturing (i.e., relatively thin areas and small holes) have been noted in single-use and multi-use chemically-resistant gloves (Canning *et al.* 1998; Dashner and Habel 1988; Sansone and Tewari 1978; and NIOSH 2001). In our studies, we selected gloves from the same box and lot to minimize variability. However, gloves from a single manufacturer and even from the same lot may differ substantially and may not be representative of all glove sources. Consequently, we do not attempt to generalize our results to all batches within the same manufacturer or that of different manufacturers. Studying the effects of variability in glove quality on permeation was outside the scope of our study. However, measurements besides thickness may be necessary to assess homogeneity of the tested material, such as pinhole testing of the test material.

Many physical, chemical, and behavioral variables can affect the performance of protective clothing and these variables are difficult to replicate in controlled experiments. Several authors (Cherrie *et al.* 2004; and Klingner and Boeniger 2002) recommend workplace monitoring to determine the efficacy of glove performance and worker exposures during actual use conditions. Studies with both laboratory and field permeation experiments, such as those by Gunderson *et al.* (1989), provide stronger evidence to determine recommendations for personal protective clothing. Our approach is a mid-point between controlled laboratory experiments and field assessment, representing a worst-case scenario of dermal exposure to polymerizing materials. Our results are not yet sufficient to assure infallible protection of workers in actual spray-situations. Further laboratory and field experiments are proposed in our larger grant application (NIOSH R01 OH009364-01), which has been accepted.

More research studying the effectiveness of coveralls and other protective clothing is also needed for the collision repair industry. We considered gloves a priority because they typically present the first barrier against dermal exposure (Boman *et al.* 2004). There is also conflicting information about the performance of coveralls; most are chosen based on comfort or price, and little is known on their protection against isocyanates. Coveralls are reused for up to a year (Chapter 3) so permeation studies with coveralls should consider this variable.

The permeation panel results showed measurable differences in permeation based on glove material, thickness, and time. These parameters should be included in specific recommendations about glove performance. This work demonstrated that nitrile gloves, when changed frequently, may help prevent dermal exposure and consequently work-related asthma.

Thin latex (4mil) gloves were not protective against isocyanates. Recommendations to painters to avoid using thin latex gloves have the bonus that will also help avoid the development of allergic reactions typical of latex products (Boman *et al.* 2004)

These results will be useful to both industry and government agencies because they will allow them to help inform painters about the gloves that are more protective. SHARP determined that this industry is a good candidate for a "research to practice" intervention, comprising both an educational campaign and technical assistance to improve dermal protection (Whittaker and Whitaker 2009). These preliminary studies demonstrate the need to develop an effective outreach strategy to share these findings with the collision repair community. Part of this strategy would include further understanding painters and business owner's motivators and preferences for adopting best practices for glove use.

6.6. Conclusions

There is a need to assess efficacy of gloves against isocyanates. Painters are currently using gloves, such as thin disposable latex, that are not protective against isocyanates. Isocyanates are known to cause work-related asthma. Exposures to isocyanates can compromise painters' health and ultimately their careers. Previously, testing of gloves was not possible because isocyanates exhibit low volatility and water solubility. Further, isocyanates in clear coat are contained in a complex and polymerizing material that is difficult to test. More data could be gathered with the permeation panel for different gloves, coveralls, and clear coat formulations. There is also a need to evaluate the influence of solvents on isocyanate permeation.

Our initial recommendation (Chapter 6) to ensure isocyanate dermal protection is that painters use nitrile gloves, ideally 8 mil or thicker. Thin nitrile gloves (4-5mil) are acceptable as long as they are used within a 20 minute time frame. In order to avoid any potential for permeation, disposable gloves should be changed frequently. Thin latex gloves (4mil) are the most popular gloves because they are inexpensive, comfortable, and elastic, but they provide little protection against isocyanates. Thin latex gloves allow immediate breakthrough of isocyanates at a permeation rate of 2.9 ng/cm^2-min. Further research is needed to provide permeation information for more glove types and other dermal protective clothing.

6.7. Notes to Chapter 6

Berardinelli SP (1988): Prevention of occupational skin disease through use of chemical protective gloves. Dermatol. Clin. 6:115–119

Boman A, Estlander T, and Wahlberg JE. Protective Gloves for Occupational Use. 2nd Ed. CRD Press. Published by Informa Health Care, (2004). 343 pgs

Canning KM, Jablonski W, and McQuillan PB (1998): Quantification of surface defects on chemically protective gloves following their use in agriculture. Ann. Agric. Environ. Med. 5:45-56

Cherrie JW, Semple S, and Brouwer D (2004): Gloves and dermal exposure to chemicals: proposals for evaluating workplace effectiveness. Ann. Occup. Hyg. 48(7):607-15. Epub 2004 Sep 23

Daschner FD and Habel H (1988)" HIV prophylaxis with punctured gloves? Infect. Control. 8:184-186

U.S. Environmental Protection Agency (EPA) (1999): Choosing the right gloves for painting cars. U.S. Environmental Protection Agency. Publication EPA/744-F-00-005. Updated June 2000. Available at http://www.epa.gov/dfe/pubs/auto/gloves/gloves.pdf, accessed January 2007

Gunderson EC, Kingsley BA, Witham CL, and Bromberg DC (1989): A practical study in laboratory and workplace permeation testing. Appl Ind Hyg 4(12):324-329

Klingner TD and Boeniger MF (2002): A critique of assumptions about selecting chemical resistant gloves: a case for workplace evaluation of glove efficacy. AOEHJ 17(5):360-367. Available at http://www.clilabs.com/clidownloads.htm (file: GLOVEPAP1-final.pdf), accessed July 2006

Mickelsen RL and Hall RC (1987): A breakthrough time comparison of nitrile and neoprene glove materials produced by different manufacturers. AULA 48(ll):941-947

The National Institute for Occupational Safety and Health (NIOSH) (2001): Recommendations for Chemical Protective Clothing: A Companion to the NIOSH Pocket Guide to Chemical Hazards. Available at http://www.cdc.gov/niosh/ncpc/ncpc2.html, Accessed March 2009

Oppl R (2001): Chemical protective gloves — in-use protection time vs. standard breakthrough time. Miljoe-Chemie, Hamburg, Germany. [Abstract 196] New Orleans, LA: American Industrial Hygiene Conference & Exposition

Occupational Safety & Health Administration (OSHA) (1999): Sampling for surface contamination. In: OSHA Technical Manual, Section II, Chapter 2. Salt Lake City, Utah: OSHA Technical Center, p 1-16

Perkins JL and Pool B (1997): Batch lot variability in permeation through nitrile gloves. AIHA J. 58:474-479

PPG Industries (1997): PPG Two-Component Polyurethane Coating Systems Guidelines for Safe Use. PAM 9379 8/97

Sanson EB and Tewari YB (1978): The permeability of laboratory gloves to selected solvents. AIHA J. 39:169-174

Sparer J, Stowe MH, Bello D, *et al.*(2004): Isocyanate exposures in autobody shop work: the SPRAY study. J Occup. Environ. Hyg. (9):570-81

Whittaker SG. and Reeb-Whitaker C (2009): Characterizing the Health and Safety Needs of the Collision Repair Industry. J. Occup. Environ. Hyg. 6(5):273-282

Chapter 7
SUMMARY

7.1. Summary

This dissertation focused on isocyanate permeation of gloves commonly used in the collision repair industry. Gloves remain the main dermal barrier for autobody painters during mixing and spraying processes. However, painters are currently using gloves, such as thin disposable latex, that are not protective against isocyanates. Isocyanates are known to cause work-related asthma both via inhalation or dermal exposures. Isocyanates exposures can then compromise painters' health and ultimately their careers. Previously, testing of gloves was not possible due to the inherent low volatility and water solubility of isocyanates. Further, isocyanates in clear coat are contained in a complex, polymerizing material that is difficult to test. There is a need to assess efficacy of gloves against isocyanates.

The permeation panel developed for this research is a field-testing device that can provide measures of permeation for several test materials simultaneously. Loading measures ensure uniformity of clear coat throughout the panel and provide a means for normalization of the data. The panel has no moving parts, is inexpensive, easy to clean, reusable, and its coating is chemically resistant. The permeation panel succesfully provided permeation data under typical spray application conditions. This was presented in the development of the permeation panel study, Chapter 5.

Information on the typical painter's work practices was needed to support the development of the permeation panel. Survey data and field observations collected during the UNC-SHARP study (Chapter 3) helped inform us about work practices during the mixing and spray application of the clear coat formulations. In addition, field data also described typical spray application durations; the most common clear coat formulations; gloves, coveralls, and respirators used; and other factors. This information helped with the decision as to what materials to test with the permeation panel. The use of dermal PPE in the collision repair industry was summarized in Chapter 3. The rationale for choosing the clear coat formulations was stated in Chapters 5 and 6.

Another piece of the puzzle was to determine which solid media to use with the permeation panel. The development of an objective analysis method for the colorimetric

SWYPE surface sampling technique provided a valuable visual tool during permeation field experiments, as well as a quantitative assessment of permeation. The RGB analysis combined with the SWYPE is an improvement over existing qualitative or semi-quantitative colorimetric isocyanate SWYPE tests (Chapter 2). The RGB analysis of the SWYPE has the advantage of not only preserving images of the samples, but also reducing reader-to-reader variability.

In the search for solid media to measure isocyanates, understanding of the current isocyanate air sampling filter methods was needed. The inter-method comparison in Chapter 4 provided not only understanding of the different methods, but also a relative performance with the EH Lab OSHA 42/PV2034 to validate results from the objective colorimetric method and permeation panel. We found that the modified OSHA 42/PV2034 method performed reasonably well compared to other methods and has the ability to measure oligomers within a typical mix of isocyanates in a hardener. Therefore, the use of OSHA 42/PV2034 method to validate the SWYPE RGB analysis in Chapter 2 and to provide permeation experiments in Chapter 5 and 6 was appropiate. The inter-method study brings to light the challenges faced when comparing different isocyanate analytical methods. Different methods report results in different units that make direct comparison sometimes impossible. Further, each method identifies a different set of isocyanate species depending on the method's capability.

Our initial recommendation (Chapter 6) to ensure isocyanate dermal protection is that painters use nitrile gloves, ideally 8 mil or thicker. Thin nitrile gloves (4-5mil) are acceptable as long as they are used within a 20 minute time frame. In order to avoid any potential for permeation, disposable gloves should be changed frequently. Thin latex gloves (4mil) are the most popular because they are inexpensive, comfortable, and elastic, but they provide little protection against isocyanates. Thin latex gloves allow immediate breakthrough of isocyanates at a permeation rate of 2.9 ng/cm^2-min.

Although tests were performed with representative clear coat formulations, these results may not represent the entire spectrum of clear coat formulations and do not account for the permeation of solvents through the gloves. However, these recommendations form the basis of future studies to further understand dermal protection against coatings.

7.2. Future Studies

Production of isocyanates and automotive paints worldwide is increasing. Even though the easiest solution to avoid workplace exposure would be to eliminate isocyanates, these chemicals are invaluable materials that would be hard to substitute. Clear coats, in particular, require isocyanates because they must resist environmental etch, bird droppings, car wash machines, and other outside influences (Dupont 2009). Isocyanates may not be substituted in the near future but new isocyanate products including water-based coatings and blocked-isocyanate technology, may eventually replace current formulations. Even if these product substitutions take place, there would still be the need to test to assure painter's safety.

Although waterborne technology is not new, it is growing in importance, spurred by new environmental regulations in California and elsewhere (DTSC 2007). We did not find autobody shops in Washington State using these coatings. Although they are less toxic, less flammable, and yield less environmental emissions (low volatile organic compounds or VOCs), one of the reasons for not switching to water-based paints is the expense required to add another spraying system (DTSC 2007). There are no commercial clear coat waterborne formulations yet, and the few that exist do not pass quality standards. Further, water-based paints can take longer to dry, which can result in increased costs. Some products are available that reduce drying times significantly (Mercer 2006) but many autobody shops are resistant to change; this may change as product advancements go forward.

Blocked-isocyanate technology for auto paints may hold promise, even in water-based paints, but there is a concern about the health effects of the blocking agent when it is released using heat. These so called 'blocked isocyanates' are stable at room temperature, even when mixed with polyols. They become reactive once the system is heated to an activation temperature, normally called the unblocking temperature. As the temperature rises the isocyanate unblocks, liberating NCO groups, which are then free to react with polyols to form the urethane polymer. The free blocking agent either remains in the coating or is removed by evaporation (www.gdspublishing.com/ic_pdf/apdinfra/baxe.pdf. Accessed May 20, 2009).

Regardless of the possibilities for substitution of the traditional coating formulations, there is a great need to address painters' health and safety practices, specifically for dermal protection. Suggestions for future studies revolve around projects with a technical and social emphasis. Technical projects are mainly geared toward gathering permeation data for different materials and improvements to the current equipment and procedures. In addition, field studies should be conducted to validate data obtained with the permeation panel. Social projects are ultimately geared towards social marketing campaigns, education, and training of painters to improve work practices and reduce the burden of work-related asthma. More permeation panel testing, in-use field testing, and focus groups were proposed as part of the larger NIOSH grant application (NIOSH R01 OH009364-01).

Further research with the permeation panel is needed to provide permeation information for additional glove types and clear coat formulations. Further, there is a need to test other dermal protective clothing, in particular coveralls. There is also a need to determine the effect of solvent in isocyanate permeation. The use of the permeation panel has the potential to measure different permeants with different polymerizing formulations. These dissertation results are not yet sufficient to assure infallible protection of workers in actual spray situations; further laboratory and field experiments are proposed in a larger grant application (NIOSH R01 OH009364-01), which has been submitted for review.

To improve measures of permeation using the permeation panel, there is a need to study further the role that derivatization reagents play in the permeation process. Other solid media could then be used for the measurement of solvents or other permeants.

Although oligomers are large molecules that are not expected to permeate, we do not yet understand the mechanisms of mass transfer. It is important to study oligomer permeation because 1) oligomers are present in higher concentrations than monomer in the clear coat formulations so the potential for exposure is higher, and 2) like monomers, they can also elicit sensitization. However, to measure oligomers, more sensitive analytical methods may be required.

Current analytical methods for the measurement of isocyanates would benefit from the commercialization of oligomer standards. Besides improving agreement between methods, it would facilitate the creation of workplace polyisocyanate exposure limit standards in Washington State. Further, analytical chemistry method development points to a method that uses UV/FLD coupled with MS (or MS-MS). This powerful combination would bring the advantages associated with both detectors: UV/FLD would be able to measure total NCO-mass of isocyanates, monomers and oligomers, and the MS detector can then check for specificity of the different species. The MS would also provide lower detection limits. Method development for an UV-MS system was proposed as part of the larger NIOSH grant application (NIOSH R01 OH009364-01).

Standardization of permeation panel experiments is crucial to minimize the variability among panels and within panels. When using the same painter, variations among panels can be mainly attributed to differences in temperature, loading, and clear coat. To control loading, it is important to keep constant the number of passes of the spray gun and the time interval between applications. Variation within a panel can be mainly attributed to small variations in sampling time, quality of the test material, and loading homogeneity. Most these variables can be controlled with a systematic field approach. The standardization process ultimately would involve automation by a robotic hand for the spraying of the panel.

In terms of social emphasis projects, there are training and research opportunities with auto painters to improve the use of safety practices, in particular the use of dermal PPE, implementation of respiratory protection programs, and the use of eye protection. This industry would also benefit from an intervention to decrease the use of thin latex, which provides little protection against solvents or isocyanates.

Overall, we found that auto painters' PPE choices were usually determined by their smoking status, years spray painting, and frequency of use and type of dermal PPE. We concluded that these determinants affected PPE choices depending on painter's attitudes towards adoption of PPE use. Those who use PPE understand that frequency of use and type of gloves are important factors that affect protection. In addition, behaviors such as smoking were statistically significantly associated with dermal PPE outcome variables. Further, comfort, convenience, and experience of the painter appeared to influence their PPE choices.

There is a need to identify additional workplace factors and employer and employee preferences that may obstruct or facilitate adoption of effective dermal PPE. In the case of gloves, it is important to understand whether variables other than price and dexterity are important (for example color). In the case of coveralls, reasons behind high reuse should be further studied. Use of focus groups would be essential to retrieve the information from painters and managers to improve PPE use. Comments from a painter/trainer suggest that black nitrile gloves, as supposed to typical purple or blue, were highly desired among his students. We expect that color, marketing, and knowledge of effectiveness impact glove-use decisions. (A marketing video promoting these gloves to auto repair workers can be found online at: http://www.ammex.com/getintheblack/video2.htm. Accessed March 2009).

Finally, a "social marketing" intervention strategy would be the next ideal step. This approach would use the barriers and benefits to adopting sustainable safe work practices as the foundation of an educational and technical assistance campaign. Social marketing utilizes the behavior change tools from social science research to promote information, attitudes, values and behaviors.

7.3. Conclusions

In the preceding chapters, a new field-testing device to test dermal protective clothing against sprayed coatings was developed and tested. With a clear understanding of painters' work practices, commonly-used gloves and clear coat formulations, spray application process, and permeation measurements, the permeation panel provides the means to measure permeation under typical work conditions.

Colorimetric pads and coated air sampling filters used as solid media can provide measures of permeation when used with the permeation panel. Improvements with the permeation panel include further understanding of the effect of the derivatization reagent on the solid media as well as robotic automation of the spray application. Future studies to understand the effect of solvents on isocyanate permeation is needed. Also, more permeation data on different types of gloves and coveralls is necessary to provide painters better protection against isocyanates. Lastly, results from the permeation panel should be compared with exposure assessment of painters using the tested materials.

Social studies, including focus groups, interventions, and social marketing are essential for effecting behavior change in the workplace. Gloves by themselves are not the solution. A joint effort among workers and business owners to improve administrative and engineering controls is needed. An effective PPE program, which includes respiratory, dermal, and eye protection programs, is necessary to assure comprehensive dermal protection of workers.

We hope that this dissertation and suggestions for future research directions will help the industrial hygiene community better understand isocyanate permeation in dermal protective clothing. Most importantly, with future studies auto-body painters will be provided better dermal protection information with which to make informed decisions in the workplace. This understanding will ultimately contribute to improved public health.

7.4. Notes to Chapter 7

DTSC (2007) "Waterborne Coatings. Document No. 801. Department of Toxic Substances Control" Available at

www.dtsc.ca.gov/PollutionPrevention/ABP/upload/TD_FS_WaterbourneCoatings.pdf - 2007-02-08, accessed May 20, 2009

Dupont (2009) “Paint & Coatings for Metal Exterior” Available at http://www2.dupont.com/Automotive/en_US/products_services/paintCoatings/metalExterior.html#Clearcoat, accessed May 20, 2009

Mercer (2006) “New Paint Technologies in 2006 Posted 5/13/2006 By Rachael J. Mercer. AutoInc.Online edition” Available at http://www.asashop.org/autoinc/may2006/collision.htm, accessed May 20, 2009

BIBLIOGRAPHY

Akbar-Khanzadeh F, Bisesi MS, and Rivas RD (1995): Comfort of personal protective equipment. Appl. Ergon. 26(3):195-8

Akbar-Khanzadeh F (1998): Factors contributing to discomfort or dissatisfaction as a result of wearing personal protective equipment. J. Hum. Ergol. (Tokyo) 27(1-2):70-5

Afifi AA, Clark V, and May S: Computer-aided Multivariate Analysis. Contributor Virginia Clark, Susanne May. Published by CRC Press, (2004) 489 pages

Anna DH: Chemical Protective Clothing, 2nd edition. (2003), 530 pages

American Thoracic Society (2003): American Thoracic Society statement: Occupational contribution to the burden of airway disease. Am. J. Respir. Crit. Care. Med. 167(5):787–797

ASTM F739-07 Standard Test Method for Permeation of Liquids and Gases through Protective Clothing. Materials under Conditions of Continuous Contact. Annual book of ASTM standards by American Society for Testing and Materials. Philadelphia, Pa: ASTM, 1970-2001. 7 Edition. Vol. 11.03

Bakerly ND, Moore VC, Vellore AD, et al. (2008): Fifteen-year trends in occupational asthma: data from the Shield surveillance scheme. Occup. Med. (Lond) 58(3):169-74

Bayer Corporation (1997): The chemistry of polyurethane coatings: A general reference manual. Pittsburgh, PA: Bayer Corporation.

Bayer Material Science LLC: *DESMODUR N 3400 Aliphatic Polyisocyanate* [Product Bulletin] Pittsburgh, Pa.: Bayer MaterialScience, (2002)

Bello D, Streicher RP, Woskie SR (2002): Evaluation of the NIOSH draft method 5525 for determination of the total reactive isocyanate group (TRIG) for aliphatic isocyanates in autobody repair shops. National Institute for Occupational Safety and Health. J. Environ. Monit. 4(3): 351-360

Bello D, Woskie SR, Streicher RP, et al. (2004): Polyisocyanates in occupational environments: a critical review of exposure limits and metrics. Am. J. Ind. Med. 46(5):480-91

Bello D, Woskie SR, Streicher RP, et al. (2005): A laboratory investigation of the effectiveness of various skin and surface decontaminants for aliphatic polyisocyanates. J. Environ. Monit. 7:716- 721

Bello D, Herrick CA, Smith TJ, et al. (2007a): Skin Exposure to Isocyanates: Reasons for Concern. Environ. Health Perspect. 115(3):328-35

Bello D, Sparer J, Redlich CA, et al. (2007b): Slow curing of aliphatic polyisocyanate paints in automotive refinishing: a potential source for skin exposure. J. Occup. Environ. Hyg. 4(6):406-11

Bello D, Redlich CA, Stowe MH, *et al.* (2008) Skin exposure to aliphatic polyisocyanates in the auto body repair and refinishing industry: II. A quantitative assessment. Ann. Occup. Hyg. 52(2):117-124

Berardinelli SP (1988): Prevention of occupational skin disease through use of chemical protective gloves. Dermatol. Clin. 6:115-119

Boman A, Estlander T, and Wahlberg JE: Protective Gloves for Occupational Use. 2nd Ed. CRD Press. Published by Informa Health Care, (2004). 343 pgs

BobeldijkIvana D, Karlsson A, Pronk J *et al.* (2008): Validation of Transferability of DBA Derivatization and LC–MS/MS Determination Method for Isocyanates via an Interlaboratory Comparison. Ann. Occup. Hyg. 52(8):757-763

Boutin M, Dufresne A, Ostiguy C and Lesage J (2006): Determination of Airborne Isocyanates Generated During the Thermal Degradation of Car Paint in Body Repair Shops. Ann. Occup. Hyg. 50(4):385-393

Canning KM, Jablonski W, McQuillan PB (1998): Quantification of surface defects on chemically protective gloves following their use in agriculture. Ann. Agric. Environ. Med. 5:45-56

Ceballos DM, Yost MG, Whittaker SG and Camp J (2007): "Isocyanate Surface Sampling in the Puget Sound Collision Repair Industry." Abstract. Poster 45 presented at the American Industrial Hygiene Conference & Expo, Philadelphia, PA. June 3-6

Ceballos DM, Yost MG, Whittaker SG, *et al.* (2009): Objective Color Scale for the SWYPE Surface Sampling Technique Using Computerized Image Analysis Tools. J. Occup. Environ. Hyg. (in press)

Chang FK, Chen ML, Cheng SF, Shih TS, and Mao IF (2007): Dermal absorption of solvents as a major source of exposure among shipyard spray painters. J. Occup. Environ. Med. 49(4):430-6

Cherrie JW, Semple S, and Brouwer D (2004): Gloves and dermal exposure to chemicals: proposals for evaluating workplace effectiveness. Ann. Occup. Hyg. 48(7):607-15. Epub 2004 Sep 23

Collin-Hansen I, Stowe M, Ibrahim K, *et al.* (2006): Field evaluation of gloves and protective clothing against organic solvents during auto body spray painting [Abstract]. In: American Industrial Hygiene Association Conference 2006, Chicago, IL. Available at http://www.aiha.org/abs06/po119.htm, accessed 19 January 2007

Cowley S, Else D, and LaMontagne A (2004): Increasing the adoption of OHS risk controls in small business: can social marketing help to achieve change? J. Occup. Health Saf. Aust. Nz. (Cch. Aust.) 20(1):69-77

Creely KS, Hughson GW, Cocker J, et al. (2006): Assessing isocyanate exposures in polyurethane industry sectors using biological and air monitoring methods. Ann. Occup. Hyg. 50:609–21

Daschner FD, Habel H (1988). HIV prophylaxis with punctured gloves? Infect. Control. 8:184-186.

Department of Health, Washington State (2009): Tobacco Prevention and Control Program, Progress Report, March 2009. DOH Pub. 340-130

DTSC (2007) "Waterborne Coatings. Document No. 801. Department of Toxic Substances Control" Available atwww.dtsc.ca.gov/PollutionPrevention/ABP/upload/TD_FS_WaterbourneCoatings.pdf - 2007-02-08, accessed May 20, 2009.

Dupont (2009) "Paint & Coatings for Metal Exterior" Available at http://www2.dupont.com/Automotive/en_US/products_services/paintCoatings/metalExterior.html#Clearcoat, accessed May 20, 2009.

Efron, B.: The jackknife, the bootstrap, and other resampling plans, In The Society of Industrial and Applied Mathematics CBMS-NSF Monographs, 38 (1982).

England E, Key-Schwartz R, Lesage J, *et al.* (2000): Comparison of sampling methods for monomer and polyisocyanates of 1,6-hexamethylene diisocyanate during spray finishing operations. Appl. Occup. Environ. Hyg. 15(6):472-8

Ehntholt DJ, Cerandolo DL, Bodek I, Schwope AD, Royer MD, Nielsen AP (1990) A test method for the evaluation of protective glove materials used in agricultural pesticide operations. AIHA J. 51:462–468

U.S. Environmental Protection Agency (EPA) (1999): Choosing the right gloves for painting cars. U.S. Environmental Protection Agency. Publication EPA/744-F-00-005. Updated June 2000. Available at http://www.epa.gov/dfe/pubs/auto/gloves/gloves.pdf, accessed January 2007

U.S. Environmental Protection Agency (EPA) (2005). Revised Automotive Refinishing Industry Isocyanate Profile. U.S. Environmental Protection Agency. January 2005. Available at www.epa.gov/opptintr/dfe/pubs/auto/profile/index.htm, accessed October 2005.

Erjefalt I and Persson CG. (1992) Increased sensitivity to toluene diisocyanate (TDI) in airways previously exposed to low doses of TDI. Clin. Exp. Allergy. 22(9):854-62

Evans PG, McAlinden JJ, Griffin P (2001): Personal protective equipment and dermal exposure. Appl. Occup. Environ. Hyg. 16(2):334-7

Fent K, Jayaraj K, Gold A, Ball L, and Nylander-French L (2006): Tape-strip sampling for measuring dermal exposure to 1,6-hexamethylene diisocyanate. Scan. J. Work Environ. Health. 32(3):225–231

Fent KW, Gaines LG, Thomasen J, *et al.* (2008): Quantification and statistical modeling of dermal exposure to monomeric and polymeric 1,6-hexamethylene diisocyanate. J. Environ. Monit. 10:500-507

Fent KW, Trelles Gaines LG, Thomasen JM,*et al.* (29009) Quantification and Statistical Modeling--Part I: Breathing-Zone Concentrations of Monomeric and Polymeric 1,6-Hexamethylene Diisocyanate. Ann. Occup. Hyg. Submitted

Fisher L.D. and Van Belle G. Biostatistics: A methodology for the health sciences. Wiley interscience. US. (1993). page 900. total 991 pages

Gaiao N, Martins VL, Lyra S, *et al.* (2006): Digital image-based titrations. Anal. Chim. Acta. 570(2):283-90

Gagne S, Lesage J, Ostiguy C, Cloutier Y, Van Tra H (2005): Quantitative determination of hexamethylene diisocyanate (HDI), 2,4-toluene diisocyanate (2,4-TDI) and 2,6-toluene diisocyanate (2,6-TDI) monomers at ppt levels in air by alkaline adduct coordination ionspray tandem mass spectrometry. J. Environ. Monit. 7(2):145-150

Garrod AN, Phillips AM, Pemberton JA (2001): Potential exposure of hands inside protective gloves - a summary of data from non-agricultural pesticide surveys. Ann. Occup. Hyg. 45:55-60

Gates D, Brehm B, Hutton S, Singler M, and Poeppelman A (2006) Changing the Work Environment to Promote Wellness A Focus Group Study. AAOHN J. 4(12):515-20

Geer LA, Curbow BA, Anna DH, Lees PS, and Buckley TJ (2006): Development of a questionnaire to assess worker knowledge, attitudes and perceptions underlying dermal exposure. Scand. J. Work Environ. Health. 32(3):209-18

Geer LA, Anna D, Curbow B, *et al* (2007): Survey assessment of worker dermal exposure and underlying behavioral determinants. J. Occup. Environ. Hyg. 4(11):809-20

Gunderson EC, Kingsley BA, Witham CL, and Bromberg DC (1989): A practical study in laboratory and workplace permeation testing. Appl. Ind. Hyg. 4(12):324-329

Henneken H, Vogel M, and Karst U (2007): Determination of airborne isocyanates. Anal. Bioanal. Chem. 387(1):219-36. Epub 2006 Nov 14.

Herrick CA, Xu L, Wisnewski AV, *et al.* (2002): A novel mouse model of diisocyanate-induced asthma showing allergic-type inflammation in the lung after inhaled antigen challenge. J. Allergy Clin. Immunol. 109(5):873-878

Health and Safety Executive (HSE) (2005a). Work-related Asthma. Health and Safety Executive. Statistics. Available at www.hse.gov.uk/statistics/causdis/asthma.htm, accessed November 2005.

Health and Safety Executive (HSE) (2005b). Table THORR05: Occupational asthma: estimated number of cases reported by chest and occupational physicians to SWORD/OPRA and estimated rates per 100,000 workers per year, by occupation. Health and Safety Executive. Available at www.hse.gov.uk/statistics/Tables/thorr05.htm, accessed November 2005.

Health and Safety Laboratory (HSL) (1993): Preparation of samples for the HSE diisocyanate AQUA scheme. Report # IR/L/SP/93/01. UK: Health and Safety Executive. (1993)

Imai FH and Berns RS: "High-Resolution Multi-Spectral Image Archives - A Hybrid Approach." Available at: http://www.cis.rit.edu/people/faculty/berns/PDFs/cic6_Imai.pdf, accessed July 20, 2006

Jepsen, JR, Sparre-Jorgensen, A., and Kyst, A (1985): Hand protection for car-painters, Contact Derm. 13(5):317-20

Klingner TD and Boeniger MF. (2002) A critique of assumptions about selecting chemical resistant gloves: a case for workplace evaluation of glove efficacy. AOEHJ. 17(5):360-367. Available at http://www.clilabs.com/clidownloads.htm (file: GLOVEPAP1-final.pdf), accessed July 2006

Liu Q and Wisnewski AV (2003). Recent developments in diisocyanate asthma. Ann. Allergy Asthma Immun. 90:35-41

Liu Y, Sparer J, Woskie SR, *et al.* (2000): Qualitative Assessment of Isocyanate Skin Exposure in Auto Body Shops: A Pilot Study. Am. J. of Ind. Med. 37(3):265-274

Liu Y, Stowe MH, Bello D, Sparer JA, *et al.* (2005): "Surface and skin decontamination of aliphatic isocyanates: a field study." Abstract for Poster 66 presented as part of the International Conference Occupational and Environmental Exposures of Skin to Chemicals. Stockholm, Sweden, June 12-15, 2005. Available at http://www.cdc.gov/niosh/topics/skin/OEESC2/AbPost066Liu.html, accessed August 7, 2006

Liu Y, Stowe M, Bello D, *et al.* (2006): Respiratory Protection from Isocyanate Exposure in the Autobody Repair and Refinishing Industry. J. Occup. Environ. Hyg. 3(5):234-249

Liu Y, Bello D, Sparer JA, *et al.* (2007): Skin Exposure to Aliphatic Polyisocyanates in the Auto Body Repair and Refinishing Industry: A Qualitative Assessment. Ann. Occup. Hyg. 51:429-439

Marand A, Karlsson D, Dalene M and Skarping G (2005): Solvent-free sampling with di-n-butylamine for monitoring of isocyanates in air. J. Environ. Monit. 7:335-343

Marshall M, Li K, Kaufman M, Lawrence B, and McKenrick L (2002): Auto Repair Industry Evaluation Report. Published by the Local Hazardous Waste Management Program Public Health – Seattle & King County. Environmental Health Division. December 23, 2002

Mercer (2006) "New Paint Technologies in 2006 Posted 5/13/2006 By Rachael J. Mercer. AutoInc.Online edition" Available at http://www.asashop.org/autoinc/may2006/collision.htm, accessed May 20, 2009

Mickelsen RL, Roder MM, and Berardinelli SP (1986): Permeation of chemical protective clothing by three binary solvent mixtures. Am. Ind. Hyg. Assoc. J. 47(4):236-40

Mickelsen RL and Hall RC (1987): A breakthrough time comparison of nitrile and neoprene glove materials produced by different manufacturers. AULA 48(ll):941-947

Misimi E, Mathiassen JR, and Erikson U (2007): Computer vision-based sorting of Atlantic salmon (Salmo salar) fillets according to their color level. J. Food Sci. 72(1):S030-5

The National Institute for Occupational Safety and Health (NIOSH) (1996): NIOSH Alert: Preventing Asthma and Death from Diisocyanate Exposures. National Institute of Occupational Safety and Health. Cincinnati, OH. DHHS (NIOSH) Publication No. 96-111. 1996. Available at http://www.cdc.gov/niosh/asthma.html, accessed March 2009

The National Institute for Occupational Safety and Health (NIOSH) (2001): Recommendations for Chemical Protective Clothing: A Companion to the NIOSH Pocket Guide to Chemical Hazards. Available at http://www.cdc.gov/niosh/ncpc/ncpc2.html, accessed March 2009

The National Institute for Occupational Safety and Health (NIOSH) (2003): NIOSH Manual of Analytical Methods. P. C. Schlecht and P. F. O'Connor, (eds). NIOSH, Cincinnati, OH, 4th edn., Method 5525, Isocyanates, total (MAP), Issue 1, 3rd supplement, 2003, 154. Available at http://www.cdc.gov/niosh/nmam/pdfs/5525.pdf, Cincinnati: National Institute for Occupational Safety and Health, accessed June 2008

The National Institute for Occupational Safety and Health (NIOSH) (2004): A Summary of Health Hazard Evaluations: Issues Related to Occupational Exposure to Isocyanates, 1989 to 2002. Available at http://www.mass.gov/envir/ota/pubs/wbfull.pdf, accessed July 2006

The National Institute for Occupational Safety and Health (NIOSH) (2005): NIOSH Pocket Guide to Chemical Hazards. Publication No. 2005-149. Cincinnati, OH:National Institute for Occupational Safety and Health. Available at http://www.cdc.gov/niosh/npg/, accessed 12 January 2007

Oppl R (2001). Chemical protective gloves — in-use protection time vs. standard breakthrough time. Miljoe-Chemie, Hamburg, Germany. [Abstract 196] New Orleans, LA: American Industrial Hygiene Conference & Exposition.

Occupational Safety & Health Administration (OSHA) (1989): OSHA 42 Analysis Method

"Diisocyanates" Available at http://www.osha.gov/dts/sltc/methods/organic/org042/org042.html (Accessed July 15, 2006).

Occupational Safety & Health Administration (OSHA) (1996): "Centers for disease control and prevention, NIOSH health hazard evaluation report 95-0311-2593. Martin's Carstar, Inc., Lakewood, Colorado" Available at http://www.osha.gov/SLTC/autobody/docs/cdc002.html#Isocyanates (Accessed July 15, 2006).

Occupational Safety & Health Administration (OSHA) (1997a): "Aromatic isocyanate surface contamination sampling and evaluation techniques" Available at http://www.osha.gov/SLTC/isocyanates/mrl_inte.html, accessed July 15, 2006

Occupational Safety & Health Administration (OSHA) (1997b): OSHA Technical manual, Occupational Skin Exposure Chapter 2. Available at http://www.osha.gov/dts/osta/otm/otm_ii/otm_ii_2.html, accessed July 15, 2006

Occupational Safety & Health Administration (OSHA) (1999): Sampling for surface contamination. In: OSHA Technical Manual, Section II, Chapter 2. Salt Lake City, Utah: OSHA Technical Center, p 1-16

Occupational Safety & Health Administration (OSHA) (2002): 1,6-Hexamethylene Diisocyanate sampling and analytical method W 4002. "1,6-Hexamethylene Diisocyanate" Available at http://www.osha.gov/dts/sltc/methods/validated/w4002/w4002.html, accessed July 15, 2006

Pauluhn J (2008): Brown Norway rat asthma model of diphenylmethane-4,4'-diisocyanate (MDI): impact of vehicle for topical induction. Regul Toxicol. Pharmacol. 50(1):144-54

Perkins JL, Pool B (1997): Batch lot variability in permeation through nitrile gloves. AIHA J. 58:474-479

Pilin A, Pudil F, and Bencko V (2007): Changes in colour of different human tissues as a marker of age. Int. J. Legal Med. 121(2):158-62

Polettini A: Applications of LC-MS in Toxicology, Pharmaceutical Press, (2006), pp. 275.

PPG Industries (1997): PPG Two-Component Polyurethane Coating Systems Guidelines for Safe Use. PAM 9379 8/97

Pronk A, Yu F, Vlaanderen J, *et al.* (2006a): Dermal, inhalation, and internal exposure to 1,6-HDI and its oligomers in car body repair shop workers and industrial spray painters. Occup. Environ. Med. 63(9):624-31

Pronk A, Tielemans E, Skarping G, *et al.* (2006b) Inhalation exposure to isocyanates of car body repair shop workers and industrial spray painters. Ann. Occup. Hyg. 50(1):1-14

Quandt SA, Arcury TA, Austin CK, and Saavedra RM (1998): Farm-worker and farmer perceptions of farmworker agricultural chemical exposure in North Carolina. Hum. Organ. 57(3): 359-68

Rattray NJ, Botham PA, Hext PM, *et al.* (1994) Induction of respiratory hypersensitivity to diphenylmethane-4 4'-diisocyanante (MDI) in guinea pigs. Influence of route of exposure. Toxicology. 88:15-30

Redlich CA, Bello D, Wisnewski AV (2007): Isocyanate exposures and health effects. . In: Environmental and occupational medicine (Rom WN, ed). Philadelphia, PA 2007: Lippincott-Raven, 502-516.

Sanderson WT, Ringenburg V, and Biagini R (1995): Exposure to commercial pesticide applicators to the herbicide Alachlor. AIHA J. 56:890-897

Sanson EB and Tewari YB (1978): The permeability of laboratory gloves to selected solvents. AIHA J 39:169-174

Safety & Health Assessment & Research for Prevention, (SHARP) Washington State Department of Labor and Industries (2000): Workers' Compensation Based Surveillance of Asthma, Hospitalized Burns, and Adult Blood Lead Levels in Washington State, 1994-1998. SHARP report 64-1-2000. Olympia, Washington. July 2000

Safety & Health Assessment & Research for Prevention, (SHARP) Washington State Department of Labor and Industries (2003): Work-Related Asthma in Washington State: A Review of Worker's Compensation Claims from 1995-2002. SHARP report 64-6-2003. Olympia, Washington. December 2003

Safety & Health Assessment & Research for Prevention, (SHARP) Washington State Department of Labor and Industries (2005): Health and Safety in Washington State's Collision Repair Industry: A Needs Assessment. Technical report 69-4-2005. SHARP, Olympia, Washington, December 2005. Available at http://www.lni.wa.gov/Safety/Research/Collision/Repair/Default.asp, accessed March 17, 2007

Shoemaker JP, Garland CW and Steinfeld JI: Experiments in Physical Chemistry, McGraw-Hill, Inc., (1974), pp. 34-39

Sparer J, Stowe MH, Bello D, *et al.* (2004): Isocyanate exposures in autobody shop work: the SPRAY study. J. Occup. Environ. Hyg. 1(9):570-81

Streicher RP, Arnold JE, Ernst MK, and Cooper CV (1996): Development of a novel derivatization reagent for the sampling and analysis of total isocyanate group in air and comparison of its performance with that of several established reagents. AIHA J 57(10): 905-913.

Streicher RP, Reh CM, Key-Schwartz RJ, *et al.* (2000): Determination of airborne isocyanate exposure: considerations in method selection. AIHA J. 61(4):544-56. Review

Streicher R, Reh CM, Key-Schwartz RK, *et al.* (2002): Selecting Isocyanate Sampling and Analytical Methods. Appl. Occup. Environ. Hyg. 17 (3):157-162

Taylor J: An Introduction to Error Analysis, University Science Books, Mill Valley CA, (1982)

Trelles Gaines LG, Fent KW, Flack SL, *et al.* (2009): Urine 1,6-Hexamethylene Diamine (Hda) Levels Among Workers Exposed To 1,6-Hexamethylene Diisocyanate (HDI). In preparation

Tremblay P, Lesage J, Ostiguy C, and Tra HV (2003): Investigation of the competitive rate of derivatization of several secondary amines with phenylisocyanate (PHI), hexamethylene-1,6-diisocyanate (HDI), 4,4'-methylenebis(phenyl isocyanate) (MDI) and toluene diisocyanate (TDI) in liquid medium. Analyst. 128(2): 142-149

Toyota Motor Corporation (1991): Toyota Fundamental Painting Procedures. Pub. No. BRM024E. Edited by Body & Paint Service Division. Published by Overseas Service Division. Japan.

Vaughan E (1993): Chronic exposure to an environmental hazard: Risk perceptions and self protective behavior. Health Psychol. 12:74-85

Vandenplas O, Cartier A, Lesage J, *et al* (1993) prepolymers of hexamethylene diisocyanate as a cause of occupational asthma. J. Allergy Clin. Immunol. 91:850-61

Whittaker SG and Reeb-Whitaker C (2009): Characterizing the Health and Safety Needs of the Collision Repair Industry. J. Occup. Environ. Hyg. 6(5):273-282

Woskie SR, Sparer J, Gore RJ, *et al.* (2004): Determinants of isocyanate exposures in auto body repair and refinishing shops. Ann. Occup. Hyg. 48(5):393–403

Appendix A

CHAPTER ABSTRACTS

A.1. Objective Surface Colorimetric Sampling (Chapter 2)

Title: **Objective Color Scale for the SWYPE Surface Sampling Technique Using Computerized Image Analysis Tools**

Abstract

Colorimetric SWYPE pads are useful tools for identifying unpolymerized aliphatic isocyanates on a variety of surfaces. This technique has been used in auto body shops to determine the presence of hexamethylene diisocyanate (HDI) and other aliphatic isocyanates that are important constituents of many automotive coatings. SWYPEs have the advantage of being relatively inexpensive, rapid, and portable. The color change elicited by aliphatic isocyanates (from yellow to red) provides a visual indication of the extent of surface contamination. In an attempt to quantify isocyanate contamination based on the colorimetric response, an objective color scale was developed for isocyanate loading. Sampled pads were digitized on a calibrated portable flatbed scanner and red-green-blue (RGB) histograms of SWYPE images were created. A calibration curve was created from a series of reference images derived from SWYPEs loaded with an isocyanate-containing product. The SWYPE RGB analysis allowed for quantification over a range of isocyanate loadings: from ~0.01 to 24.0 μg/cm^2, with reproducibility of >90%, accuracy >90%, and a surface extraction efficiency of >90%. RGB analysis exhibited a lower detection limit than visual scoring (~3 μg versus ~10 μg). The colorimetric response was cross-validated with a high-performance liquid chromatography quantitative assay. When combined with RGB analysis, SWYPE colorimetric wipes represent a rapid and inexpensive method to assess objectively surface contamination with aliphatic polyisocyanates.

A.2. Survey of Dermal Protection in Autobody Shops (Chapter 3)

Title: **Survey of Dermal Protection in Washington State Collision Repair Industry**

Abstract

Isocyanates in auto paints are known irritants, sensitizers, and can cause occupational asthma in the collision repair industry. Dermal exposure to isocyanates is significant in these shops and can contribute to painter's disease onset. Information about spray painters' use of dermal personal protective equipment (PPE) in Washington State was collected during field visits using an industrial hygiene survey. Information on the frequency and type of dermal PPE was summarized from survey data and field observations. In addition, demographic, health, and work determinants were evaluated for their effect on painters' dermal PPE choices. Dermal PPE outcome variables studied included frequency of glove use, type of glove use, thickness of glove use, and frequency of coverall use. Survey data reported that 50% of shops used latex gloves, 38% used nitrile gloves, and 8% used none. Sixty nine percent of painters always used gloves while 63% always used coveralls. Even though overspray presents an opportunity for dermal exposure in the neck and face, only 18.7% of painters used respirators that covered their head. Overall, we found that auto painters' PPE choices were usually determined by frequency and type of dermal PPE. Painters who always used coveralls were more likely to use gloves (OR=7.9, p=0.061, 95%CI: 1.4771-43.4783, Cox & Snell R2=0.185) and painters using nitrile gloves were more likely to use gloves frequently (Pearson chi square p=0.079). Also, we found that dermal PPE outcomes were associated to smoking status, for example, ever smokers tended to use gloves and coveralls more frequently (Pearson chi-square p_{gloves}=0.05 and $p_{coveralls}$=0.01). Ever smokers included those that have quite smoking and may be more concerned with respiratory disease. Paint job frequency had an effect on painters dermal PPE choices, for example, painters who painted more jobs per month used coveralls more frequently (independent t-test p=0.038, 95%CI: -85.164 to -2.669). We suggest that other factors affecting dermal PPE choices were comfort, convenience, and painter's experience. Exact logistic regressions and random sample calculations corroborated logistic regression results thus we concluded that painter's observations were independent of shop. Because of the small sample size studied, there is need for future research to further understand painters and business owner's motivators and preferences for adopting best practices for dermal PPE use. There are training and research opportunities with auto painters to improve the use of safety practices, in particular the use of dermal PPE to reduce work-related asthma.

A.3. Isocyanate Analytical Method Comparison (Chapter 4)

Title: **Determination of Isocyanate Concentrations in a Sample of Commercial Hardener – An Isocyanate Analytical Method Comparison Study**

Abstract

Aliphatic diisocyanates are widely used in the collision repair industry as components of catalyst hardeners in two-part polyurethane coating systems. Exposure to isocyanates in the auto-body industry has been associated with increased risk for work-related asthma, therefore the importance of measuring isocyanate exposures. This current study critically compares methods for analyzing the isocyanates present in a common and representative bulk sample of clear coat hardener, as well as comparing the metrics for reporting results. The methods compared were: modified LC/UV-FLD NIOSH 5525 using 1-(9-anthracenylmethyl)piperazine or MAP as derivatization reagent, LC-MS using 1-(2- methoxyphenyl)piperazine (MPP) as derivatization reagent, LC/UV-FLD OSHA 42/PV2034 using 1-(2-pyridyl)piperazine (PPZ) as derivatization reagent, and modified LC/UV-FLD Omega Iso-Chek using MPP and 9-(methylaminomethyl)anthracene (MAMA) in a dual filter system. A bulk sample was selected for analysis in order to avoid the variability associated with the sampling of airborne isocyanates, in particular during collection from an air sample. In overall, the key issues on which the methods here compared differed from each-other are: 1) derivatization reagent, 2) chromatography and detection, 3) standards used for calibration, and 4) reported units. We concluded that the main challenges when comparing isocyanate analytical methods were: 1) metrics used when reporting results were different and some times not directly comparable, especially if manufacturer's proprietary information or titration data were not available, which is common for field samples, and 2) each method provides a different set of isocyanate species depending on the method's capability. The authors suggest caution when comparing results from different isocyanate analytical methods. Using the same metrics, as possible, and having enough information about the content of isocyanates species is key for a fair comparison. Each method showed strengths and weaknesses that seemed to be mostly related to the type of detector used. The next step in method development points to a method that uses UV/FLD coupled with MS (or MS-MS). This powerful combination would bring the advantages associated with both detectors: UV/FLD would be able to measure total NCO-mass of isocyanates including specific monomers and oligomers that can then be identified by the MS detector. The MS would also provide lower detection limits than if UV/FLD was used alone.

The refinement of a wider set of standards would be essential in the future development of a new LC/UV/FLD-MS method.

A.4. Permeation Panel Development (Chapter 5)

Title: **Development of a Permeation Panel to Test Dermal Protective Clothing Against Sprayed Coatings**

Abstract

Permeability and breakthrough time data for low volatility and low water solubility chemicals, such as isocyanates or pesticides, are limited. The only data available usually provide information for pure compounds or mixtures with only one or two solvents for a few dermal protective materials. Unfortunately, behavior in complex mixtures and in particular mixtures that polymerize or cure, like coatings, paints, foams, or glues is different. Lack of data is not surprising because conventional permeation testing methods do not apply. We developed a novel device, called a permeation panel, for field-testing dermal protective clothing. The panel provides objective data to evaluate the protection efficacy of materials; up to 8 test materials can be measured at once and simulate actual sprayed-on operations. Solid media placed behind the tested material was used to collect permeating chemicals, in this case isocyanates. The solid media was impregnated with a derivatization reagent for stabilization until analysis. Impregnated solid media used to measure isocyanate permeation included 1-(2-pyridyl)-piperazine (PPZ) coated fiber glass filters and SWYPE colorimetric pads. Both PPZ filters and SWYPE provided usable estimates of permeation. PPZ filters provided quantitative permeation measurements by modified OSHA 42/PV2034 method analysis. SWYPE provided immediate estimates by visual scoring and semi quantitative estimates by the RGB analysis. A minimum of 12 teflon filters were attached between the permeation cells to measure loading. Mass gain of dry paint on the loading filters was used to determine the homogeneity of the sprayed-on material loading. Permeation panel characterization results suggested that the permeation panel is a viable method that can be used to assess dermal protective clothing performance. Loading assessment determined that the sprayed-on material had a thickness of approximately 0.06mm and fairly homogeneous mass loading throughout the panel (up to 13%CV). Temperature inside the panel was stable (72 +/- 1 F) as well as relative humidity (50 +/-1%). Permeation variability was assessed by one-way ANOVA for factors such as day, paint, and panel; with only panel having a significant difference in permeation for both PPZ (F

= 8.1 p = 0.013) and SWYPE (F = 14.4 p = 0.002). Standardization of experiments is crucial to diminish the variability among panels. Results from the permeation panel can be used to provide recommendations to workers for improving their work practices and reducing illnesses linked to dermal exposures, such as dermatitis and work-related asthma.

A.5. Permeation Panel Experiments (Chapter 6)

Title: **Evaluation of Protective Gloves Against Aliphatic Isocyanate Paints Used In The Collision Repair Industry**

Abstract

Painters in auto body shops are exposed to a variety of hazardous chemicals, particularly isocyanates, used in hardeners of two-part paint systems and present in high concentrations in the final "clear" coat. While inhalation of isocyanate aerosols and vapors has long been recognized as a primary cause of work-related asthma, growing evidence suggests that skin exposure may be an important route of exposure. Only limited and conflicting information is available on the effectiveness of protective gloves for spray painters, focused largely on comfort, elasticity, and solvent resistance rather than resistance to isocyanates. This is not surprising, because conventional permeation testing methods do not work with low volatility, low water solubility agents, complex mixtures, or materials that polymerize or cure, like isocyanate-based paint. We developed a novel device, called a permeation panel, for field-testing protective clothing. The panel provides objective data to evaluate the efficacy of gloves for protection against isocyanates. Several glove materials can be tested at once and simulate actual spray painting operations. Fivety percent of autobody shops in Washington State use thin latex gloves, however; permeation panel experiments suggested that thin latex gloves were not protective against isocyanates. Thin latex gloves showed consistently more isocyanate permeation than thin nitrile gloves measured by three different methods: 1-(2-pyridyl)-piperazine (PPZ) coated fiber glass filters analyzed by modified OSHA 42/PV2034, SWYPE colorimetric pads analyzed by RGB analysis, and MAMA coated fiber glass filters analyzed by modified Iso-Chek. Thin latex (4 mil) reported a permeation starting immediately, at a rate of 2.9 ng/min-cm^2 and thin nitrile (5 mil) after 30 minutes. Thicker gloves (8-14 mil) performed better than thinner gloves with thin latex performing the worst. We recommend that workers do not use thin (4-5ml) latex gloves for mixing or spray painting since there is ample evidence of breakthrough within typical usage times. Thin nitrile gloves provide better protection than

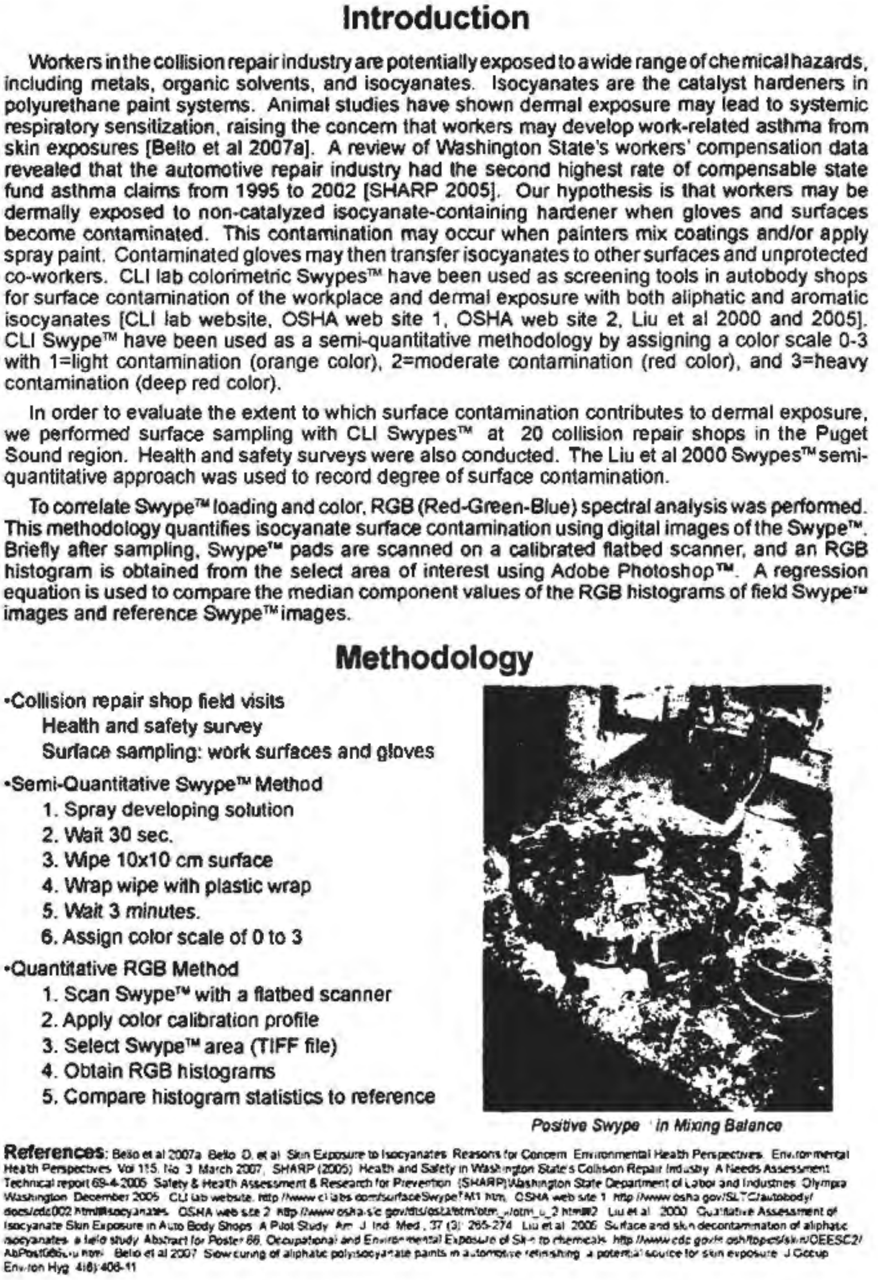
thin latex, only if they are changed frequently, at least every 20 minutes, which is as long as a typical paint application. Painters should use good work practices to also avoid skin exposure in other areas besides their hands to prevent work-related asthma.

Appendix B

SWYPE RGB ANALYSIS DATA

B.1. Ceballos *et al.* 2007 Poster (Chapter 2)

Ceballos, D.M., M.G. Yost, S.G. Whittaker, and J. Camp: "Isocyanate Surface Sampling in the Puget Sound Collision Repair Industry." Abstract. Poster 45 presented at the American Industrial Hygiene Conference & Expo, Philadelphia, PA. June 3-6, 2007.



Introduction

Workers in the collision repair industry are potentially exposed to a wide range of chemical hazards, including metals, organic solvents, and isocyanates. Isocyanates are the catalyst hardeners in polyurethane paint systems. Animal studies have shown dermal exposure may lead to systemic respiratory sensitization, raising the concern that workers may develop work-related asthma from skin exposures [Bello et al 2007a]. A review of Washington State's workers' compensation data revealed that the automotive repair industry had the second highest rate of compensable state fund asthma claims from 1995 to 2002 [SHARP 2005]. Our hypothesis is that workers may be dermally exposed to non-catalyzed isocyanate-containing hardener when gloves and surfaces become contaminated. This contamination may occur when painters mix coatings and/or apply spray paint. Contaminated gloves may then transfer isocyanates to other surfaces and unprotected co-workers. CLI lab colorimetric Swypes™ have been used as screening tools in autobody shops for surface contamination of the workplace and dermal exposure with both aliphatic and aromatic isocyanates [CLI lab website, OSHA web site 1, OSHA web site 2, Liu et al 2000 and 2005]. CLI Swype™ have been used as a semi-quantitative methodology by assigning a color scale 0-3 with 1=light contamination (orange color), 2=moderate contamination (red color), and 3=heavy contamination (deep red color).

In order to evaluate the extent to which surface contamination contributes to dermal exposure, we performed surface sampling with CLI Swypes™ at 20 collision repair shops in the Puget Sound region. Health and safety surveys were also conducted. The Liu et al 2000 Swypes™ semi-quantitative approach was used to record degree of surface contamination.

To correlate Swype™ loading and color, RGB (Red-Green-Blue) spectral analysis was performed. This methodology quantifies isocyanate surface contamination using digital images of the Swype™. Briefly after sampling, Swype™ pads are scanned on a calibrated flatbed scanner, and an RGB histogram is obtained from the select area of interest using Adobe Photoshop™. A regression equation is used to compare the median component values of the RGB histograms of field Swype™ images and reference Swype™ images.

Methodology

- Collision repair shop field visits
  - Health and safety survey
  - Surface sampling: work surfaces and gloves
- Semi-Quantitative Swype™ Method
  1. Spray developing solution
  2. Wait 30 sec.
  3. Wipe 10x10 cm surface
  4. Wrap wipe with plastic wrap
  5. Wait 3 minutes.
  6. Assign color scale of 0 to 3
- Quantitative RGB Method
  1. Scan Swype™ with a flatbed scanner
  2. Apply color calibration profile
  3. Select Swype™ area (TIFF file)
  4. Obtain RGB histograms
  5. Compare histogram statistics to reference

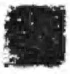
Positive Swype™ in Mixing Balance

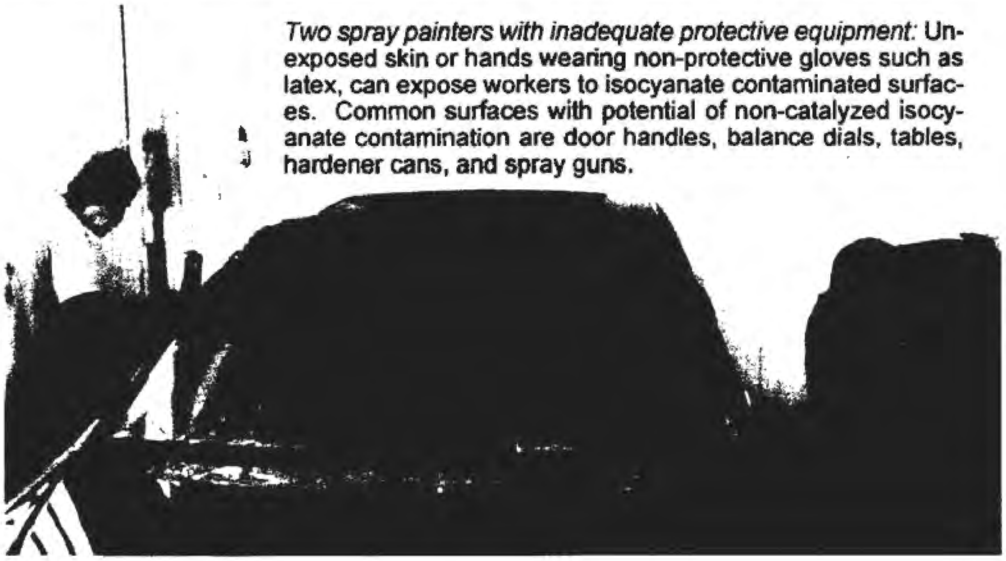
References: Bello et al 2007a Bello D. et al Skin Exposure to Isocyanates Reasons for Concern Environmental Health Perspectives. Environmental Health Perspectives Vol 115, No 3 March 2007, SHARP (2005) Health and Safety in Washington State's Collison Repair Industry A Needs Assessment Technical report 69-4-2005 Safety & Health Assessment & Research for Prevention (SHARP) Washington State Department of Labor and Industries Olympia Washington December 2005 CLI lab website. http //www cl labs com/surfaceSwype™1 htm, OSHA web site 1 http //www osha gov/SLTC/autobody/docs/cdc002 html#isocyanates. OSHA web site 2 http //www osha-slc gov/dts/osta/otm/otm_ii/otm_ii_2 html#2 Liu et al 2000 Qualitative Assessment of Isocyanate Skin Exposure in Auto Body Shops A Pilot Study Am J Ind Med., 37 (3) 265-274 Liu et al 2005 Surface and skin decontamination of aliphatic isocyanates a field study Abstract for Poster 66, Occupational and Environmental Exposure of Skin to chemicals http //www cdc gov/niosh/topics/skin/OEESC2/AbPost066Liu html Bello et al 2007 Slow curing of aliphatic polyisocyanate paints in automotive refinishing a potential source for skin exposure J Occup Environ Hyg 4(6) 406-11

Continued on next page

Swype™ Semi-Quantitative Data

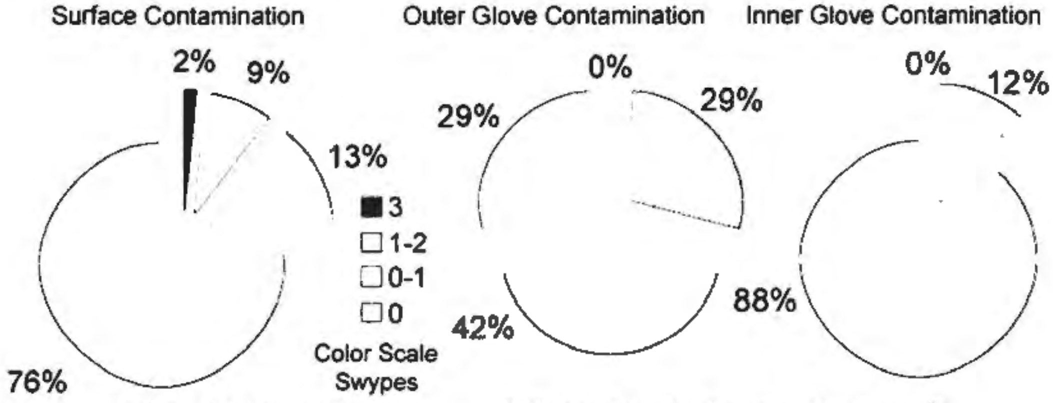
Swype™ Loading Scale for Bayer Desmodour N3400:
Loaded aluminum foil surfaces as references

Load	0 ug	3.5 ug	31 ug	62 ug	124 ug	186 ug	>100 mg
Color	Yellow		Yellow/ Orange		Orange/ Red		Deep Red
Swype™							
Color Scales	0		1		2		3
Contamination	No		Slight		Moderate		High



Two spray painters with inadequate protective equipment: Unexposed skin or hands wearing non-protective gloves such as latex, can expose workers to isocyanate contaminated surfaces. Common surfaces with potential of non-catalyzed isocyanate contamination are door handles, balance dials, tables, hardener cans, and spray guns.

Isocyanate Surface Contamination in the Puget Sound Collision Repair Industry



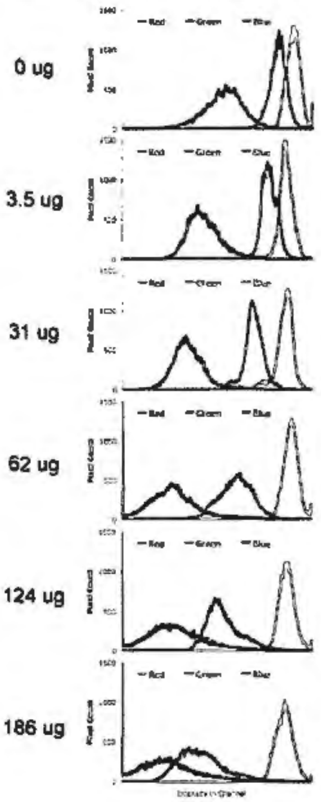
20 shops visited, 122 Swypes™

8 Shops, 24 pair of gloves, 96 Swypes™

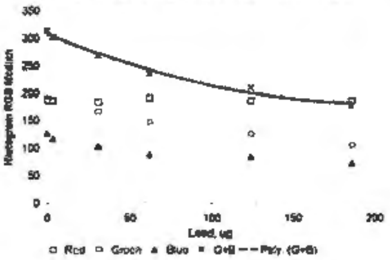
Continued on next page

Swypes™ Characterization and Validation

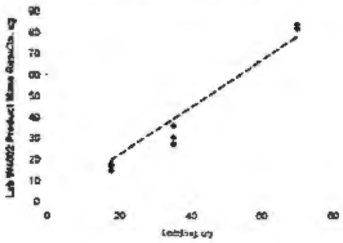
RGB Histograms per loading



RGB Method versus W4002



Swypes™ RGB Calibration, R² 0.98



Ghost Wipes W4002 Calibration, R² 0.96

Swypes™ loading is proportional to color intensity, and the sum of Green and Blue channel values provides the largest signal range for calibration.

The next phase of this evaluation will include a parallel side-by-side comparison of Swypes™ and Ghost Wipes method W4002 in a field situation. Swypes™ color scale data has been succesfully compared with quantitative wipes analyzed by NIOSH 5525 [Bello et al, 2007].

Conclusions

Swypes™ have the advantages of being fast, economical, visual, and easy to use. They have the disadvantages of not being specific for a particular isocyanate but general to NCO groups. Another disadvantage is that mineral oil (developing solution) can be a workplace hazard if not cleaned after sampling. Swypes™ surface sampling has great potential when combined with the RGB analysis method described here. However, many variables affect the quantification of Swype™ color, such as wetting agent (oil), light, time, loading, type of surface and isocyanate, roughness, dirt and other interferences. Oil and plastic wrap, for example, help preserve color. It was determined that when using oil and plastic wrap there is no significant loss of color within 20 minutes of fully developed color. Laboratory RGB method characterization determined Swypes™ detection limit (LOD) to be ~ 10 ug N3400 product (CLI lab: 3-5ug lab LOD and Liu et al 2000: 50ug field LOD), replicates with a coefficient of variation < 9%, and extraction efficiency > 90% (determined on aluminum surfaces).

In the Puget Sound Region, 90% of surfaces with positive contamination were inside the paint mixing room. Consequently, surface contamination outside the mixing room does not appear to be a significant contributor to dermal exposure. Most gloves were contaminated with isocyanates on the glove's outer surface (71%) and occasionally on the inner surface (12%). Although widespread surface contamination of collision repair shops does not appear to be a significant problem, we recommend painters to improve mixing practices and change gloves after each mixing or painting task.

Acknowledgements: To Neal McConnell for helping with the implementation of the RGB methodology, his constant support, and technical assistance. Thanks also to SHARP field assistants Rob Anderson, Carolyn Whitaker, Erika Jenkins, and Tammy Clawson; to University of North Carolina, Chapel Hill, Professor Leena Nylander-French and field assistants Linda Gaines, Kenny Fent, Sheila Flack, Jen Thomasen; to Russell Dills, Jacqui Ahmad, and Jianbo Yu at the Environmental Health Laboratory, UW, for their help and advise in regards to chemical analysis; and to funding by the National Occupational Research Agenda Project.

B.2. SWYPE RGB Calibration for N3400 (Chapter 2)

Color Scale	File	Cal #	Load µg		Red	Green	Blue
0	scan0008	0	0	mean	189.95	187.55	128.92
				sd	11.64	11.87	16.35
				median	189	187	127
	scan0013	1	3.5	mean	187.2	185.06	119.07
				sd	9.75	9.8	12.96
				median	187	185	117
1	scan0012	2	31	mean	184.41	166.32	104.29
				sd	12.13	12.67	14.95
				median	185	166	102
	scan0015	3	62	mean	191.67	147.03	90.76
				sd	11.76	18.73	18.6
				median	191	147	88
2	scan0014	4	124	mean	188.78	130.42	87.97
				sd	12.41	17.94	19.28
				median	187	126	84
	scan0016	5	186	mean	187.41	108.44	76.44
				sd	13.14	18.2	19.35
				median	187	105	72
3 or positive control	scan0007	6		mean	175.08	93.94	73.46
				sd	9.6	12.05	13.31
				median	174	92	71

B.3. OSHA W4002 Calibration for Chromabase 7775S (Chapter 2)

Cal #	**Hardener Load**	**HDI**	**IPDI**	**Oligomers**
	μg bulk	**μg/sample**	**μg/sample**	**μg/sample**
Cal 1	97.4	0.15	0.16	4.5
Cal 1b	97.4	0.18	0.23	4.2
Cal 2	243.5	0.16	0.23	11
Cal 2c	243.5	0.19	0.23	9.5
Cal 3	389.6	0.21	0.23	16
Cal 4	487	0.16	0.18	23

B.4. SWYPE RGB Calibration for Chromabase 7775S (Chapter 2)

Color Scale	File	Cal #	Load µg		Red	Green	Blue
0	ppp167	blank	0	mean	224.69	203.6	116.33
				stdev	9.42	10.99	25.43
				median	223	201	114
0	ppp168		48.7	mean	232.68	190.09	123.17
				stdev	11.18	22.34	30.56
				median	233	190	125
0	ppp169		48.7	mean	217.93	177.85	97.51
				stdev	8.84	11.81	23.83
				median	218	177	97
0	ppp171	1	97.4	mean	224.31	185.97	107.43
				stdev	9.72	17.39	28.12
				median	225	188	107
1	ppp172		194.8	mean	220.7	142.46	76.02
				stdev	9.25	20.68	34.3
				median	220	142	75
1	ppp173	2	243.5	mean	223.11	154.32	105.09
				stdev	12.7	23.25	32.02
				median	222	154	105
1	ppp174	2	243.5	mean	220.46	152.64	98.89
				stdev	9.63	24.51	30.13
				median	220	153	99
1	ppp175	2	243.5	mean	221.56	156.03	104.85
				stdev	13.06	23.46	29.63
				median	221	157	106
1	ppp176	3	389.6	mean	216.72	143.33	81.5
				stdev	10.25	18.8	26.77
				median	216	141	80
2	ppp177	4	487	mean	213.93	138.71	90.62
				stdev	105.2	29.06	29.78
				median	214	143	90
2-3	ppp178		974	mean	214.61	121.42	79.8
				stdev	10.92	27.61	31.33
				median	215	123	80

Appendix C

SURVEY DERMAL PPE DATA

C.1.a Baseline Charateristics, Quantitative Variables (First visit)

UNC ID	SHARP ID	Worker	Age yr	Weight lbs	Height in	BMI	Time Spray Painting yr	Times painting this month
0911	184	A	29	200	70.5	28.3	2	130
1011	163	A	28	175	67	27.4	10	50
1111	34	A	39	170	67	26.6	7	50
1211	658	A	32	180	70	25.8	12	60
1221	658	B	59	255	68	38.8	35	24
1311	196	B	32	165	67	25.8	4.5	32
1411	101	A	22	215	70	30.8	3	160
1511	642	A	41	200	72	27.1	10	20
1521	642	B	23	205	74	26.3	2	12
1611	128	A	37	215	73	28.4	19	60
1711	162	A	35	154	64	26.4	3	40
1811	260	B	43	160	65	26.6	12	40
1821	260	A	21	175	68.5	26.2	2.5	40
1911	12	A	24	165	69	24.4	5	60
1921	12	B	22	125	64	21.5	5	200
1931	12	C	35	190	70	27.3	17	25
2011	102	A	23	250	76	30.4	0.25	160
2111	74	A	41	170	70.5	24.0	22	80
2211	124	A	33	200	69	29.5	15	60
2311	227	A	37	220	73	29.0	15	100
2411	129	A	33	265	71	37.0	15	72
2511	63	B	38	230	72	31.2	14	30
2711	204	A	34	190	72	25.8	16	70
2811	250	A	51	160	67	25.1	32	60
2911	660	A	36	220	70	31.6	20	160
2921	660	B	30	145	66	23.4	5	40
3011	8	A	45	204	74	26.2	25	140
3021	8	B	43	224	71	31.2	27	8
3111	659	A	28	170	71	23.7	10	20
3211	137	A	29	215	66	34.7	5	10
3311	32	A	25	215	71	30.0	0.5	5
3411	279	A	38	160	65	26.6	0.42	120

C.1.b. Baseline Charateristics, Categorical Variables (First visit)

UNC ID	Hispanic	Race	Skin Type	Smoker	Past Smoker	Smoker Status
	N=no Y=yes	W-white B-black H-hispanic O-other M-mixed A-Asian N-Native American	A-Burns very easily B-Burns easily C-Tans easily D-Brown E-Black	N=no Y=yes	N=no Y=yes	0=never 1=past 2=current
0911	N	W	C	N	N	0
1011	N	W	A	N	Y	1
1111	Y	H	B	N	N	0
1211	N	W	B	N	N	0
1221	N	W	C	N	N	0
1311	N	W	C	Y		2
1411	N	W	B	Y		2
1511	N	W	C	N	N	0
1521	N	W	C	N	Y	1
1611	N	W	A	N	N	0
1711	N	A	D	N	N	0
1811	Y	O	D	N	Y	1
1821	N	M	D	N	N	0
1911	N	W	C	N	Y	1
1921	N	W	B	Y		2
1931	N	W	C	N	N	0
2011	N	W	B	Y		2
2111	N	W	C	N	N	0
2211	N	W	B	Y		2
2311	N	W	A	N		0
2411	N	N	D	Y		2
2511	N	W	C	Y		2
2711	N	W	B	N	Y	1
2811	N	W	C	N	Y	1
2911	N	W	A	N	Y	1
2921	Y	M	C	N	Y	1
3011	N	M	C	N	N	0
3021	N	W	B	N	Y	1
3111	N	W	B	N	N	0
3211	N	W	B	Y		2
3311	N	W	B	Y		2
3411	N	W	C	N	N	0

C.2.a Type of Glove Use (First visit)

UNC ID	Glove Type	Glove Thickness (U=Unknown, Tn=Thin, M=Medium, Tk=Thick)	Glove Model
0911	Latex	Tn	
1011	Latex	Tn	
1111	Latex	Tn	
1211	None	U	
1221	Latex	Tn	
1311	Nitrile	Tn	
1411	Latex	Tn	
1511	Latex	Tn	Microflex Diamond Grip MF-300-L
1521			
1611	Nitrile	M	Microflex Supreno
1711	Latex	Tn	Microflex Diamond Grip Latex MF300-L
1811	Latex	Tn	
1821	Latex	U	
1911	Other	Tk	0320005 MIM / 217180996i W62T CE
1921	Latex	M	Microflex Safegrip Powder-free Latex (blue)
1931			
2011			
2111	Latex	Tk	Gloveworks Heavy Duty 8 mil textured industrial latex ILHD46100
2211	Nitrile	Tn	ProGuard 8646 food service/gen purpose powdered
2311	Latex	U	
2411	None		
2511	Latex		
2711	Nitrile	U	Gloveworks industrial nitrile powdered Ammex
2811	Nitrile	M	Microflex Supreno SE
2911	Nitrile	U	Nitrile Extreme
2921	Nitrile	M	SAS Safety Corp 8 mil 12 inch powder free
3011	Nitrile	M	Microflex Supreno SE
3021	nitrile		
3111	Nitrile	M	Glove Plus heavy duty 8 mil extra long 12 inch powder free
3211	Latex	Tk	Thickster SAS 6603 12 mil
3311	Nitrile	Tn	
3411	Latex	Tn	Performance Select Latex 432-202

C.2.b. Type of Respirator Use (First visit)

UNC ID	Respirator Type
0911	Replaceable half face air purifying respirator
1011	Powered air purifying respirator
1111	Disposable half face air purifying respirator
1211	Disposable half face air purifying respirator
1221	Disposable half face air purifying respirator
1311	Replaceable half face air purifying respirator
1411	Air line half face respirator
1511	Air line helmet or hood respirator
1521	
1611	Air line helmet or hood respirator
1711	Replaceable half face air purifying respirator
1811	Full face air purifying respirator
1821	Replaceable half face air purifying respirator
1911	Disposable half face air purifying respirator
1921	Air line helmet or hood respirator
1931	
2011	Powered air purifying respirator
2111	Disposable half face air purifying respirator
2211	Replaceable half face air purifying respirator
2311	Disposable half face air purifying respirator
2411	Replaceable half face air purifying respirator
2511	Replaceable half face air purifying respirator
2711	Air line half face respirator
2811	Replaceable half face air purifying respirator
2911	Replaceable half face air purifying respirator
2921	Disposable half face air purifying respirator
3011	Replaceable half face air purifying respirator
3021	
3111	Air line helmet or hood respirator
3211	Disposable half face air purifying respirator
3311	Disposable half face air purifying respirator
3411	Replaceable half face air purifying respirator

C.2.c. Type of Coverall Use (Three visits)

UNC ID	Visit	Coverall Make	UNC ID	Visit	Coverall Make
0911	1		2012	2	Maaco
0912	2	Shoot Suit	2013	3	Maaco
0913	3	Shoot Suit	2111	1	
1011	1		2112	2	Mipa
1012	2	SAS Safety	2113	3	Mipa
1111	1	Wears shoot suit with hood	2211	1	Uses Wesco nylon shoot suit with hood
1211	1		2212	2	Wesco Auto Supply
1212	2	Shoot Suit	2213	3	Shoot Suit
1213			2311	1	
1221	1		2312	2	Shoot Suit
1222	3	cotton	2411	1	
1311	1	Wears shoot suit with hood	2412	2	
1312	2	Shoot Suit	2413	3	
1313	3	PPG	2511	1	Hood on shoot suit down
1321	2	Hi-life	2512	2	Shoot Suit
1411	1	Wears shoot suit with fabric hood	2513	3	Shoot Suit
1412	2	Shoot Suit	2711	1	SAS moonsuit coverall
1413	3	Aramark	2712	2	SAS moonsuit coverall
1511	1		2713	3	SAS moonsuit coverall
1512	2	SAS Safety	2811	1	Shoot Suit
1513	3	SAS Safety	2812	2	Shoot Suit
1521			2813	3	Shoot Suit
1611	1		2911	1	Shoot Suit
1612	2	Shoot Suit	2912	2	Shoot Suit
1613	3	Shoot Suit	2913	3	Shoot Suit
1711	1	Wore shoot suit	2921	1	Akzo Nobel
1712	2	Kleen Guard	2922	3	Akzo Nobel
1713	3	Shoot Suit	3011	1	SAS Safety
1811	1	Wore coveralls	3012	2	
1812	2	SAS Safety	3013	3	SAS Safety
1813	3	SAS Safety	3021	1	SAS Safety
1821	1		3022	2	
1822	2	SAS Safety	3023	3	SAS moonsuit coverall
1823	3	SAS Safety	3111	1	
1911	1		3112	2	
1912	2	SAS Safety	3113	3	
1913		SAS Safety	3211	1	
1921	1		3212	2	Mipa
1922	2	Shoot Suit	3213	3	Mipa
1923	3	Shoot Suit	3311	1	Shoot Suit
1931			3312	2	Shoot Suit
1932	2	Shoot Suit	3411	1	SAS Safety
1933	3	PPG	3412	2	SAS Safety
2011	1				

C.3. Frequency of PPE Use (First Visit)

	N=Never, S=Seldom, U=Usually, A=Always				
UNC ID	Gloves	Long Sleeves	Coveralls	Hat	Goggles
0911	U	U	U	U	N
1011	A	N	A	N	A
1111	A	A	A	A	N
1211	N	S	N	N	N
1221	U	N	N	N	N
1311	A	A	A	S	N
1411	A	A	A	A	N
1511	A	S	N	S	S
1521	A	A	A	N	N
1611	A	N	A	A	A
1711	U	A	U	N	N
1811	A	A	S	S	A
1821	A	U	A	S	N
1911	A	A	A	S	S
1921	U	N	A	N	U
1931	U	N	N	N	A
2011	A	N	A	N	A
2111	A	N	A	N	S
2211	A	N	A	A	S
2311	U	A	A	N	N
2411	S	N	N	N	N
2511	A	A	A	N	N
2711	A	N	A	A	N
2811	A	N	A	U	N
2911	A	N	A	U	S
2921	A	A	A	A	S
3011	A	N	U	S	S
3021	A	N	A	N	N
3111	U	S	S	A	A
3211	A	N	N	N	N
3311	A	S	U	U	S
3411	U	N	A	A	N

Continued on next page

	N=Never, S=Seldom, U=Usually, A=Always					
UNC ID	**Repleable half face air purifying respirator**	**Disposable half-face air purifying respirator**	**Full face air purifying respirator**	**Air line full face respirator**	**Air line helmet or hood respirator**	**Powered air urifying respirator**
0911	A	N	N	N	N	N
1011	S	N	N	N	N	A
1111	A			N		
1211	A	N	N	N	N	N
1221	N	A	N	N	N	N
1311	A	N	N	N	N	N
1411	S	N	N	A	N	N
1511	A	N	N	N	A	N
1521	A	N	N	N	N	N
1611	N	N	N	A	N	N
1711	A	N	N	N	N	N
1811	N	N	A	N	N	N
1821	A	N	N	N	N	N
1911	A	A	N	S	N	N
1921	U		N	U		N
1931	U	N	N	N	N	A
2011	N	N	N	A	N	N
2111	A	A	N	N	N	N
2211	U	N	N	N	N	N
2311	A	N	N	N	N	N
2411	U	N	N	N	N	N
2511	A	N	N	N	N	N
2711	N	N	N	N	N	A
2811	A	N	N	N	N	N
2911	A	N	N	N	N	N
2921	A	N	N	N	N	N
3011	A	N	N	N	N	N
3021	A	N	N	N	N	N
3111	S	N	N	N	A	N
3211	A	N	N	N	N	N
3311	A	N	N	N	N	N
3411	A	N	N	N	N	N

Appendix D

INTERMETHOD COMPARISON DATA

D.1. Modified Iso-Chek Method Data (Chapter 4)

ID	lab number	N3300	Z4470	corr. Z4470	N3400	N100	HDI	corr. HDI	IPDI
		µg	µg	µg	µg	µg	µg	µg	µg
MOP1	08A0298	1.4	5	3.5	7.3	0.3	0.08	0.015	0.030
MOP2	08A0299	10.7	31.4	22.0	56.1	0.4	0.08	0.015	0.170
MOP3	08A0300	10.4	33.5	23.5	57.2	0.4	0.21	0.145	0.150
MOP4	08A0301	0.3	1.8	1.3	0.9	0.5	0.12	0.055	0.000
MOP5	08A0302	0.5	0.5	0.4	0.2	0.5	0.10	0.035	0.000
MOP6	08A0303	13.1	40.8	28.6	71.5	0.7	0.37	0.305	0.200
MOP7	08A0304	52.7	164.0	114.8	290.8	1.8	0.66	0.595	0.800
MOP8	08A0305	10.7	37.7	26.4	59.3	0.2	0.25	0.185	0.170
MOP9	08A0306	2.4	5.8	4.1	8.1	0.6	0.11	0.045	0.040
MOP10	08A0307	54.4	179.4	125.6	323.5	10.2	0.91	0.845	0.920
MOP11	08A0308	0.4	2.0	1.4	0.5	0.5	0.05	0.000	0.030
MOP12	08A0309	0.1	0.7	0.5	0.9	0.4	0.09	0.025	0.000
MOP13	08A0310	0.7	0.4	0.3	0.2	0.3	0.15	0.085	0.000
MOP14	08A0311	55.1	185.0	129.5	336.9	10.8	0.75	0.685	0.860
MOP15	08A0312	14.7	53.6	37.5	87.6	2.0	0.27	0.205	0.200
MOP16	08A0313	14.3	47.9	33.5	83.4	2.7	0.31	0.245	0.290
MOP17	08A0314	0.4	1.3	0.9	1.1	0.4	0.10	0.035	0.000
MOP18	08A0315	1.6	5.2	3.6	9.0	0.4	0.12	0.055	0.000
BL1							0.06	0.000	0.000
BL2							0.07	0.005	0.000

D.2. MS Method Data (Chapter 4)

Sample ID	Date Analyzed	HDI (µg)	Biuret (µg)	Uretidone (µg)	Isocyanurate (µg)
1	2/25/2008	0.012	0.069	0.26	0.93
2	2/25/2008	0.096	0.41	1.3	6.3
3	2/25/2008	0.12	0.51	1.6	7.6
4	2/25/2008	<LOD	<LOD	0.068	0.099
5	2/25/2008	<LOD	<LOD	<LOD	<LOD
6	2/25/2008	0.13	0.59	1.8	8.7
7	2/25/2008	0.48	2.5	5.9	26
8	2/25/2008	0.13	0.41	2.9	6.7
9	2/25/2008	0.012	0.069	0.28	0.95
10	2/25/2008	0.51	2.9	7.2	29
11	2/25/2008	<LOD	<LOD	<LOD	0.057
12	2/25/2008	<LOD	<LOQ	0.042	0.096
13	2/25/2008	<LOD	<LOD	<LOD	<LOD
14	2/25/2008	0.47	2.5	6.2	27
15	2/25/2008	0.13	0.63	1.9	8.9
16	2/25/2008	0.13	0.62	1.9	8.8
17	2/25/2008	<LOD	<LOD	0.043	0.088
18	2/25/2008	0.012	0.058	0.31	0.98

D.3. Modified NIOSH 5525 Method Data (Chapter 4)

ID	HDI µg NCO	pHDI µg NCO	pIPDI µg NCO	Total µg NCO	Isocyanurate µg NCO	Uretidone µg NCO	Biuret µg NCO	NOTES
1	0.0123	1.017	0.572	1.601	0.205	0.437	0.037	
2	0.0006	0.113	0.062	0.176	0.020	0.034	0.002	
3	0.0005	0.113	0.05	0.163	0.020	0.034	0.002	
4	0.0006	0.119	0.062	0.182	0.019	0.033	0.002	
5	<0.001	<0.005	<0.005	- BLANK	0.001	0.002	0.000	
6	-	-	-	-				LOST Spilled during transport
7	0.3027	34.3	17.3	51.9	6.003	12.034	1.372	
8	0.0007	0.115	0.075	0.191	0.022	0.032	0.003	Uretidinedione peak small compared to isocyanurate. Likely overestimation of the pHDI component.
9	0.006	1.11	0.58	1.69	0.215	0.292	0.017	
10	0.3676	34.48	18.04	52.9	6.697	14.588	1.298	Sample had precipitated. Diluted to 5mL.
11	<0.001	<0.005	<0.005	BLANK	0.000	0.002	0.000	
12	0.0013	0.106	0.069	0.166	0.023	0.032	0.002	
13	<0.001	<0.005	<0.005	BLANK	0.000	0.001	0.000	
14	0.3557	39.5	21.1	61	8.340	17.801	1.690	Sample had precipitated. Diluted to 5mL.
15	0.0813	12.5	5.73	18.3	2.224	0.268	0.036	Uretidinedione peak small compared to isocyanurate. Likely overestimation of the pHDI component.
16	0.0813	9.18	4.89	14.2	1.894	3.677	0.357	
17	0.0113	1.21	0.62	1.83	0.228	0.333	0.024	
18	<0.001	0.076	0.04	0.116	0.016	0.000	0.000	pIPDI clearly quantifiable. pHDI had only one main peak. If this is not a real spike,then this sample must been contaminated. Sample had precipitated. Diluted to 5mL.

D.4. Modified OSHA 42/PV2034 Data (Chapter 4)

Sample ID	HDI µg/sample	NCO-HDI µg/sample	NCO-Oligomers µg/sample	Total NCO µg/sample
1	<0.05	<0.03	1.2	1.2
2	0.07	0.04	4.7	4.7
3	0.1	0.06	8.8	8.8
4	<0.05	<0.03	0.4	0.4
5	<0.05	<0.03	<0.3	0.0
6	0.1	0.07	12	11.8
7	0.4	0.2	59	59.0
8	0.09	0.04	5.9	5.9
9	<0.05	<0.03	1.2	1.2
10	0.5	0.2	57	57.4
11	<0.05	<0.03	<0.3	0.0
12	<0.05	<0.03	<0.3	0.0
13	<0.05	<0.03	<0.3	0.0
14	0.4	0.2	57	57.5
15	0.1	0.07	13	13.5
16	0.1	0.07	14	14.1
17	<0.05	<0.03	<0.3	0.0
18	<0.05	<0.03	1.2	1.2

D.5. Isocyanate Analytical Method Comparison Protocol (Chapter 4))

Determination of Isocyanate Concentrations in a Sample of Commercial Hardener – An Interlab Study

Objectives:

- Determine the intra- and inter-lab variability of the isocyanate analysis of an aliquot of a commercial hardener used in the collision repair industry.
- Understand the strengths and weaknesses of the analytical methods used by different labs.
- Investigate and compare the ability of each method to quantify individual isocyanate species as well as the total isocyanate content of the sample based on the monomer and oligomer calibration curves.

Conditions of participation:

- The University of Washington (UW) will take the lead in coordinating the effort, including summarizing results and conclusions.
- The spike levels on individual filters will be unknown to the participating labs.
- Labs will abide by the procedures described in this document unless there are method-specific reasons for non-compliance. Any divergence from the enclosed procedures must be discussed with UW staff prior to analysis.
- We acknowledge that a comprehensive comparison of method performance must address both sampling and analytical issues. However, for the purposes of this exercise, we will concern ourselves only with analytical issues.
- Participating labs agree that resulting data will be reported in oral and written presentations, including technical reports and peer-reviewed publications. All participants will have the opportunity to comment on any presentation prior to release. The identities of participating labs and staff will be held confidential, upon request. Participants will be named as co-authors in any presentation of these data (unless anonymity is requested).
- The MSDS of the product to be tested will be provided in a separate communication. As requested by the manufacturer, product-specific information must not be provided in any thesis, presentation, report, or publication.

Product information:

The hardener product contains both HDI and IPDI monomers and oligomers.
According to the manufacturer:

1) %NCO should range from 16.0- 17.2, the referenced test method is ASTM D1638-74
2) Theoretical HDI: 0.24% mass monomer/total mass product and 47.9% mass oligomer/total mass product.
3) Theoretical IPDI 0.25% mass monomer/total mass product and 35.5% mass oligomer/total mass product.

4) 2 & 3 are not analyzed for each batch; values are dependant on isocyanate resin supplier data. However, total solids should range +/- 1.2% around the 83.91 wt% solids listed on the MSDS.

Note: Labs may perform their own NCO titrations, preferably in triplicate. The procedure is provided in Appendix I. The UW lab will provide their titration result to all labs.

Methods

Participating lab supplies required

Participating labs will ship filters and derivatization solutions to the UW. To minimize filter handling by the UW, the participating labs will ship at least 20 filters in individual containers (these containers will be returned to the labs, when they will contain the spiked filters plus derivatization solution). Labs will also ship a sufficient volume of prepared derivatization solution to accommodate 20 filters.

Sample preparation

A UW analyst will dissolve the hardener in toluene to load 1, 10, 100, and 400 μg bulk product/filter (justification for these levels is provided in Appendix II). These will be prepared in triplicate. Three blank filters will be spiked with an aliquot of the toluene used to prepare the spiking solutions.

The filters will be allowed to dry at room temperature for 2-5 minutes. The loaded filters and three blanks will be placed in derivatization solution and shipped to the participating labs on ice packs. The amount of material spiked on the filters will not be provided to the labs; each filter will be designated a code with the identification key kept by UW and SHARP.

Sample handling at the labs

Samples should be removed from shipping containers immediately and stored according to the lab's typical methodology.

Samples should be analyzed as soon as possible. If any delay is necessary, storage times should not exceed those recommended by the particular lab method. If analysis is delayed or exceeds established holding times, this fact should be noted on the report.

Samples should be analyzed for HDI monomer and HDI oligomers plus IPDI monomer and IPDI oligomers, as possible. It is suggested to report total NCO content of the sample. This may or may not be the sum of all individual species. Additionally, each lab should ideally provide the equivalent NCO content of each species, if the NCO content is not the primary metric used by the lab. This is required in order to make comparisons and estimate method bias.

Reporting of Results

a) Brief method description or reference to established methods,
b) Date samples received from the UW, storage conditions and duration, analysis date, and notes recording unusual situations or conditions,
c) Analytical results for the spiked filters and blanks,
d) Reporting limits,
e) Calibration range,
f) Procedural blanks and QCs,
g) Chromatogram of the bulk product and one of the each level (If possible, examine bulk material by HPLC/MS to determine the monomeric/prepolymeric profile)

Results:

The data for all labs will be compiled by UW and SHARP. Because the spike levels will be unknown to the labs, UW and SHARP will calculate percent recoveries for each spike level as well as variability within each level and other statistics.

A final report will be sent to the participating labs, where the labs will be identified by a code.

References

Bello, Dhimiter *et al*. Polyisocyanates in occupational environments: A critical review of exposure limits and metrics. American Journal of Industrial Medicine, Volume 46, Issue 5 ,June 2004, pp. 480 - 491

Liu, Youcheng; Stowe, Meredith; Bello, Dhimiter; Woskie, Susan; Sparer, Judy; Gore, Rebecca; Youngs, Fred; Cullen, Mark; Redlich, Carrie. Respiratory Protection from Isocyanate Exposure in the Autobody Repair and Refinishing Industry. Journal of Occupational and Environmental Hygiene, Volume 3, Number 5, May 2006, pp. 234-249(16).

For further information contact:

Steve Whittaker, Ph.D.
Toxicologist
SHARP Program
Department of Labor & Industries
P O Box 44330 Olympia WA 98504-4330
Phone: 360-902-5663 / FAX: 360-902-5672
E-mail: whiw235@LNI.wa.gov

Michael Yost, PhD
Professor of Environmental and Occupational Health Sciences
University of Washington
Health Sciences Center, Room F-225
Box 357234 Seattle, WA 98195-7234
Phone: 206 685-7243 / Fax: 206 616-2687
Email: airion@u.washington.edu

Russell Dills, PhD.
Director Environmental Health Lab
University of Washington
Health Sciences Center, Room F-461a
Box 357234 Seattle, WA 98195-7234
Phone: 206 543-3263 / Fax: 206 543-9616
e-mail: russ1@u.washington.edu

Diana Ceballos, MS
PhD Student Environmental and Occupational Hygiene
University of Washington
Health Sciences Center, Room F-224
Box 357234 Seattle, WA 98195-7234
Phone: 206 685-4471 / Fax: 206 616-2687
Email: dmco25@u.washington.edu

Appendix I

Titration of NCO

The isocyanates are unstable and so they are titrated before use in order to ensure that no polymerized species are present. This titration does not distinguish between isomers and is not specific to isocyanate.

1- Prepare a solution of dibutylamine (DBA) in toluene by mixing 60 ml (11.11%) of DBA with 480ml (88.88%) of toluene. (0.65936N)
2- Dissolve 0.1g of bromophenol blue in 100ml of methanol. Add dilute sodium hydroxide (0.1M) dropwise with stirring until the solution is blue.
3- Weigh approximately 2-3g of each *product* accurately into each of 3 flasks (3 replicates).

4- Pipette 50ml of the DBA solution into each of the sample flasks and into 3 further flasks to serve as blanks. [3 blanks + 3 replicates per each product].
5- Swirl the flasks to mix their contents. Gentle warming on a hot plate may be needed to dissolve the products and speed up the completion of the reaction.
6- Add 100ml of isopropanol and 3-4 drops of the bromophenol blue solution to each of the flasks.
7- Titrate the contents of the flasks against 1 molar hydrochloric acid. The end point is a color change from blue to pale yellow. **Blank titres should agree to within 0.1ml. If not the titration should be repeated.** The blank titre should be about 32 ml.
8- Calculate the percentage NCO in the samples as follows:

$$\%NCO = \frac{HCl\_molarity * (mean\_blank - titre) * 4.2}{sample\_weight}$$

Please contact Dr. Dhimiter Bello directly if you have any questions (Dhimiter_Bello@uml.edu).

Appendix II - Spiking Level Justification and Species Estimate

The hardener will be spiked on filters to yield concentrations based on the UK standards (Bello *et al.* 2004; Liu *et al.* 2006). Assuming a sampling time of 8 hours and a sampled air volume of 1 m^3:

- HSE 8 hr TWA =20 µg NCO/m^3 = 20 µg NCO/filter
- HSE 15-min STEL = 70 µg NCO/m^3 = 70 µg NCO/filter

(1) Very Low Level: 1% of TWA

1% of 20 µg NCO/filter = 0.2 µg NCO/filter
Assuming 17% NCO in the bulk product:
0.2/0.17 =1.176 µg bulk product/filter,
With rounding, "Very Low" spiking level is **1 µg bulk product/filter**

(2) Low Level: 10% of TWA

10% of 20 µg NCO/filter = 2 µg NCO/filter
Assuming 17% NCO in the bulk product:
2/0.17 =11.76 µg bulk product/filter,
With rounding, "Low" spiking level is **10 µg bulk product/filter**

(3) Medium Level: 100% of TWA

100% of 20 µg NCO/filter = 20 µg NCO/filter
Assuming 17% NCO in the bulk product:
20/0.17 = 117.6 µg bulk product/filter,
With rounding, "Medium" spiking level is **100 µg bulk product/filter**

(4) High Level: 100% of STEL

100% of 70 µg NCO/filter = 70 µg NCO/filter
Assuming 17% NCO in the bulk product:

70/0.17 = 412 µg bulk product/filter.
With rounding, "High" spiking level is **400 µg bulk product/filter**

Expected Masses per Filter

Level	**Bulk Product µg**	**NCO µg (17%*)**	**HDI monomer vg (0.24%*)**	**HDI Polymer vg (47.9%*)**	**IPDI monomer µg (0.25%*)**	**IPDI oligomer µg (35.5%*)**
1 (Very Low)	1	0.17	0.0024	0.479	0.0025	0.355
2 (Low)	10	1.7	0.024	4.79	0.025	3.55
3 (Med)	100	17	0.24	47.9	0.25	35.5
4 (High)	400	68	0.96	191.6	1.0	142.0

*Percentage provided by hardener manufacturer

D.6. Summary Method Characteristics (Chapter 4)

Methods	**Modified NIOSH 5525**	**2-MP LC/MS**	**OSHA 42/PV2034**	**Modified Iso-Chek**
Abbreviation	**NIOSH**	**MS**	**OSHA**	**ISO**
Characteristics				
Brief method description or reference to established methods	NIOSH 5525 with modifications as published in Bello *et al.* 2002* Gradient as published in Bello *et al.* AOH 2008	Standards synthesized and prepared as in Fent *et al.* 2008	OSHA method 42/PV2034 with modified chromatography to allow resolution of the analytes**	Modified Omega Iso-Chek for isocyanates dual filter cassettes
Derivatization reagent	1-(9-anthracenylmethyl)piperazine (MAP) in acetonitrile 10 ml solution (MAP provided by NIOSH)	1-(2-methoxyphenyl)piperazine (2-MP) in toluene 5ml solution after filter were spiked	0.1 mg 1-(2-pyridyl)-piperazine (PPZ)	Monomer uses MAMA (9-N-methylaminomethyl anthracene/OMEGA cat#J-ISO-5); Second filter (oligomers) uses 2-MP toluene solution
Instrumet	LC-FLD/UV	LC/MS	LC-FLD/UV	LC-FLD/UV
Filter	Quartz fiber filters	Pre-impregnated glass fiber filters	Pre-impregnated glass fiber filter (SKC 225-9002)	Monomer uses pre-impregnated glass fiber filter. Oligomers uses PTFE filter
Conditions different than method	None	None	None	None
Analysis date	Feb 5, Feb 12 and Feb 19, 2008. Value reported is the average of three analyses.	31-Jan-08	6-Feb-08	31-Jan-08
Notes recording unusual situations or conditions	Some samples precipitated and one was lost during shipping	None	None	None

*A new stainless steel column was used instead of the PEEK column, because this column type has been discontinued.

**The IPDI monomer results are invalid due to the artifactual formation of IPDI PPZ derivative presumably from the oligomer. In over time, the level of IPDI monomer increased in the extracts

Continued on next page

Methods	**Modified NIOSH 5525**	**2-MP LC/MS**	**OSHA 42/PV2034**	**Modified Iso-Chek**		
Abbreviation	**NIOSH**	**MS**	**OSHA**	**ISO**		
Method Characteristics						
Reporting limits (LOD and LOQ)	With background subtraction, the LOD is <1 ng NCO for HDI, conservatively <4ng NCO LOQ: reported same as LOD, 0.001µg HDI-NCO, 0.005 µg polymeric HDI-NCO, 0.005 µg polymeric IPDI-NCO	LOD was 2 and 8 fmol/µL for HDI and the oligomers, respectively. Equivalent LOD of 3.4 pg HDI LOQ was 5 and 20 fmol/µL for HDI and the oligomers, respectively. Equivalent LOQ of 8.4 pg HDI	LOQs: HDO 0.05µg, IPDI 0.05 µg, Oligomers 0.5 µg; LODs: same	**Analyte**	**LOQ (µg)**	**LOD (µg)**
				HDI Monomer	0.11	0.005
				IPDI Monomer	0.13	0.004
				HDI Uretidone	4.8	2.8
				HDI Biuret	1.9	1.7
				HDI Isocyanurate	5	1.2
				IPDI Oligomer	15.7	1.7
Procedural blanks and QCs	Recovery reported was 76.9-89% - no correction performed Average method precision was 4.4RSD% for the monomer and 3.4% for the total reactive isocyanate groups (Bello *et al.* 2002)	From calibration standards: precision RSD% 2-15, accuracy 82-112% of nominal	Accuracy over 90% of nominal value based on standards	HDI monomer	93.8	
				IPDI monomer	91.7	
				HDI Uretidone	158.6	
				HDI Biuret	87.8	
				HDI Isocyanurate	107.6	
				IPDI olig Iso	98.4	

Continued on next page

Methods **Abbreviation** **Characteristics**	**Modified NIOSH 5525** **NIOSH**	**2-MP LC/MS** **MS**	**OSHA 42/PV2034** **OSHA**	**Modified Iso-Chek** **ISO**	
Additional Data	Uretidinedione contributes 33.3% of the total NCO content of the product, Isocyanurate 15.1%, biuret 3.2% and the other two major peaks (RT 13.52 and 15.16 min) ~5.4 and 5.2% each. FLD Calibration (HDI) r^2=0.995 UV Calibration (HDI) r^2=1 HDI and IPDI monomer standards provided by NIOSH (Sigma purified reported in JEM Bello *et al.* 2000) Both HDI and IPDI calibrations (calibration coefficients differed by only 4%) were performed but all calculations were based on HDI calibration	Urea derivative of HDI (HDIU) (w = 1/x2, R2 = 0.999), urea derivative of biuret (BU) (w = 1/x2, R2 = 0.992) The urea derivative of isocyanurate (IU) (w = 1/x2, R2 = 0.995) Isocyanurate polynomial equation ($w = 1/x^2$, $R^2 = 0.996$)	HDI Calibration r^2=0.9958 – HDI Restek standard Lot#A042997 expires 01/30/09 IPDI Calibration r^2=0.9955 – IPDI Aldrich standard, Lot#03003PB expires 06/13/08	**Analyte** HDI monomer IPDI monomer HDI Dimer/ Uretidone Biuret Isocyanurate IPDI Oligomer	**Standard used** SKC Cat#225-9055 standards are already derivitized with the mama SKC Cat#225-9055 standards are already derivitized with the mama Desmodur 3400-N (Bayer bulk) Desmodur N100 (Bayer bulk) Desmodur N3300A (Bayer bulk) Desmodur Z4470-BA (Bayer bulk)

D.7. Detection and Quantitation Limit Substitution Values for the Different Methods (Chapter 4)

Methods Limits	Modified NIOSH 5525 NCO µg	2-MP LC/MS µg	OSHA 42/PV2034 µg	Modified Iso-Chek µg
LOD				
HDI Monomer	0.001	0.0000034	0.05	0.005
IPDI Monomer			0.05	0.004
HDI Dimer/Uretidone	0.005	0.00003936		2.8
HDI Biuret	0.005	0.00004032		1.7
HDI Isocyanurate	0.005	0.00004		1.2
IPDI Oligomer	0.005			1.7
NCO Oligomers			0.3	
<LOD=LOD/2				
HDI Monomer	0.0005	0.0000017	0.025	0.0025
IPDI Monomer			0.025	0.002
HDI Dimer/Uretidone	0.0025	0.00001968		1.4
HDI Biuret	0.0025	0.00002016		0.85
HDI Isocyanurate	0.0025	0.00002		0.6
IPDI Oligomer	0.0025			0.85
NCO Oligomers			0.15	
LOQ				
HDI Monomer	0.001	0.0000084	0.05	0.11
IPDI Monomer			0.05	0.13
HDI Dimer/Uretidone	0.005			4.8
HDI Biuret	0.005			1.9
HDI Isocyanurate	0.005			5
IPDI Oligomer	0.005			15.7
NCO Oligomers			0.3	
<LOQ=(LOQ-LOD)/2+LOD				
HDI Monomer	N/A	0.0000059	N/A	0.0575
IPDI Monomer			N/A	0.067
HDI Dimer/Uretidone	N/A	0.00001968	N/A	3.8
HDI Biuret	N/A	0.00002016	N/A	1.8
HDI Isocyanurate	N/A	0.00002	N/A	3.1
IPDI Oligomer	N/A		N/A	8.7
NCO Oligomers				

*LOQ was used instead of the LOD since LOQ has not been determined

D.8. NCO Conversion Factors (Chapter 4)

Component	Equivalent Weight[a] Product	Molecular Weight (MW) of Isocyanate	Conversion Factor[b]
[i]HDI monomer $C_8H_{12}N_2O_2$	84.1	168	2
[i]HDI oligomer, N-100 biuret (22%NCO) $C_{23}H_{38}N_7O_5$	191	492	4.55
[i]HDI oligomer, isocyanurate (21.6%NCO) 3300A-N $C_{24}H_{36}N_6O_6$	195	504	4.64
[ii]HDI oligomer, dimer (21.6%NCO) 3400-N	42/0.216=194	~500	1/0.216=4.62
[i]IPDI monomer $C_{12}H_{18}N_2O_2$	111.1	222	2.64
[ii]IPDI oligomer (12.1%NCO) 4470Z-BA $C_{36}H_{54}N_6O_6$ (70%product+30%solvent)	42/0.121=347	666	0.7/.121=5.79

[i] AJIM Bello *et al.* 2004

[ii] Method L&I 0067, Table 3 (Modified Iso-Chek)

[a] Equivalent Weight (EW) = MW / #NCO

[b] Factor = EW / 42, where, Mass = Mass NCO * EW / 42 (42 is the equivalent weight of one NCO)

D.9. Robust Regression SPSS Output-Weighted Least Squares Analysis (Chapter 4)

HDI monomer WISHA Method

Model Summary

Multiple R	.975
R Square	.950
Adjusted R Square	.947
Std. Error of the Estimate	.061
Log-likelihood Function Value	24.479

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Regression	1.059	1	1.059	286.499	.000
Residual	.055	15	.004		
Total	1.115	16			

Coefficients

	Unstandardized Coefficients		Standardized Coefficients			
	B	Std. Error	Beta	Std. Error	t	Sig.
(Constant)	-.026	.018			-1.461	.165
HDI	.617	.036	.975	.058	16.926	.000

HDI monomer MS method

Model Summary

Multiple R	.997
R Square	.994
Adjusted R Square	.993
Std. Error of the Estimate	.022
Log-likelihood Function Value	70.731

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Regression	1.269	1	1.269	2516.832	.000
Residual	.008	16	.001		
Total	1.277	17			

Coefficients

	Unstandardized Coefficients		Standardized Coefficients			
	B	Std. Error	Beta	Std. Error	t	Sig.
(Constant)	-.001	.000			-1.894	.076
HDI	.443	.009	.997	.020	50.168	.000

HDI monomer OSHA method

Model Summary

Multiple R	.979
R Square	.958
Adjusted R Square	.956
Std. Error of the Estimate	.086
Log-likelihood Function Value	56.274

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Regression	2.718	1	2.718	367.095	.000
Residual	.118	16	.007		
Total	2.837	17			

Coefficients

	Unstandardized Coefficients		Standardized Coefficients			
	B	Std. Error	Beta	Std. Error	t	Sig.
(Constant)	.021	.002			11.612	.000
HDI	.353	.018	.979	.051	19.160	.000

HDI monomer ISO-CHEK method

Model Summary

Multiple R	.958
R Square	.918
Adjusted R Square	.913
Std. Error of the Estimate	.095
Log-likelihood Function Value	28.027

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Regression	1.614	1	1.614	180.012	.000
Residual	.143	16	.009		
Total	1.757	17			

Coefficients

	Unstandardized Coefficients		Standardized Coefficients		t	Sig.
	B	Std. Error	Beta	Std. Error		
(Constant)	.030	.012			2.464	.025
HDI	.597	.045	.958	.071	13.417	.000

IPDI Monomer ISO-CHEK method

Model Summary

Multiple R	.989
R Square	.977
Adjusted R Square	.976
Std. Error of the Estimate	.062
Log-likelihood Function Value	39.377

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Regression	2.662	1	2.662	687.121	.000
Residual	.062	16	.004		
Total	2.724	17			

Coefficients

	Unstandardized Coefficients		Standardized Coefficients		t	Sig.
	B	Std. Error	Beta	Std. Error		
(Constant)	.002	.005			.337	.740
IPDI	.734	.028	.989	.038	26.213	.000

NCO-HDI oligomers NIOSH method

Model Summary

Multiple R	.973
R Square	.947
Adjusted R Square	.943
Std. Error of the Estimate	3.323
Log-likelihood Function Value	-43.536

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Regression	2948.916	1	2948.916	267.072	.000
Residual	165.625	15	11.042		
Total	3114.541	16			

Coefficients

	Unstandardized Coefficients		Standardized Coefficients			
	B	Std. Error	Beta	Std. Error	t	Sig.
(Constant)	-1.092	.975			-1.120	.280
NCOHDIolig	1.067	.065	.973	.060	16.342	.000

NCO-HDI oligomers MS method

Model Summary

Multiple R	.988
R Square	.977
Adjusted R Square	.975
Std. Error of the Estimate	.142
Log-likelihood Function Value	17.233

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Regression	11.965	1	11.965	594.168	.000
Residual	.282	14	.020		
Total	12.247	15			

Coefficients

	Unstandardized Coefficients		Standardized Coefficients			
	B	Std. Error	Beta	Std. Error	t	Sig.
(Constant)	.011	.001			7.582	.000
NCOHDIolig	.264	.011	.988	.041	24.376	.000

NCO-HDI oligomers ISO-CHEK method

Model Summary

Multiple R	.990
R Square	.980
Adjusted R Square	.979
Std. Error of the Estimate	.106
Log-likelihood Function Value	-17.584

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Regression	8.857	1	8.857	791.039	.000
Residual	.179	16	.011		
Total	9.037	17			

Coefficients

	Unstandardized Coefficients		Standardized Coefficients			
	B	Std. Error	Beta	Std. Error	t	Sig.
(Constant)	.935	.045			20.942	.000
NCOHDIolig	2.140	.076	.990	.035	28.125	.000

NCO-IPDI oligomers NIOSH method

Model Summary

Multiple R	.973
R Square	.946
Adjusted R Square	.943
Std. Error of the Estimate	1.741
Log-likelihood Function Value	-32.544

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Regression	800.649	1	800.649	264.277	.000
Residual	45.444	15	3.030		
Total	846.092	16			

Coefficients

	Unstandardized Coefficients		Standardized Coefficients		t	Sig.
	B	Std. Error	Beta	Std. Error		
(Constant)	-.604	.511			-1.182	.255
NCOIPDIolig	.750	.046	.973	.060	16.257	.000

NCO-IPDI oligomers ISO-CHEK method

Model Summary

Multiple R	.988
R Square	.976
Adjusted R Square	.974
Std. Error of the Estimate	.204
Log-likelihood Function Value	-.987

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Regression	27.130	1	27.130	650.354	.000
Residual	.667	16	.042		
Total	27.797	17			

Coefficients

	Unstandardized Coefficients		Standardized Coefficients		t	Sig.
	B	Std. Error	Beta	Std. Error		
(Constant)	.125	.020			6.375	.000
NCOIPDIolig	.835	.033	.988	.039	25.502	.000

NCO- HDI and IPDI oligomers NIOSH method

Model Summary

Multiple R	.973
R Square	.947
Adjusted R Square	.943
Std. Error of the Estimate	5.049
Log-likelihood Function Value	-50.647

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Regression	6822.657	1	6822.657	267.687	.000
Residual	382.312	15	25.487		
Total	7204.969	16			

Coefficients

	Unstandardized Coefficients		Standardized Coefficients			
	B	Std. Error	Beta	Std. Error	t	Sig.
(Constant)	-1.696	1.482			-1.145	.270
NCOolig	.932	.057	.973	.059	16.361	.000

NCO- HDI and IPDI oligomers OSHA method

Model Summary

Multiple R	.971
R Square	.943
Adjusted R Square	.940
Std. Error of the Estimate	.900
Log-likelihood Function Value	-30.313

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Regression	215.233	1	215.233	265.965	.000
Residual	12.948	16	.809		
Total	228.181	17			

Coefficients

	Unstandardized Coefficients		Standardized Coefficients			
	B	Std. Error	Beta	Std. Error	t	Sig.
(Constant)	.059	.145			.405	.691
NCOolig	.843	.052	.971	.060	16.308	.000

NCO- HDI and IPDI oligomers ISO-CHEK method

Model Summary

Multiple R	.992
R Square	.984
Adjusted R Square	.983
Std. Error of the Estimate	.096
Log-likelihood Function Value	-19.663

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Regression	9.260	1	9.260	1011.738	.000
Residual	.146	16	.009		
Total	9.406	17			

Coefficients

	Unstandardized Coefficients		Standardized Coefficients			
	B	Std. Error	Beta	Std. Error	t	Sig.
(Constant)	1.073	.046			23.129	.000
NCOolig	1.607	.051	.992	.031	31.808	.000

Total isocyanates NIOSH method

Model Summary

Multiple R	.973
R Square	.947
Adjusted R Square	.944
Std. Error of the Estimate	33.171
Log-likelihood Function Value	-82.651

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Regression	295098.3	1	295098.335	268.189	.000
Residual	16505.073	15	1100.338		
Total	311603.4	16			

Coefficients

	Unstandardized Coefficients		Standardized Coefficients			
	B	Std. Error	Beta	Std. Error	t	Sig.
(Constant)	-11.171	9.734			-1.148	.269
Total	.782	.048	.973	.059	16.376	.000

Total isocyanates OSHA method

Model Summary

Multiple R	.971
R Square	.944
Adjusted R Square	.940
Std. Error of the Estimate	2.295
Log-likelihood Function Value	-64.327

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Regression	1410.355	1	1410.355	267.679	.000
Residual	84.301	16	5.269		
Total	1494.656	17			

Coefficients

	Unstandardized Coefficients		Standardized Coefficients			
	B	Std. Error	Beta	Std. Error	t	Sig.
(Constant)	.443	.982			.451	.658
Total	.706	.043	.971	.059	16.361	.000

Total isocyanates ISO-CHEK method

Model Summary

Multiple R	.992
R Square	.983
Adjusted R Square	.982
Std. Error of the Estimate	.099
Log-likelihood Function Value	-48.769

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Regression	9.305	1	9.305	951.353	.000
Residual	.156	16	.010		
Total	9.461	17			

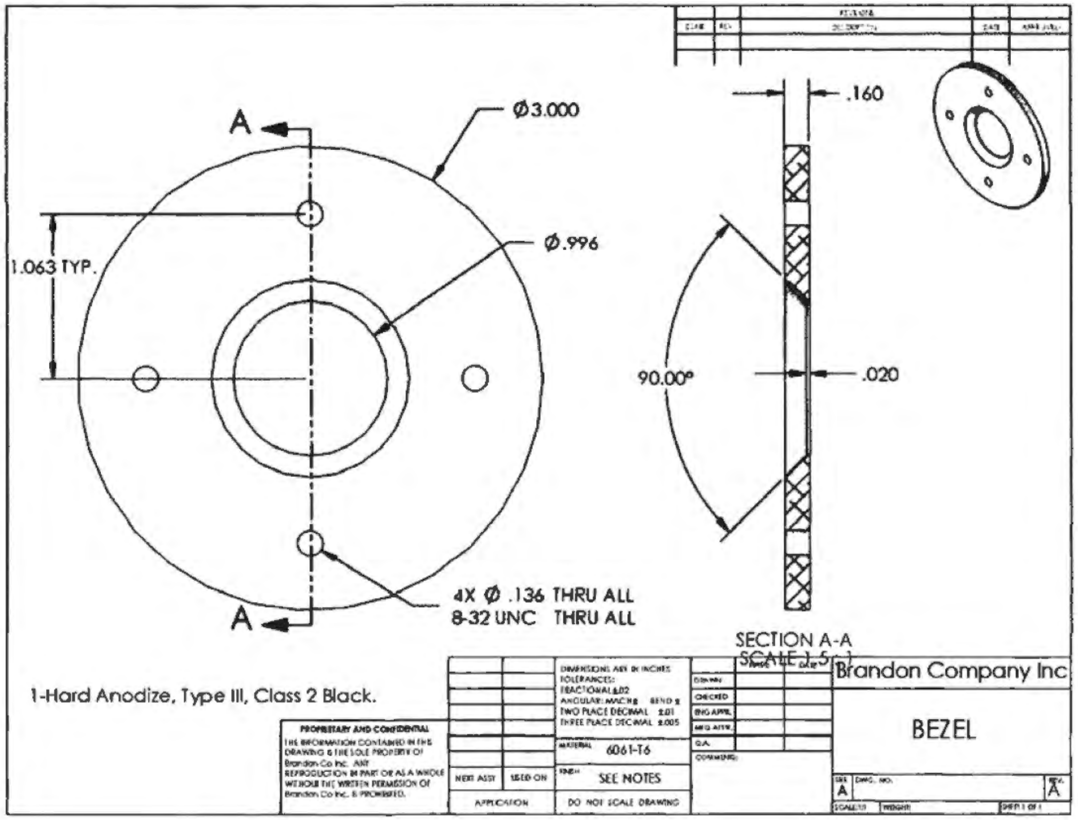
Coefficients

	Unstandardized Coefficients		Standardized Coefficients			
	B	Std. Error	Beta	Std. Error	t	Sig.
(Constant)	5.165	.231			22.359	.000
Total	1.005	.033	.992	.032	30.844	.000

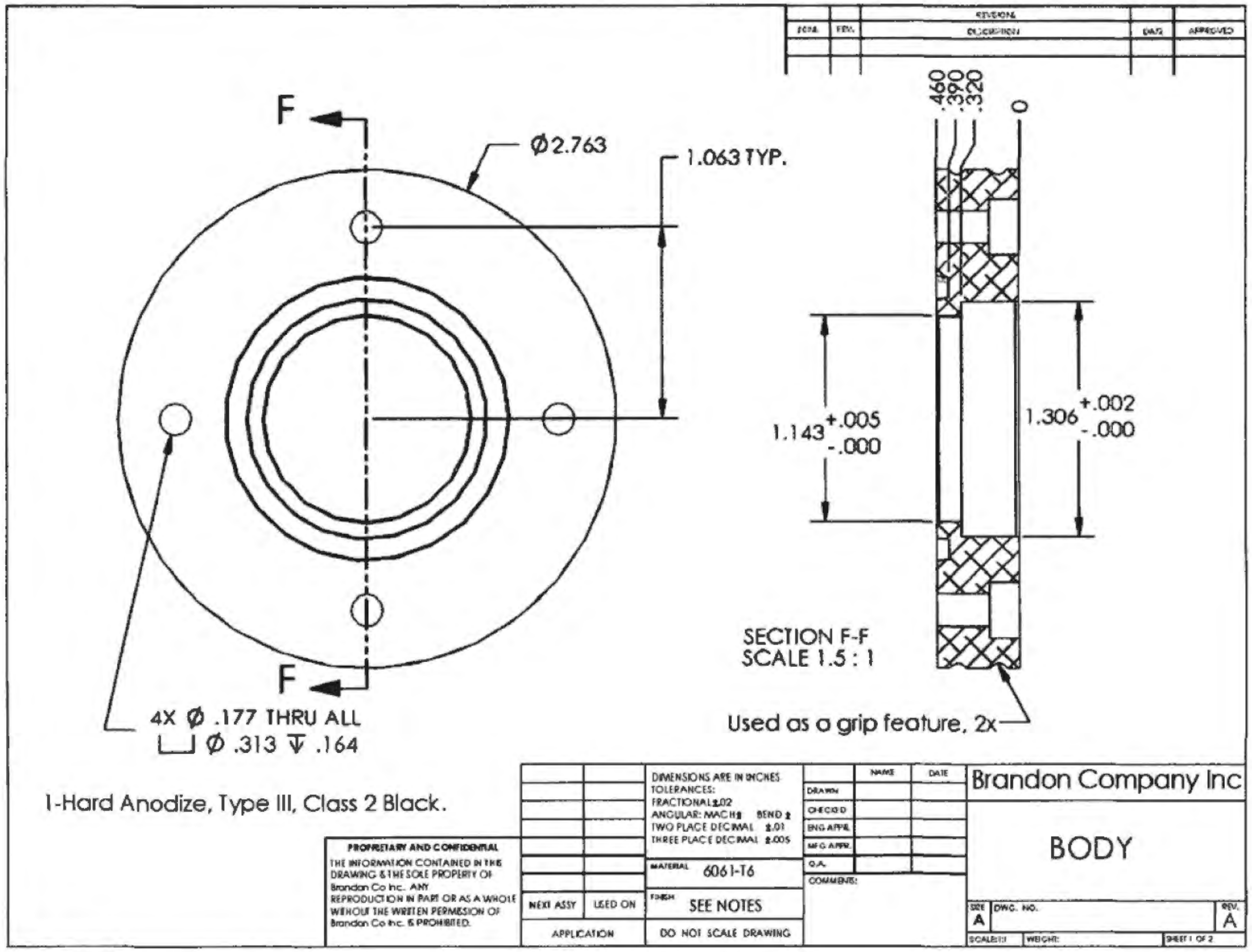
Appendix E

PERMEATION PANEL DATA

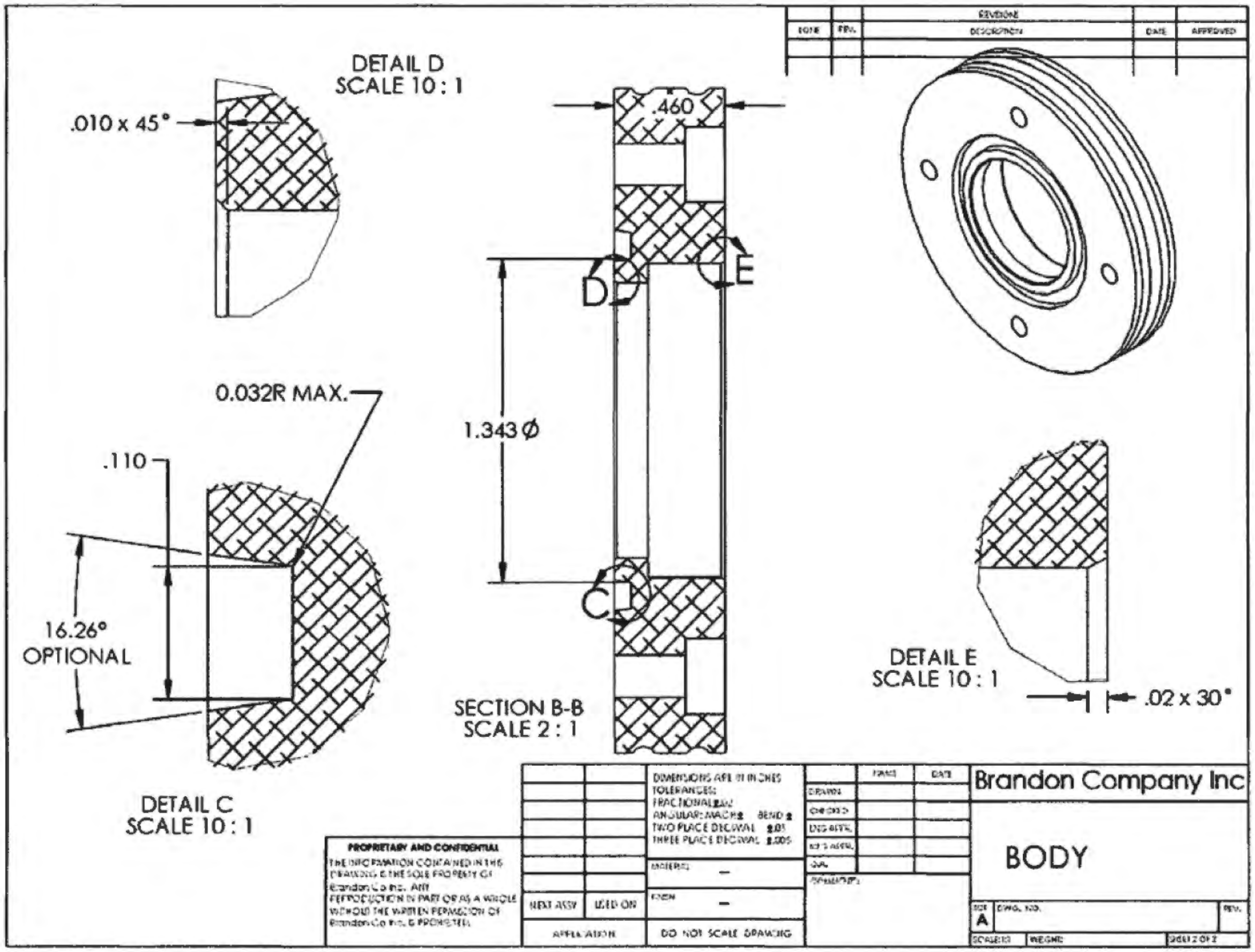
E.1. Drawing of the Permeation Cell Parts (Chapter 5)



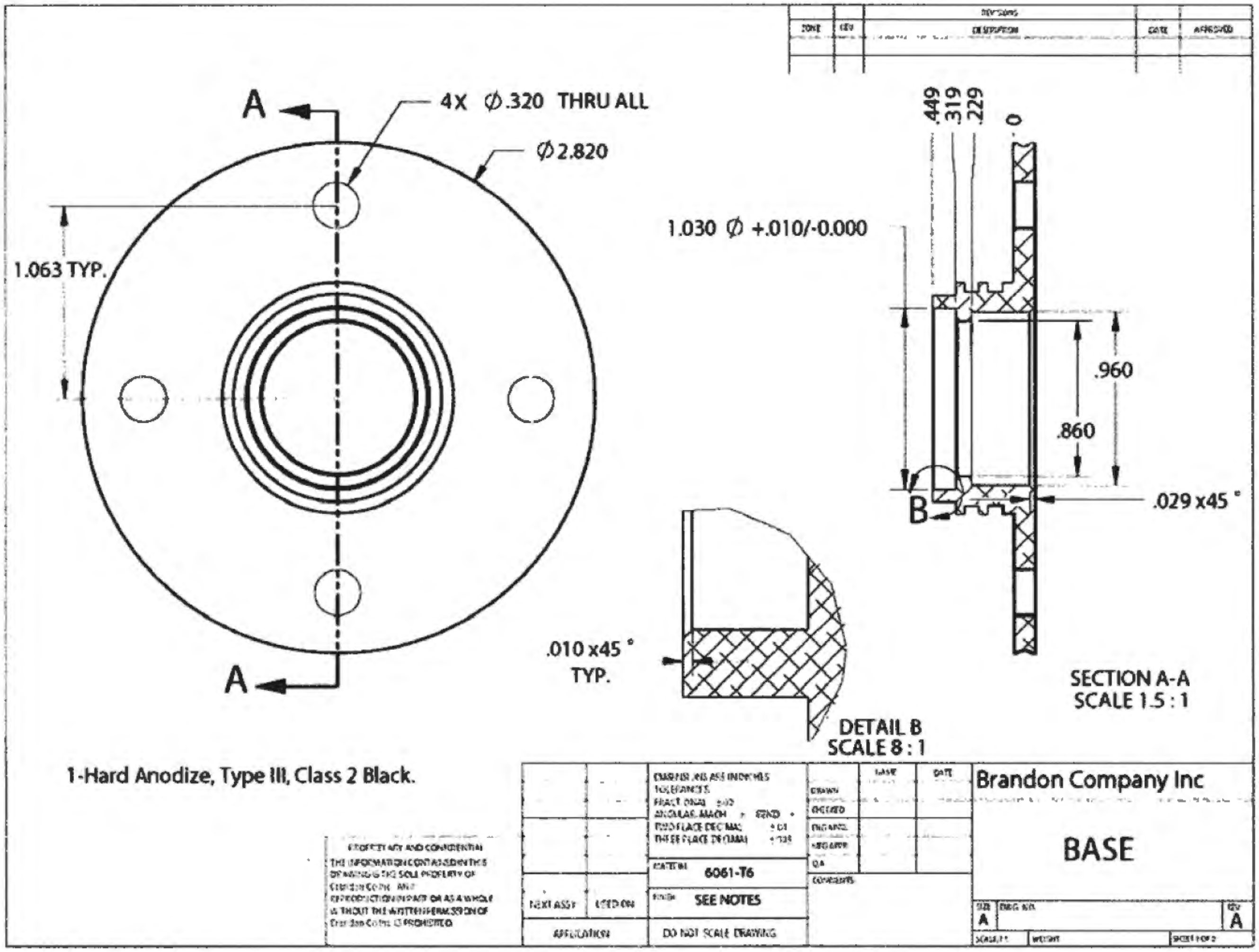
Continued on next page



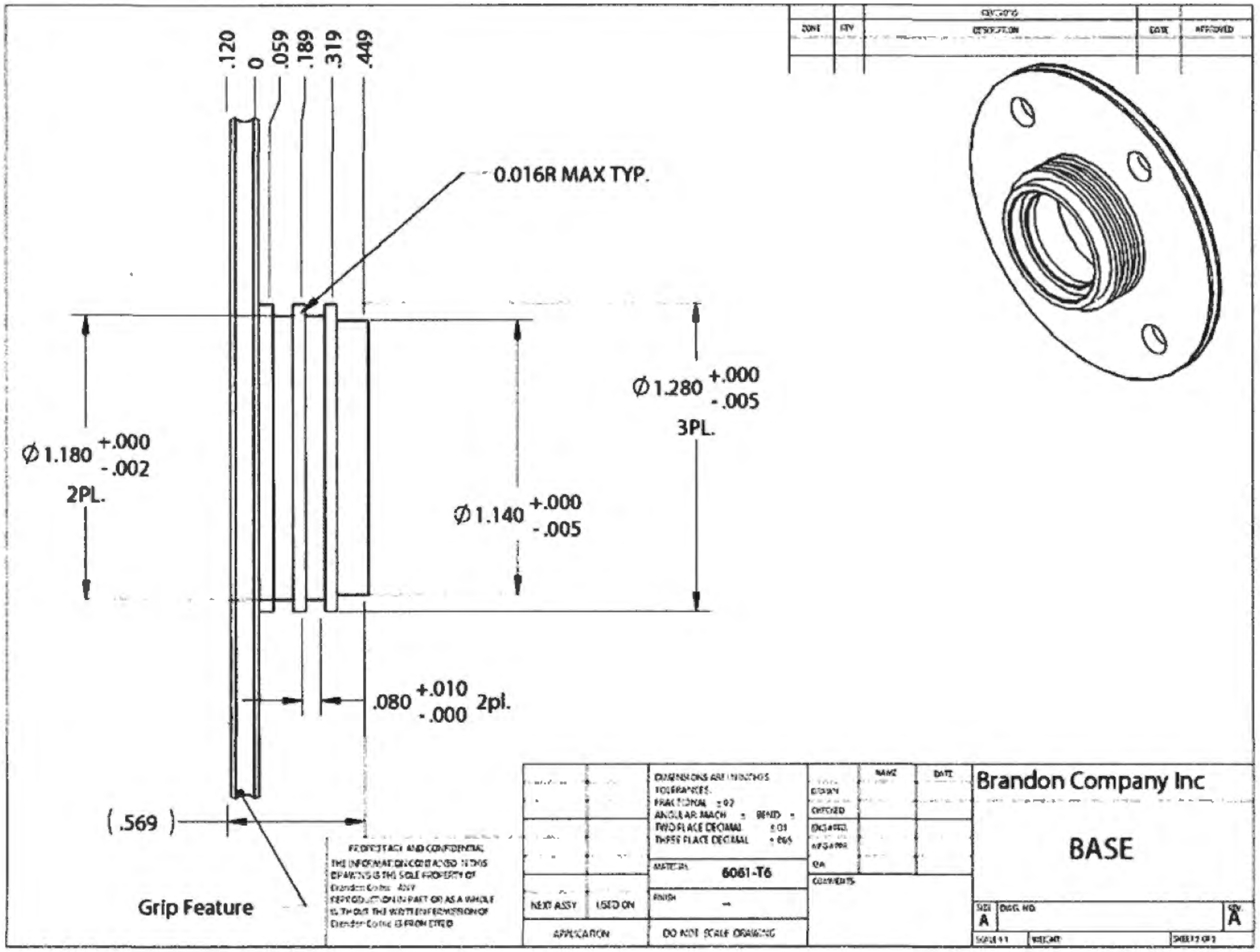
Continued on next page



Continued on next page



Continued on next page

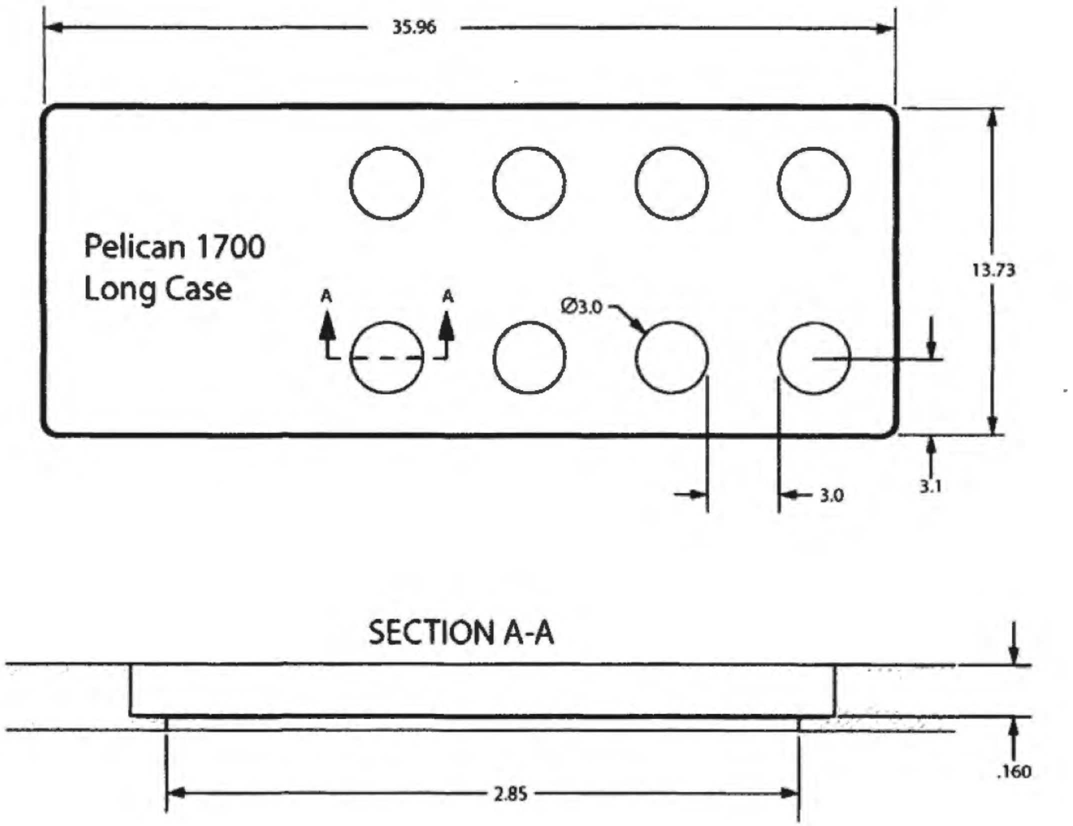


Continued on next page

The modified permeation cell used accessories presented, as follows:

- Edmund #NT46-098 high ar 1" dia TS window glued with 100% silicone sealant (Silicone II, clear household glue)
- Screws were McMaster#92185A194, Type 316 Stainless Stl Socket Head Cap Screw 8-32 Thread, 1/2" Length. Screw required hexagonal 9/64" head Allen wrench
- The body O-ring was a McMaster# 2418T148 SOFT BUNA-N n O-ring, AS568A dash number 126
- The top base O-ring was a McMaster#9262K649, metric buna-n O-ring, 1.5mm width, 29 mm id
- The bottom base O-ring was a McMaster# 9262K648, metric BUNA-N O-ring, 1.5mm width, 28mm id

E.2. Drawing of the Permeation Panel (Chapter 5)



E.3. SOP: Permeation Panel Experiments (Chapter 5)

Objective: Measure permeation of test materials using the permeation panel under spraying conditions

Materials

Equipment

Permeation panels (with 16 cells, 8 for each panel, 3 parts per each cell)

Permeation cell spare parts

- O-rings: Body O-ring McMaster# 2418T148 SOFT BUNA-N n O-ring, AS568A dash number 126. Top base O-ring McMaster#9262K649, metric buna-n O-ring, 1.5mm width, 29 mm id. Bottom base O-ring McMaster# 9262K648, metric BUNA-N O-ring, 1.5mm width, 28mm id.
- Glass windows (Edmund#NT46-098 high ar 1" dia TS)
- Screws (McMaster#92185A194, Type 316 Stainless Stl Socket Head Cap Screw 8-32 Thread, 1/2" Length))

Instruments

Balance Metler toledo AT261 Delta range

Thickness gauge

Spatial Anemometer ALNOR model RVA501

HOBO External Data Loggers (Model H08-004-02; Onset Computer Corporation)

Timer

Camera and/or video camera

Transport

Cooler and box to place the filters

Frozen blue ice packs

Permeation Samples

1-(2-pyridyl)-piperazine (PPZ) coated filters (SKC 225-9002)

SWYPE (CLI lab, part No. 1023)

Test material

Paraffin paper to seal cassettes

Loading Samples

PTFE filters (Zefluor 47mm 0.5μm Supported PTFE P/N P5PQ047 Pall – Life Sciences)

Filter holders

Thick aluminum foil

Masking tape

RGB Analysis

Scanner and laptop computer

Plastic wrap

White background (20 pages of regular white paper)

Tools

1 inch diameter paper punch (paper shaper)

Leather punch (Deluxe Rotary Punch)

Handle picks (in case an O-ring needs to be removed or moved)

Hexagonal 9/64" head allen wrenches to tighten screws

Miscellaneous

Labeling tape

Masking paper

Marker

Pen

Sample collection data sheet

Sample labels

Ziploc bags different sizes

Scissors

Tweezers

Razor blade

Silicone glue (Silicone II, clear household glue)

Pre made labels for the cells (using ideally a label maker so the label doesn't fade with solvent)

Alcohol or acetone squirt bottle
Kimwipes

Personal Protective Equipment
Respirator
Steel-toed boots
Eye protection
Hearing protection
Nitrile gloves (ideally 8 mil)
Wear long sleeves shirt, pants, and disposable coveralls

Preparing for Permeation Panel Experiment

1. Freeze blue ice packs

Prepare Test Material

2. Prepare dermal protective materials by cutting with scissors material approximately 3 inch diameter.
3. Mark holes with a pattern in each glove material. The pattern can be made by placing the bezel on a paper and marking the holes with a pen on the paper.
4. Punch holes with a leather punch. Cardboard underneath the test material facilitates the cut. Use the larger leather punch hole size (3/16 inch)
5. Measure with a thick gauge the thickness of the test material and record value tied to a permeation cell label.

Preparing Permeation Cells

6. Label each permeation cell 1x-16x. The x will be a letter from a-z indicating the sampling day (e.g. Oct 13 = e, so sampling ports are 1e-16e)
7. Cut media (SWYPE or filter) with cleaned 1 inch diameter paper shaper (cleaned with a swab and alcohol) inside a free-isocyanate hood. Always cut extra filters for field and lab blanks.
8. Assemble bezel-test material-body, making sure test material outer surface is to the outside of the cell.

9. Assemble permeation cells (mostly the base) in a clean isocyanate-free hood assuring that there is no air gap in between the test material and the media (SWYPE/filter). Use the base window to make sure that the media is aligned and centered. Try making test material surface as flat as possible, without wrinkles or bubbles.
10. Place masking tape on the bezel, especially on the section that is closest to the test material to make sure that the metal doesn't get in contact with the paint. Surface area matters in permeation experiments. The masking tape can be placed in advance to save time during the day of the experiment.

Prepare Loading Ports

11. Prepare loading ports by cutting approximately 60mm by 60mm thick aluminum with masking tape over and a centered 1" punch hole – thick aluminum could be used from a cookie sheet. If needed, flatten cookie sheet before use.
12. Name loading ports and respective filter holders 18x-41x. The x will be a letter from a-z indicating the sampling day (e.g. Oct 13 = e, so loading ports are 18e-41e) so there are at least 12 loading ports per panel.
13. Pre-weigh PTFE filters in the EH lab Metler toledo AT261 Delta range balance with the help of an antistatic device. Always have extra loading ports and filters. Always calibrate the balance before use by weighing calibrant weights that are close to the weight of the PTFE filters, to make sure balance is in good working condition.

Prepare Permeation Panel

14. Assemble permeation panel with sampling and loading ports right before going to the spray facility:
    - Load the permeation cells,
    - Cover the top of the panel with masking tape to hold the permeation cells in place,
    - Place loading ports in between permeation cells,
    - Use masking tape to secure loading ports.
15. Place masking paper on top of all ports to protect them during transport. Tape can be used to secure the masking paper.

On-site Preparation

16. Place temperature remote sensor device inside the panel before closing.
17. Mask panels so that all test material are exposed to the paint and PTFE filters are aligned. If test materials are not exposed, use a paper cuter to remove any interfering tape, making sure the test material is not punctured.
18. Mask around the permeation panel with paper and tape to avoid clear coat on the surfaces and help cover the case against overspray.
19. Label with a marker the permeation cells and loading ports on the outside of the panel for ease during the unloading of samples.

Permeation Panel Set-Up

Safety considerations: Always wear nitrile gloves while handling the panel. Use long sleeves and ideally a coverall. Anyone inside the spray booth should wear at least a half-face dual cartridge air purifying respirator (with OV/P100 cartridge).

20. Place HOBOs and panels inside the paint booth for temperature conditioning.
21. Take pictures with a camera to record position of the panel relative to the booth and final distribution of test materials within the panel.
22. Set temperature inside the booth depending on the sprayed-on material used (control by turning on and off the burner).
23. Measure flow in the booth to determine running conditions by taking several samples in each of the floor vents.
24. Open field blanks and store away appropriately (place SWYPE in plastic wrap and scan immediately. Place filters in cassettes and seal with paraffin and place inside a cooler with blue ice)
25. Painter spray panels for few seconds (approximately 18 sec) in two separate applications, with approximately 7 minutes between applications. During each spraying application, each line of sampling ports had at least two horizontal passes of paint: a first one left to right and a second one right to left. The panel had then a total of approximately six horizontal passes of paint.
26. Record spraying times both with a timer and a video camera. Video can be used afterwards to verify times noted.
27. Leave panel inside the temperature controlled booth for the duration of the experiment.

28. Record permeation times starting at the end of the second (final) spraying application.

Collection of Permeation Samples

29. Take panel outside the booth to be disassembled for sample collection except during permeation rate experiments, when each cell is taken outside the booth at its specific time point (cutting the edges of the cells help disassemble cells from the panel). Replicate samples need to be disassembled as simultaneous as possible, ideally with the help of several volunteers.
30. Change to a fresh pair of nitrile gloves after opening cells and before handling filters. Or use a two person team: one open the cell, other person handles the samples (filters).
31. Label samples according to the permeation cell number.
32. Handle media with clean forceps (clean forceps with alcohol or acetone and Kimwipes between use). After closing filter cassettes put them inside a labeled Ziploc bag and inside a cooler with blue ice.
33. Record times at when each test material was removed.

Collection of Loading Samples

34. Remove loading filters by cutting through loading holders and with the help of tweezers. Place the loading filters into respectively labeled filter holders.

Collection of paint component bulk samples

35. Always collect new cans of product if bulk analysis is needed. Do not take samples from the can because solvents and isocyanates concentrations are bound to change. Alternatively, a sample of the freshly mixed paint taken with a pipetter can be placed into derivatization reagent for later analysis following Fent *et al.* 2008 method.

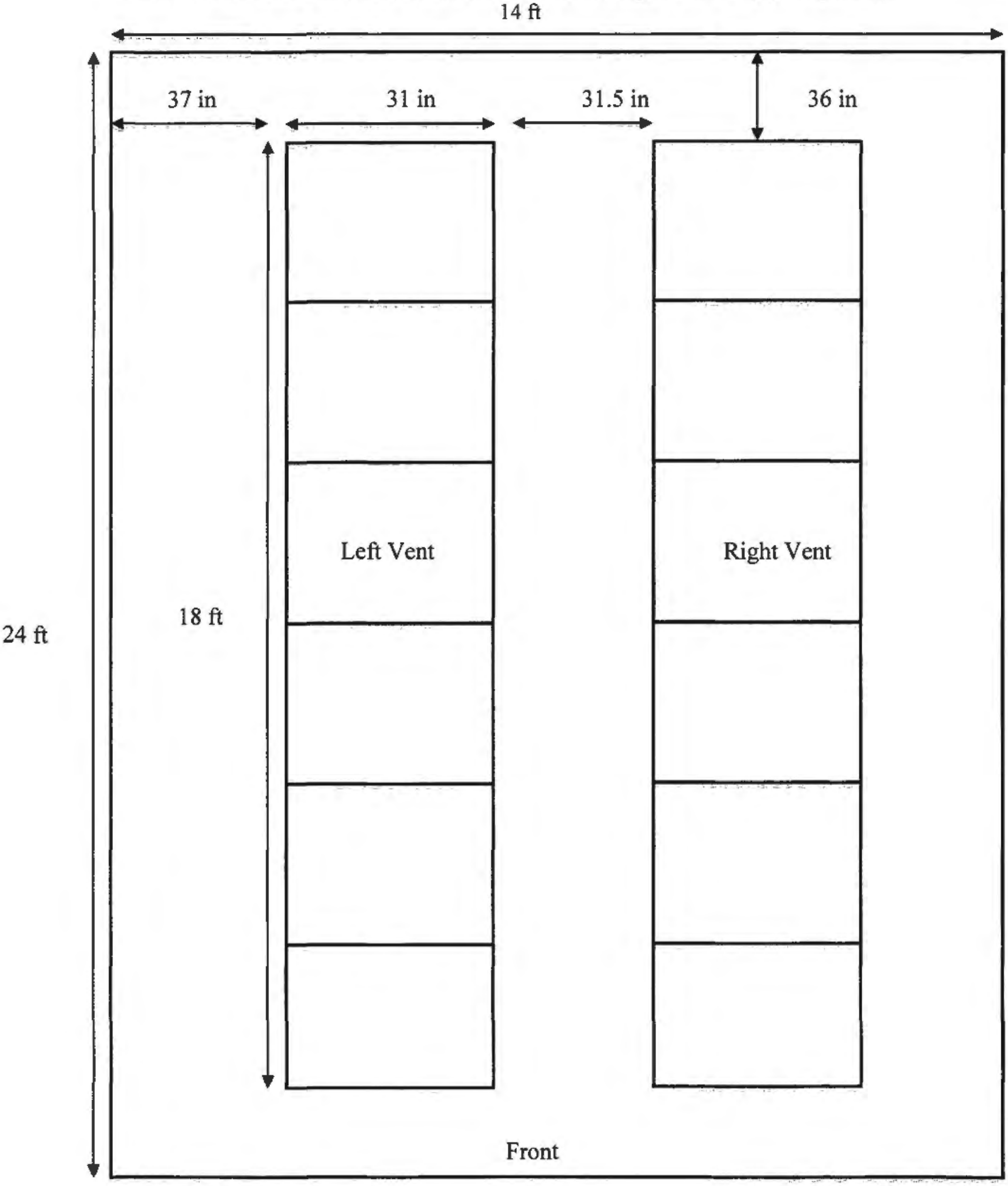
Disassembly of Permeation Panel

36. Take out all the remaining masking tape off the cells, wipe cells with acetone or alcohol to clean as much as possible all paint residue.
37. Store individual cells in small transparent plastic bags closed with tape in a box to prevent cells falling or breaking during transport.

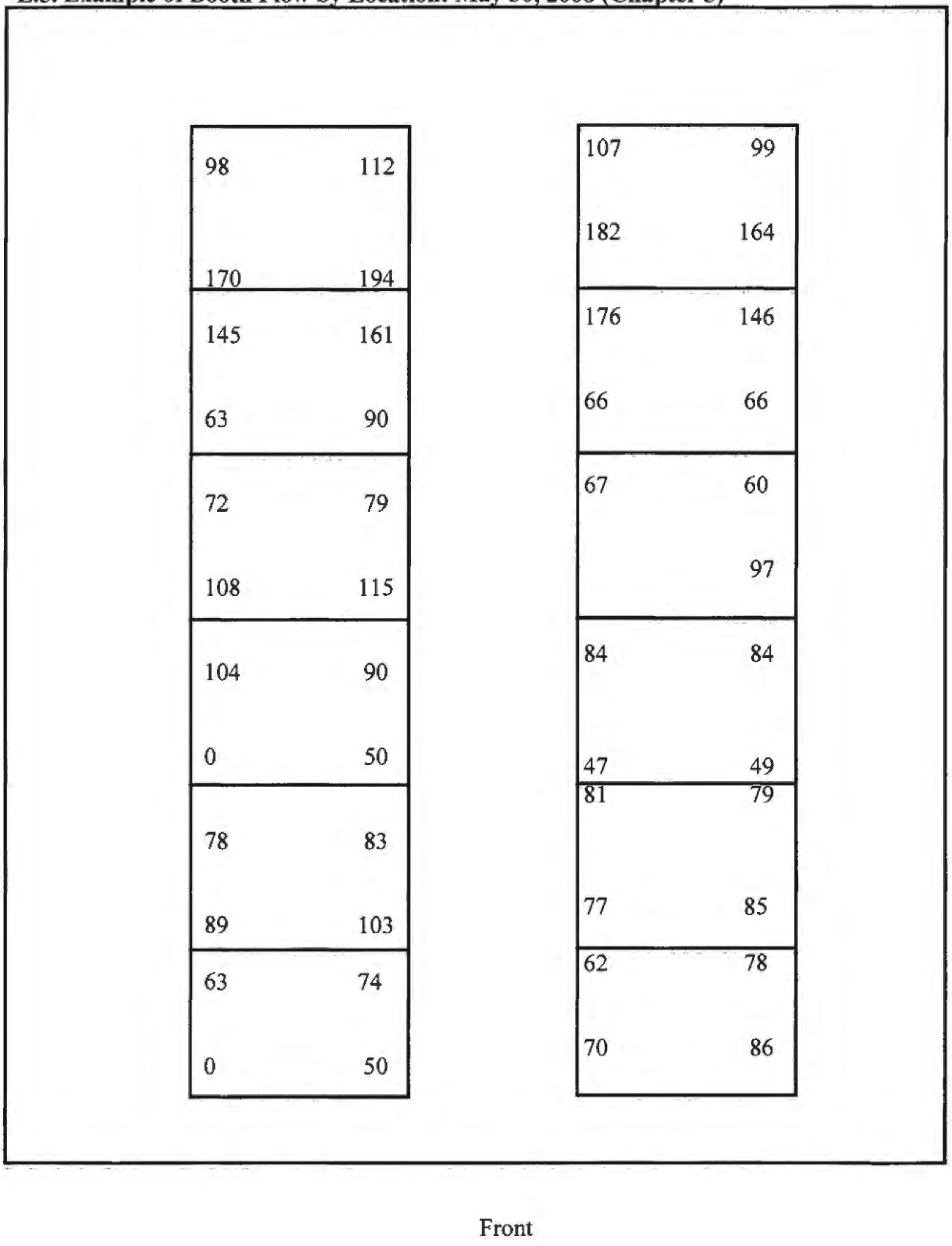
Post Preparation

38. Send filters (samples and blanks) for analysis immediately (they need to be frozen with no ice).
39. Send analysis request including MSDSs of products used and bulk samples. Provide the lab extra media filters for their blanks and calibration.
40. Clean cells according to SOP (Appendix X) inside a hood.
41. Loading ports are post-weighed after paint is dry, ideally after a week of the experiment. If necessary, ports can be dried in vacuum oven (only vacuum) to make sure paint is completely dry before weighing.

E.4. Booth Floor Plan and Dimensions (booth height was 9 ft) (Chapter 5)



E.5. Example of Booth Flow by Location: May 30, 2008 (Chapter 5)



E.6. Booth Flow Data (Chapter 5 and 6)

	Linear Velocity, LFM	
Date	Left Vent	Right Vent
5/27/2008	134	104
	96	120
	69	55
	49	86
		73.3
5/28/2008	118	123
	121	114
	202	230
	203	169
	179	197
	202	178
	71	80
	83	83
	80	77
	86	69
	130	129
	131	100
	105	88
	124	90
	46	50
	66	59
	97	60
	107	80
	89	93
	117	95
	50	87
	51	96
	56	80
	46	80

Continued on next page

Date	Linear Velocity, LFM Left Vent	Right Vent
5/29/2008	98	107
	112	99
	170	182
	194	164
	145	176
	161	146
	63	66
	90	66
	72	67
	79	60
	108	97
	115	84
	104	84
	90	47
	0	49
	50	81
	78	79
	83	77
	89	85
	103	62
	63	78
	74	70
	0	86
	50	
10/13/2008	81	80
	152	90
	155	166
	66	61
	67	71
	124	107
	122	85
	64	53
	91	100
	96	134
	51	133
	63	140

Continued on next page

	Linear Velocity, LFM	
Date	**Left Vent**	**Right Vent**
10/28/2008	185	120
	270	220
	225	173
	86	83
	83	65
	131	119
	80	68
	67	51
	89	58
	63	57
	45	52
	63.5	61
10/29/2008	185	144
	270	259
	158	232
	83	100
	102	75
	137	121
	82	90
	58	15
	86	48
	84	65
	46	66
	42	71

Continued on next page

	Linear Velocity, LFM	
Date	**Left Vent**	**Right Vent**
10/30/2008	180	155
	250	270
	200	235
	80	90
	91	70
	126	123
	104	106
	55	45
	107	51
	54	69
	45	75
	50	70
3/20/2009	121	107
	198	161
	175	168
	81	84
	90	77
	127	110
	81	100
	63	57
	100	77
	92	86
	60	107
	53	90

E.7. Loading Data 5/27/2008 and 5/28/2008 (Chapter 5)

Date	Port #	Panel	Material	Pre Weight mg	Post Weight mg	Mass Loading mg
5/27/2008	18a	I	PTFE	90.41	120.62	30.21
	19a	I	Metal tape	262.54	291.31	28.77
	20a	I	Thick aluminum square	132.32	162.62	30.3
	21a	I	Metal tape	312.14	340.97	28.83
	22a	I	Thick aluminum square	132.42	163.64	31.22
	23a	I	Metal tape	370.57	402.74	32.17
	24a	I	PTFE	92.32	127.22	34.9
	25a	I	Metal tape	384.93	416.8	31.87
	26a	I	Thick aluminum circle	470.67	506.91	36.24
	27a	I	Thick aluminum circle	594.93	630.81	35.88
	28a	I	Metal tape	379.34	414.2	34.86
	29a	I	Aluminum foil	*	*	
	30a	I	Aluminum foil	*	*	
	31a	I	Metal tape	317.69	348.64	30.95
	32a	I	PC	15.97	53.08	37.11
	33a	I	Metal tape	296.91	339.61	42.7
	34a	I	PC	*	*	
	35a	I	Metal tape	329.55	368.74	39.19

* Missing data due to error when weighing or method failed to collect a sample

Continued on next page

Date	Port #	Panel	Material	Pre Weight mg	Post Weight mg	Mass Loading mg
5/27/2008	36a	II	Thick aluminum square	132.94	168.7	35.76
	37a	II	Thick aluminum square	131.82	171.28	39.46
	38a	II	Metal tape	*	263.93	
	39a	II	Aluminum foil	79.55	122.07	42.52
	40a	II	Aluminum foil	*	*	
	41a	II	Metal tape	362.69	398.44	35.75
	42a	II	PC	*	*	
	43a	II	Metal tape	326.34	362.57	36.23
	44a	II	PC	*	*	
	45a	II	Metal tape	324.86	359.6	34.74
	46a	II	Metal tape	*	*	
	47a	II	Thick aluminum circle	520.48	556.49	36.01
	48a	II	Thick aluminum circle	554.71	587.27	32.56
	49a	II	Metal tape	*	*	
	50a	II	PTFE	89.44	126	36.56
	51a	II	Metal tape	*	*	
	52a	II	PTFE	91.05	124.7	33.65
	53a	II	Metal tape	334.23	365.09	30.86

* Missing data due to error when weighing or method failed to collect a sample

Continued on next page

Date	Port #	Panel	Material	Pre Weight mg	Post Weight mg	Mass Loading mg
5/28/2008	18b	I	PTFE	81.61	111.92	30.31
	19b	I	Thick aluminum circle	537.2	566.93	29.73
	20b	I	PTFE	79.59	113.66	34.07
	21b	I	PTFE	84.3	119.5	35.2
	22b	I	Thick aluminum circle	596.54	624.94	28.4
	23b	I	PTFE	86.03	115.09	29.06
	24b	I	PTFE	86.44	116.47	30.03
	25b	I	Thick aluminum circle	727.76	755.72	27.96
	26b	I	PTFE	81.79	113.32	31.53
	27b	I	PTFE	80.98	117.03	36.05
	28b	I	Thick aluminum circle	781.62	816.5	34.88
	29b	I	PTFE	79.42	109.75	30.33
	30b	II	PTFE	83.94	122.34	38.4
	31b	II	PTFE	82.38	124.17	41.79
	32b	II	Thick aluminum circle	582.32	622.92	40.6
	33b	II	Thick aluminum square	*	*	
	34b	II	PTFE	84.77	114.79	30.02
	35b	II	PTFE	81.68	113.32	31.64
	36b	II	PTFE	80.7	111.82	31.12
	37b	II	PTFE	81.32	116.96	35.64
	38b	II	Thick aluminum square	*	*	
	39b	II	Thick square square	*	*	
	40b	II	PTFE	82.11	113.2	31.09
	41b	II	PTFE	83.62	116.5	32.88

* Missing data due to error when weighing or method failed to collect a sample

E.8. SOP: Permeation Cells Cleaning (Chapter 5)

Objective: Clean cells in between experiments to assure cleanliness. Traces of paint carry over may interfere with future analysis and can deteriorate the coating of the cells. Care should be taken when cleaning the cells to assure that the Teflon coating of the cells doesn't come off.

Materials

- 1-methyl-2-pyrrolidinone (known as N-Methylpyrrolidone or NMP) is the most efficient cleaning agent to remove/clean/strip any paint/isocyanate/polurethane residue. BASF publishes its properties at http://www.basf.com/diols/bcdiolsnmp.html; MSDS at http://www.jtbaker.com/msds/englishhtml/m7114.htm
- Isopropyl alcohol, acetone, or paint thinner

Safety Considerations

Be very careful with NMP since it is a strong solvent and not too volatile.
Clean cells inside the hood (Morgan's lab) wearing adequate protection (lab coat, goggles, and thick heavy weight neoprene gloves on top of disposable nitrile gloves).

Cleaning Procedure

1) Clean cells with NMP in a tub inside the hood. There is no need to use too much solvent, using a paper towel to wipe the peaces with the solvent is enough.
2) Clean the cells with alcohol or acetone afterwards. The second clean up will help remove residues and assure cleanliness.
3) Sonicate cells (sonicate in EH lab F456) in a water/ Alconox powder detergent bath for at least 15 min. Dissolve a small quantity of soap in water before you place the parts in the solution. Do not use dishwasher liquid soap as it can strip the coating of the cells, only mild soap.
4) Let cells dry before assembly (or air/heat dry)
5) Store cells in acrylic holder

E.9. SWYPE Permeation Results for Characterization Experiments (Chapter 5)

Date	Original File*	Cell	Glove	Panel	Paint Formulation	Observed Color Scale
5/27/2008	Scan08527-0001	blank				
	Scan08527-0002	2a	Latex**	I	A & I	1
	Scan08527-0002	3a	Latex	I	A & I	1
	Scan08527-0002	5a	Latex	I	A & I	1
	Scan08527-0002	6a	Latex	I	A & I	1
	Scan08527-0003	10a	Latex	II	A & I	1
	Scan08527-0003	12a	Latex	II	A & I	1
	Scan08527-0003	15a	Latex	II	A & I	1
	Scan08527-0003	16a	Latex	II	A & I	1
5/28/2008	Scan08528-0002	3b	Latex	I	A & I	1
	Scan08528-0002	5b	Latex	I	A & I	1
	Scan08528-0002	6b	Latex	I	A & I	1
	Scan08528-0002	8b	Latex	I	A & I	1
	Scan08528-0004	10b	Latex	II	B & I	1
	Scan08528-0004	12b	Latex	II	B & I	1
	Scan08528-0004	14b	Latex	II	B & I	1
	Scan08528-0004	15b	Latex	II	B & I	1

*Several SWYPE samples were scanned in the same file

**Data was discarded because glove sample was mistakenly taped during the experiment

Continued on next page

	Red			Green			Blue			G+B	Load*
Cell	**mean**	**SD**	**median**	**mean**	**SD**	**median**	**mean**	**SD**	**median**	**mean**	**µg hardener**
Blank 5/27/08	246.76	6.64	248	229.17	6.71	230	179.51	10.95	180	410	<3
2a	246.16	5.71	247	228.44	5.8	229	187.81	10.53	189	418	NA**
3a	244.49	6.26	245	212.15	7.9	212	169.16	11.7	170	382	13.1
5a	244.84	6.13	246	213.31	7.15	213	161.46	13.76	163	376	18.8
6a	244.4	7.8	246	212.91	7.78	213	170.42	13.46	171	384	11.2
10a	245.96	5.13	246	219.73	6.05	220	175.54	10.63	176	396	<3
12a	245.3	8.21	247	213.71	9.76	214	169.71	12.35	171	385	10.2
15a	245.14	5.19	246	217.5	6.22	218	174.7	10.56	176	394	<3
16a	245.37	4.96	246	219.54	6.28	220	174.23	10.65	175	395	<3
3b	246.47	7.78	248	218.53	7.54	219	175.14	11.07	176	395	<3
5b	245.62	5.04	246	214.51	6.26	215	164.27	12.06	165	380	15
6b	244.94	6.12	246	214.64	6.67	215	164.77	13.36	166	381	14.1
8b	242.71	5.8	243	211.37	8.78	212	157.26	16.94	160	372	22.7
10b	245.67	5.53	246	218.43	6.26	219	173.4	12.41	175	394	<3
12b	246.62	4.8	247	222.68	5.34	223	183.55	9.23	184	407	<3
14b	244.52	5.39	245	215.95	5.94	216	168.34	12.23	170	386	9.2
15b	246.05	6.06	247	218.91	6.47	219	218.91	6.47	219	438	<3
										LOQ	3

*Calculated using RGB calibration

**Glove was taped over while the experiment by mistake so data was discarded

Continued on next page

E.10. PPZ Coated Filter Permeation Results for Characterization Experiments Analyzed by Modified OHSA42/PV2034 (Chapter 5)

Date	Cell	Panel	Material	Thickness mil	Paint Formulation	HDI µg/sample	IPDI µg/sample	Oligomers µg/sample
5/27/2008	1a	I	Latex	4	A & I	0.41	0.08	<0.5
	4a	I	Latex	4	A & I	0.34	0.06	<0.5
	7a	I	Latex	4	A & I	0.68	0.14	<0.5
	8a	I	Latex	4	A & I	0.45	0.08	<0.5
	9a	II	Latex	4.1	A & I	0.23	<0.05	<0.5
	11a	II	Latex	4.1	A & I	0.35	0.08	<0.5
	13a	II	Latex	4	A & I	0.18	<0.05	<0.5
	14a	II	Latex	4	A & I	0.26	<0.05	<0.5
5/28/2008	1b	I	Latex	4	A & I	0.23	<0.05	<0.5
	2b	I	Latex	4	A & I	0.12	<0.05	<0.5
	4b	I	Latex	4.1	A & I	0.59	0.07	<0.5
	7b	I	Latex	4.1	A & I	0.33	<0.05	<0.5
	9b	II	Latex	4	B & I	0.11	<0.05	<0.5
	11b	II	Latex	4.1	B & I	0.2	<0.05	<0.5
	13b	II	Latex	4.1	B & I	0.22	<0.05	<0.5
	16b	II	Latex	4	B & I	0.16	<0.05	<0.5
					LOQ	<0.05	<0.05	<0.5

Continued on next page

E.11. Bulk Analysis for Paint Formulations Components (Chapter 6)

Sample ID	vm&p naptha % w/w	methyl ethyl keton % w/w	methyl isobutyl ketone % w/w	toluene % w/w	ethyl benzene % w/w	p-xylene % w/w	m-xylene % w/w	o-xylene % w/w
Clear A	0.02	0.03	0.06	0.10	5.70	5.50	13.00	5.90
Duplicate Clear A	0.01	0.03	0.06	0.10	6.20	6.00	14.00	6.20
Reducer I	2	32	0.06	21	<0.01	0.02	0.04	0.02
Duplicate Reducer I	2	31	0.05	21	0.01	0.02	0.04	0.02
Hardene	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Duplicate Hardener	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01
Reducer II	27	17		9.4	1.1	1.4	3.2	0.48

Sample ID	styrene % w/w	2-heptanone % w/w	propylene glycol % w/w	ethyl 3-ethoxy propionate % w/w	methyl cyclohexane % w/w	petroleum distillates % w/w
Clear A	0.20	13.00	0.04	0.90	<0.01	1.30
Duplicate Clear A	0.20	14.00	0.04	0.90	<0.01	1.20
Reducer I	<0.01	<0.01	24	<0.01	0.4	24
Duplicate Reducer I	<0.01	<0.01	23	<0.01	0.4	24
Hardener	<0.01	17	<0.01	<0.01	<0.01	0.5
Duplicate Hardener	<0.01	17	<0.01	<0.01	<0.01	0.4
Reducer II		6	22	11		

E.12. Temperature And Relative Humidity Data (Chapter 6)

	Panel I		Booth Left Side		Booth Right Side	
Date Time	**Temperature F**	**RH %**	**Temperature F**	**RH %**	**Temperature F**	**RH %**
5/27/2009 11:11	73.15	47.50	73.15	44.50	71.43	45.72
5/27/2009 11:12	73.15	47.40	72.58	46.35	71.20	47.23
5/27/2009 11:13	73.15	47.30	73.15	47.92	71.77	49.15
5/27/2009 11:14	72.69	47.37	73.50	48.15	72.23	49.73
5/27/2009 11:15	72.46	47.40	73.84	48.07	72.69	49.75
5/27/2009 11:16	72.46	47.50	74.53	47.75	73.15	49.53
5/27/2009 11:17	72.46	47.60	74.53	47.32	73.84	49.13
5/27/2009 11:18	72.46	47.60	74.53	45.90	73.84	47.87
5/27/2009 11:19	72.46	47.60	74.53	45.15	73.84	46.75
5/27/2009 11:20	72.46	47.60	73.84	45.00	73.15	46.53
5/27/2009 11:21	72.46	47.60	73.61	45.18	73.04	46.48
5/27/2009 11:22	72.46	47.60	73.15	45.60	72.46	46.77
5/27/2009 11:23	72.46	47.60	72.92	46.00	72.12	47.15
5/27/2009 11:24	72.46	47.60	72.46	46.37	71.77	47.50
5/27/2009 11:25	72.46	47.60	72.46	46.80	71.54	47.93
5/27/2009 11:26	72.46	47.68	71.77	47.43	71.08	48.52
5/27/2009 11:27	72.46	47.70	71.77	47.70	71.08	48.87
5/27/2009 11:28	72.46	47.75	71.77	48.05	71.08	49.15
5/27/2009 11:29	72.23	47.83	71.08	48.60	70.85	49.58
5/27/2009 11:30	71.77	47.97	71.08	49.25	70.39	50.27
5/27/2009 11:31	71.77	48.10	71.08	49.70	70.39	50.75
5/27/2009 11:32	71.77	48.17	70.85	49.93	70.39	50.97
5/27/2009 11:33	71.77	48.20	70.39	50.12	70.05	51.05
5/27/2009 11:34	71.77	48.37	70.39	50.30	69.71	51.30
5/27/2009 11:35	71.77	48.43	70.39	50.73	69.71	51.63
5/27/2009 11:36	71.77	48.50	69.82	51.08	69.71	51.92
5/27/2009 11:37	71.66	48.68	69.71	51.37	69.37	52.20
5/27/2009 11:38	71.08	48.85	69.71	51.77	69.02	52.67
5/27/2009 11:39	71.08	48.90	69.71	52.15	69.02	53.03
5/27/2009 11:40	71.08	49.10	69.71	52.28	69.02	53.26

Continued on next page

	Panel II		Booth Left Side		Booth Right Side	
Date Time	**Temperature**	**RH**	**Temperature**	**RH**	**Temperature**	**RH**
	F	**%**	**F**	**%**	**F**	**%**
5/27/2008 12:40	--	--	71.77	49.53	71.77	50.13
5/27/2008 12:41	--	--	71.77	49.77	71.08	50.43
5/27/2008 12:42	--	--	71.31	49.97	71.08	50.55
5/27/2008 12:43	--	--	71.08	50.40	71.08	51.05
5/27/2008 12:44	--	--	71.08	50.80	71.08	51.40
5/27/2008 12:45	--	--	71.08	50.87	71.08	51.53
5/27/2008 12:46	--	--	71.08	51.03	71.08	51.68
5/27/2008 12:47	--	--	71.08	51.17	70.62	51.90
5/27/2008 12:48	--	--	71.08	51.48	70.39	52.25
5/27/2008 12:49	--	--	71.08	51.80	70.39	52.60
5/27/2008 12:50	--	--	70.85	52.10	70.39	52.93
5/27/2008 12:51	--	--	70.39	52.40	70.39	53.18
5/27/2008 12:52	--	--	70.39	52.60	70.39	53.40
5/27/2008 12:53	--	--	71.08	53.73	71.77	54.73
5/27/2008 12:54	--	--	72.35	52.73	73.04	52.87
5/27/2008 12:55	--	--	73.15	50.63	73.73	50.97
5/27/2008 12:56	--	--	73.73	49.87	73.84	50.60
5/27/2008 12:57	--	--	73.84	49.63	73.96	50.38
5/27/2008 12:58	--	--	74.53	49.70	74.53	50.27
5/27/2008 12:59	--	--	75.22	49.15	74.53	50.50
5/27/2008 13:00	--	--	75.45	48.58	74.53	50.62

Continued on next page

Date Time	Panel I Temperature F	RH %	Booth Left Side Temperature F	RH %	Booth Right Side Temperature F	RH %
5/28/2008 10:36	67.31	59.12	75.69	49.37	74.53	52.40
5/28/2008 10:37	68.33	59.15	75.92	48.63	74.76	51.75
5/28/2008 10:38	68.56	58.47	76.39	47.67	75.22	50.88
5/28/2008 10:39	69.02	57.97	76.27	45.97	75.22	49.45
5/28/2008 10:40	69.02	57.50	75.92	44.90	74.65	48.08
5/28/2008 10:41	69.14	57.08	75.22	44.80	74.42	47.65
5/28/2008 10:42	69.60	56.65	74.65	45.20	73.84	47.73
5/28/2008 10:43	69.71	56.27	74.30	45.67	73.27	47.98
5/28/2008 10:44	69.71	55.97	73.73	46.27	72.81	48.28
5/28/2008 10:45	69.71	55.60	73.15	46.90	72.46	48.60
5/28/2008 10:46	69.82	55.37	72.58	47.60	71.89	49.08
5/28/2008 10:47	70.28	55.02	72.12	48.30	71.77	49.57
5/28/2008 10:48	70.39	54.77	71.77	48.98	71.54	50.03
5/28/2008 10:49	70.39	54.52	71.54	49.62	71.08	50.48
5/28/2008 10:50	70.39	54.37	71.08	50.25	71.08	50.90
5/28/2008 10:51	70.39	54.13	71.08	50.77	70.74	51.37
5/28/2008 10:52	70.39	53.93	70.39	51.42	70.39	51.83
5/28/2008 10:53	70.39	53.77	70.39	51.98	70.39	52.25
5/28/2008 10:54	70.39	53.67	69.94	52.58	70.28	52.70
5/28/2008 10:55	70.85	53.43	69.71	53.10	69.71	53.15
5/28/2008 10:56	71.08	53.23	69.71	53.33	69.71	53.37
5/28/2008 10:57	71.08	53.15	69.48	53.73	69.71	53.63
5/28/2008 10:58	71.08	53.03	69.02	54.37	69.71	54.05
5/28/2008 10:59	71.08	52.83	69.02	54.83	69.25	54.57
5/28/2008 11:00	71.08	52.70	69.02	56.12	69.37	55.40

Continued on next page

	Panel II		Booth Left Side		Booth Right Side	
Date Time	Temperature	RH	Temperature	RH	Temperature	RH
	F	%	F	%	F	%
5/28/2008 11:51	69.71	54.27	70.16	57.43	70.51	57.38
5/28/2008 11:52	69.71	54.30	70.85	57.00	71.08	57.23
5/28/2008 11:53	69.71	54.50	71.54	56.13	71.66	56.68
5/28/2008 11:54	69.71	54.50	72.12	55.03	72.12	55.90
5/28/2008 11:55	69.71	54.52	72.69	54.05	72.46	55.30
5/28/2008 11:56	69.71	54.60	73.38	53.30	73.15	54.70
5/28/2008 11:57	69.71	54.60	73.84	52.20	73.38	54.03
5/28/2008 11:58	69.71	54.60	74.53	51.35	73.84	53.47
5/28/2008 11:59	69.71	54.60	74.76	50.53	73.96	52.83
5/28/2008 12:00	69.71	54.52	75.22	49.70	74.53	52.23
5/28/2008 12:01	70.39	54.40	75.80	49.00	74.53	51.73
5/28/2008 12:02	70.39	54.33	75.92	48.20	74.88	51.20
5/28/2008 12:03	70.39	54.20	75.92	46.48	74.88	49.68
5/28/2008 12:04	70.39	54.07	75.45	45.57	74.53	48.57
5/28/2008 12:05	70.39	53.93	75.11	45.42	74.19	48.15
5/28/2008 12:06	70.62	53.80	74.53	45.73	73.73	48.05
5/28/2008 12:07	71.08	53.60	73.96	46.33	73.15	48.47
5/28/2008 12:08	71.08	53.43	73.73	46.73	72.69	48.70
5/28/2008 12:09	71.08	53.30	73.15	47.30	72.46	49.00
5/28/2008 12:10	71.08	53.20	72.46	47.95	72.00	49.40
5/28/2008 12:11	71.08	53.18	72.35	48.62	71.77	49.92
5/28/2008 12:12	70.97	53.12	71.77	49.30	71.66	50.43
5/28/2008 12:13	70.51	53.18	71.77	49.68	71.08	50.75
5/28/2008 12:14	70.39	53.20	71.08	50.20	71.08	50.97
5/28/2008 12:15	70.39	53.20	71.08	50.68	70.62	51.37
5/28/2008 12:16	70.39	53.20	70.39	51.40	70.39	51.92
5/28/2008 12:17	70.39	53.20	70.39	52.08	70.39	52.45
5/28/2008 12:18	70.39	53.20	70.39	52.50	70.16	52.93
5/28/2008 12:19	70.39	53.20	69.71	52.93	69.71	53.20
5/28/2008 12:20	70.39	53.30	69.71	53.33	69.71	53.60
5/28/2008 12:21	70.39	53.30	69.71	53.88	69.71	54.03
5/28/2008 12:22	70.05	53.48	69.25	54.32	69.71	54.40
5/28/2008 12:23	69.71	53.60	69.02	54.63	69.14	54.73

Continued on next page

	Panel I		Booth Left Side		Booth Right Side	
Date Time	Temperature	RH	Temperature	RH	Temperature	RH
	F	%	F	%	F	%
5/29/2008 10:47	71.08	40.50	74.53	30.60	74.53	30.90
5/29/2008 10:48	71.08	40.40	74.53	30.53	74.53	30.90
5/29/2008 10:49	71.31	40.33	74.53	30.50	74.53	30.90
5/29/2008 10:50	71.77	40.20	74.53	30.43	74.53	30.90
5/29/2008 10:51	71.77	40.03	74.53	30.40	74.53	30.90
5/29/2008 10:52	71.77	40.00	74.53	30.40	74.53	30.90
5/29/2008 10:53	71.77	39.90	74.53	30.40	74.53	30.65
5/29/2008 10:54	71.77	39.80	74.53	30.40	74.53	30.70
5/29/2008 10:55	71.77	39.80	74.53	30.40	74.53	30.60
5/29/2008 10:56	71.77	39.80	75.22	30.30	74.53	30.60
5/29/2008 10:57	71.77	39.72	75.22	30.30	74.53	30.90
5/29/2008 10:58	71.77	39.70	75.22	30.30	74.53	30.80
5/29/2008 10:59	71.77	39.60	75.22	30.30	74.53	30.60
5/29/2008 11:00	71.77	39.50	75.22	30.30	74.53	30.80
5/29/2008 11:01	71.77	39.50	75.22	30.05	74.53	30.60
5/29/2008 11:02	71.77	39.50	75.22	30.00	74.53	30.60
5/29/2008 11:03	71.77	39.47	75.22	30.00	74.53	30.43
5/29/2008 11:04	71.77	39.40	75.22	30.00	74.53	30.60
5/29/2008 11:05	72.00	39.37	75.22	29.85	74.53	30.43
5/29/2008 11:06	72.12	39.35	75.22	29.90	74.88	30.35
5/29/2008 11:07	72.46	39.30	75.22	29.80	75.22	30.30
5/29/2008 11:08	72.46	39.10	75.22	29.80	74.99	30.33
5/29/2008 11:09	72.46	39.10	75.22	29.70	75.22	30.30
5/29/2008 11:10	72.46	39.10	75.22	29.80	75.22	30.33
5/29/2008 11:11	72.46	39.10	75.22	30.00	75.22	30.47
5/29/2008 11:12	72.46	39.10	75.22	30.00	75.22	30.50
5/29/2008 11:13	72.46	39.03	75.22	30.00	75.22	30.50
5/29/2008 11:14	72.46	39.00	75.22	30.00	75.22	30.50
5/29/2008 11:15	72.46	39.00	75.22	30.00	75.22	30.50
5/29/2008 11:16	72.46	39.00	75.22	30.00	74.53	30.60

Continued on next page

Date Time	Panel II Temperature F	 RH %	Booth Left Side Temperature F	 RH %	Booth Right Side Temperature F	 RH %
5/29/2008 11:47	72.46	39.10	75.80	29.92	75.22	30.55
5/29/2009 11:48	72.46	39.10	75.69	29.78	75.22	30.50
5/29/2008 11:49	72.46	39.10	75.92	29.90	75.22	30.50
5/29/2008 11:50	72.46	39.08	75.22	30.00	75.22	30.50
5/29/2008 11:51	72.46	39.00	75.22	30.00	75.22	30.50
5/29/2008 11:52	72.46	39.00	75.22	30.00	75.22	30.50
5/29/2008 11:53	72.46	39.00	75.22	30.00	75.22	30.50
5/29/2008 11:54	72.46	39.00	75.22	30.05	75.22	30.50
5/29/2008 11:55	72.46	39.00	75.45	29.97	75.22	30.50
5/29/2008 11:56	72.46	39.00	75.57	29.95	75.22	30.50
5/29/2008 11:57	72.46	38.97	75.92	29.90	75.22	30.50
5/29/2008 11:58	72.46	38.80	75.80	29.92	75.22	30.50
5/29/2008 11:59	72.46	38.90	75.69	29.93	75.22	30.50
5/29/2009 12:00	72.46	38.97	75.92	29.90	75.22	30.50
5/29/2009 12:01	72.46	38.80	75.92	29.85	75.22	30.40
5/29/2009 12:02	72.46	38.80	75.92	29.60	75.22	30.30
5/29/2009 12:03	72.46	38.80	75.92	29.60	75.22	30.30
5/29/2009 12:04	72.46	38.80	75.80	29.77	75.22	30.30
5/29/2009 12:05	72.69	38.77	75.22	29.70	75.22	30.30
5/29/2009 12:06	72.81	38.75	75.22	29.70	75.22	30.30
5/29/2009 12:07	73.15	38.67	75.22	29.70	75.22	30.30
5/29/2009 12:08	73.15	38.50	75.22	29.70	75.22	30.30
5/29/2009 12:09	73.15	38.50	75.22	29.70	75.22	30.30
5/29/2009 12:10	73.15	38.50	75.45	29.67	75.22	30.30
5/29/2009 12:11	73.15	38.50	75.80	29.62	75.22	30.30
5/29/2009 12:12	73.15	38.50	75.45	29.67	75.22	30.30
5/29/2009 12:13	73.15	38.50	75.92	29.60	75.22	30.30
5/29/2009 12:14	73.15	38.50	75.45	29.67	75.22	30.30
5/29/2009 12:15	73.15	38.48	75.57	29.65	75.22	30.30
5/29/2009 12:16	73.15	38.40	75.92	29.60	75.22	30.15
5/29/2009 12:17	73.15	38.40	75.92	29.60	75.22	30.15
5/29/2009 12:18	73.15	38.40	75.92	29.60	75.22	30.30

Continued on next page

	Panel I		Booth Left Side		Booth Right Side	
Date Time	Temperature	RH	Temperature	RH	Temperature	RH
	F	%	F	%	F	%
5/30/2008 11:10	73.84	33.43	77.31	29.75	76.62	30.50
5/30/2008 11:11	73.84	33.30	77.31	29.70	76.62	30.40
5/30/2008 11:12	73.96	33.28	77.31	29.70	76.62	30.40
5/30/2008 11:13	73.96	33.28	77.31	29.70	76.62	30.40
5/30/2008 11:14	74.53	33.13	77.31	29.90	76.62	30.60
5/30/2008 11:15	74.53	33.00	77.31	30.00	76.85	30.57
5/30/2008 11:16	74.53	33.00	77.31	30.00	77.31	30.60
5/30/2008 11:17	74.53	33.00	77.31	29.95	77.31	30.50
5/30/2008 11:18	74.53	33.00	77.31	29.70	77.31	30.33
5/30/2008 11:19	74.53	33.00	78.01	29.60	77.31	30.30
5/30/2008 11:20	74.53	32.87	78.01	29.60	77.31	30.30
5/30/2008 11:21	74.53	32.80	78.01	29.60	77.31	30.30
5/30/2008 11:22	74.53	32.80	78.01	29.47	77.31	30.25
5/30/2008 11:23	74.53	32.80	78.01	29.40	77.31	30.05
5/30/2008 11:24	74.53	32.80	78.01	29.25	77.31	29.80
5/30/2008 11:25	74.53	32.80	78.01	29.10	77.31	29.70
5/30/2008 11:26	74.76	32.67	78.01	29.20	77.31	29.70
5/30/2008 11:27	75.11	32.52	78.01	28.90	77.31	29.48
5/30/2008 11:28	75.22	32.50	77.31	28.15	76.85	28.82
5/30/2008 11:29	75.22	32.50	76.74	27.88	76.27	28.35
5/30/2008 11:30	75.22	32.50	76.15	27.97	75.57	28.40
5/30/2008 11:31	75.22	32.50	75.45	28.17	74.76	28.57
5/30/2008 11:32	74.99	32.53	74.76	28.52	74.07	28.92
5/30/2008 11:33	74.65	32.58	74.19	28.85	73.50	29.20
5/30/2008 11:34	74.53	32.60	73.84	29.85	73.15	30.20
5/30/2008 11:35	74.53	32.60	73.84	30.57	73.15	31.00
5/30/2008 11:36	74.53	32.60	74.19	30.65	73.61	31.17
5/30/2008 11:37	74.53	32.60	74.53	30.90	73.84	31.30
5/30/2008 11:38	74.53	32.60	74.53	31.05	73.84	31.57

Continued on next page

Date Time	Panel II Temperature F	RH %	Booth Left Side Temperature F	RH %	Booth Right Side Temperature F	RH %
5/30/2008 12:08	73.84	33.30	78.01	28.20	78.01	28.50
5/30/2008 12:09	73.84	33.30	78.01	28.07	78.01	28.50
5/30/2008 12:10	73.84	33.13	78.01	27.80	78.01	28.20
5/30/2008 12:11	74.07	33.07	78.01	28.20	78.01	28.45
5/30/2008 12:12	74.53	32.97	78.48	28.13	78.01	28.50
5/30/2008 12:13	74.53	32.80	78.36	27.80	78.01	28.20
5/30/2008 12:14	74.53	32.80	78.01	27.33	77.78	27.75
5/30/2008 12:15	74.53	32.70	77.66	26.78	77.31	27.17
5/30/2008 12:16	74.53	32.60	77.31	26.83	76.74	26.98
5/30/2008 12:17	74.53	32.60	76.50	27.02	76.15	27.27
5/30/2008 12:18	74.53	32.60	75.92	27.30	75.45	27.47
5/30/2008 12:19	74.53	32.40	75.22	27.50	74.76	27.67
5/30/2008 12:20	74.53	32.30	74.76	27.77	74.07	27.97
5/30/2008 12:21	74.42	32.32	74.19	28.28	73.73	28.47
5/30/2008 12:22	73.84	32.40	73.84	28.70	73.15	28.85
5/30/2008 12:23	73.84	32.40	73.27	29.28	72.46	29.70
5/30/2008 12:24	73.84	32.40	73.27	30.63	72.69	30.92
5/30/2008 12:25	73.84	32.65	73.84	31.03	73.15	31.40
5/30/2008 12:26	73.84	32.70	73.84	31.40	73.50	31.72
5/30/2008 12:27	73.84	32.70	74.30	31.43	73.84	31.95
5/30/2008 12:28	73.84	32.70	74.53	31.50	74.19	31.95
5/30/2008 12:29	73.84	32.90	74.76	31.57	74.53	32.07
5/30/2008 12:30	73.84	32.90	75.22	31.50	74.88	32.05
5/30/2008 12:31	73.84	32.90	75.45	31.43	75.22	31.93
5/30/2008 12:32	73.84	32.90	75.92	31.17	75.45	31.62
5/30/2008 12:33	73.84	32.90	75.92	30.85	75.92	31.23
5/30/2008 12:34	73.84	32.90	76.27	30.65	75.92	31.20
5/30/2008 12:35	73.84	32.90	76.62	30.60	76.15	31.00
5/30/2008 12:36	73.84	32.90	76.62	30.57	76.62	30.90

Continued on next page

	Panel I		Booth Left Side		Booth Right Side	
Date Time	Temperature F	RH %	Temperature F	RH %	Temperature F	RH %
10/13/2008 10:30	68.33	20.19	70.39	21.33	71.77	22.09
10/13/2008 10:31	68.33	20.19	70.39	21.33	71.77	22.09
10/13/2008 10:32	68.33	20.19	70.39	21.33	71.77	22.09
10/13/2008 10:33	68.33	20.19	70.39	21.33	71.77	22.09
10/13/2008 10:34	68.33	20.19	70.05	21.14	71.43	21.90
10/13/2008 10:35	68.33	20.19	69.71	20.95	71.08	21.71
10/13/2008 10:36	68.33	20.19	69.71	20.95	71.08	21.71
10/13/2008 10:37	68.33	20.19	69.71	20.95	71.08	21.71
10/13/2008 10:38	68.33	20.19	69.71	20.95	71.08	21.71
10/13/2008 10:39	68.33	20.19	69.71	20.95	71.08	21.71
10/13/2008 10:40	67.65	19.81	69.71	20.95	70.74	21.52
10/13/2008 10:41	67.65	19.81	69.71	20.95	70.39	21.33
10/13/2008 10:42	67.65	19.81	69.25	20.70	70.39	21.33
10/13/2008 10:43	67.65	19.81	69.02	20.57	70.39	21.33
10/13/2008 10:44	67.65	19.81	69.02	20.57	70.39	21.33
10/13/2008 10:45	67.65	19.81	69.02	20.57	70.39	21.33
10/13/2008 10:46	67.65	19.81	69.02	20.57	70.39	21.33
10/13/2008 10:47	67.65	19.81	69.02	20.57	70.39	21.33
10/13/2008 10:48	67.65	19.81	69.60	20.89	70.97	21.65
10/13/2008 10:49	67.65	19.81	70.16	21.20	71.77	22.09
10/13/2008 10:50	67.65	19.81	70.85	21.58	72.23	22.35
10/13/2008 10:51	67.65	19.81	71.54	21.96	73.04	22.80
10/13/2008 10:52	67.65	19.81	72.12	22.29	73.73	23.18
10/13/2008 10:53	67.99	20.00	72.69	22.61	74.07	23.37
10/13/2008 10:54	68.33	20.19	73.27	22.92	74.53	23.63
10/13/2008 10:55	68.33	20.19	73.84	23.24	75.11	23.95
10/13/2008 10:56	68.33	20.19	74.53	23.63	75.45	24.14
10/13/2008 10:57	68.33	20.19	74.76	23.76	75.92	24.40
10/13/2008 10:58	68.91	20.51	75.22	24.01	76.27	24.60

Continued on next page

	Panel II		Booth Left Side		Booth Right Side	
Date Time	Temperature	RH	Temperature	RH	Temperature	RH
	F	%	F	%	F	%
10/13/08 11:20	70.39	21.33	70.39	21.33	71.08	21.71
10/13/08 11:21	70.39	21.33	69.71	20.95	71.08	21.71
10/13/08 11:22	70.39	21.33	69.71	20.95	71.08	21.71
10/13/08 11:23	70.16	21.20	69.71	20.95	71.08	21.71
10/13/08 11:24	69.71	20.95	69.71	20.95	71.08	21.71
10/13/08 11:25	69.71	20.95	69.71	20.95	71.08	21.71
10/13/08 11:26	69.71	20.95	69.71	20.95	70.51	21.39
10/13/08 11:27	69.71	20.95	69.71	20.95	70.39	21.33
10/13/08 11:28	69.71	20.95	69.71	20.95	70.39	21.33
10/13/08 11:29	69.71	20.95	69.71	20.95	70.39	21.33
10/13/08 11:30	69.71	20.95	69.71	20.95	70.39	21.33
10/13/08 11:31	69.14	20.63	69.71	20.95	70.39	21.33
10/13/08 11:32	69.02	20.57	69.71	20.95	70.39	21.33
10/13/08 11:33	69.02	20.57	69.14	20.63	70.39	21.33
10/13/08 11:34	69.02	20.57	69.02	20.57	70.39	21.33
10/13/08 11:35	69.02	20.57	69.02	20.57	70.39	21.33
10/13/08 11:36	69.02	20.57	69.02	20.57	70.39	21.33
10/13/08 11:37	69.02	20.57	69.02	20.57	70.39	21.33
10/13/08 11:38	68.33	20.19	69.02	20.57	70.39	21.33
10/13/08 11:39	68.33	20.19	69.02	20.57	70.39	21.33
10/13/08 11:40	68.33	20.19	69.02	20.57	70.39	21.33
10/13/08 11:41	68.33	20.19	69.02	20.57	70.39	21.33
10/13/08 11:42	68.33	20.19	69.02	20.57	70.39	21.33
10/13/08 11:43	68.33	20.19	69.02	20.57	70.39	21.33
10/13/08 11:44	68.33	20.19	69.02	20.57	70.39	21.33
10/13/08 11:45	68.33	20.19	69.02	20.57	70.39	21.33
10/13/08 11:46	68.33	20.19	69.02	20.57	70.39	21.33
10/13/08 11:47	68.33	20.19	69.02	20.57	70.39	21.33
10/13/08 11:48	68.33	20.19	69.02	20.57	70.39	21.33

Continued on next page

	Panel II		Booth Left Side		Booth Right Side	
Date Time	**Temperature**	**RH**	**Temperature**	**RH**	**Temperature**	**RH**
	F	**%**	**F**	**%**	**F**	**%**
10/28/2008 10:36	69.02	40.55	71.77	40.27	71.77	41.70
10/28/2008 10:37	69.25	40.23	71.77	40.23	71.66	41.72
10/28/2008 10:38	69.71	39.95	71.77	40.20	71.43	41.75
10/28/2008 10:39	69.71	39.77	71.77	40.20	71.66	41.52
10/28/2008 10:40	69.71	39.60	71.77	40.20	71.77	41.70
10/28/2008 10:41	70.28	39.38	71.77	40.22	71.54	41.73
10/28/2008 10:42	70.39	39.20	71.77	40.37	71.43	41.78
10/28/2008 10:43	70.39	38.93	71.77	40.30	71.08	41.82
10/28/2008 10:44	70.39	38.90	71.77	40.50	71.66	41.95
10/28/2008 10:45	70.85	38.78	71.77	40.43	71.66	41.83
10/28/2008 10:46	71.08	38.63	71.77	40.47	71.77	41.85
10/28/2008 10:47	71.08	38.37	71.77	40.50	71.54	41.97
10/28/2008 10:48	71.08	38.27	71.77	40.50	71.77	42.00
10/28/2008 10:49	71.77	38.07	71.77	40.55	71.77	42.02
10/28/2008 10:50	71.77	37.83	71.77	40.70	71.77	42.13
10/28/2008 10:51	71.77	37.65	72.12	40.45	71.77	41.97
10/28/2008 10:52	72.12	37.35	72.35	40.27	71.77	41.85
10/28/2008 10:53	72.46	37.10	72.46	40.15	71.77	41.73
10/28/2008 10:54	72.46	37.03	72.46	40.20	71.77	41.80
10/28/2008 10:55	72.46	36.90	72.46	40.20	71.77	41.73
10/28/2008 10:56	72.46	36.77	72.46	40.20	71.77	41.77
10/28/2008 10:57	72.46	36.60	72.46	40.18	71.77	41.78
10/28/2008 10:58	72.46	36.60	72.46	40.03	71.77	41.70
10/28/2008 10:59	72.46	36.40	72.46	39.90	71.77	41.70
10/28/2008 11:00	72.46	36.40	72.46	39.77	71.77	41.52
10/28/2008 11:01	72.46	36.40	72.58	39.68	71.77	41.40
10/28/2008 11:02	72.46	36.30	72.92	39.57	71.77	41.40
10/28/2008 11:03	72.46	36.30	73.15	39.37	71.89	41.25
10/28/2008 11:04	72.58	36.28	73.15	39.33	72.35	41.12

Continued on next page

	Panel I		Booth Left Side		Booth Right Side	
Date Time	Temperature F	RH %	Temperature F	RH %	Temperature F	RH %
10/29/2008 10:41	69.71	46.13	69.71	46.13	69.71	46.13
10/29/2008 10:42	70.28	45.92	70.28	45.92	70.28	45.92
10/29/2008 10:43	70.39	45.73	70.39	45.73	70.39	45.73
10/29/2008 10:44	70.39	45.57	70.39	45.57	70.39	45.57
10/29/2008 10:45	70.39	45.43	70.39	45.43	70.39	45.43
10/29/2008 10:46	70.39	45.23	70.39	45.23	70.39	45.23
10/29/2008 10:47	70.39	45.10	70.39	45.10	70.39	45.10
10/29/2008 10:48	70.39	44.93	70.39	44.93	70.39	44.93
10/29/2008 10:49	70.39	44.83	70.39	44.83	70.39	44.83
10/29/2008 10:50	70.51	44.65	70.51	44.65	70.51	44.65
10/29/2008 10:51	70.62	44.50	70.62	44.50	70.62	44.50
10/29/2008 10:52	71.08	44.40	71.08	44.40	71.08	44.40
10/29/2008 10:53	71.08	44.40	71.08	44.40	71.08	44.40
10/29/2008 10:54	71.08	44.32	71.08	44.32	71.08	44.32
10/29/2008 10:55	71.08	44.23	71.08	44.23	71.08	44.23
10/29/2008 10:56	71.08	44.10	71.08	44.10	71.08	44.10
10/29/2008 10:57	71.08	44.00	71.08	44.00	71.08	44.00
10/29/2008 10:58	71.08	43.90	71.08	43.90	71.08	43.90
10/29/2008 10:59	71.08	43.80	71.08	43.80	71.08	43.80
10/29/2008 11:00	71.08	43.80	71.08	43.80	71.08	43.80
10/29/2008 11:01	71.08	43.77	71.08	43.77	71.08	43.77
10/29/2008 11:02	71.08	43.70	71.08	43.70	71.08	43.70
10/29/2008 11:03	71.08	43.70	71.08	43.70	71.08	43.70
10/29/2008 11:04	71.08	43.70	71.08	43.70	71.08	43.70
10/29/2008 11:05	71.08	43.70	71.08	43.70	71.08	43.70
10/29/2008 11:06	71.08	43.70	71.08	43.70	71.08	43.70
10/29/2008 11:07	71.08	43.70	71.08	43.70	71.08	43.70
10/29/2008 11:08	71.08	43.67	71.08	43.67	71.08	43.67
10/29/2008 11:09	71.08	43.50	71.08	43.50	71.08	43.50

Continued on next page

	Panel I		Booth Left Side		Booth Right Side	
Date Time	Temperature	RH	Temperature	RH	Temperature	RH
	F	%	F	%	F	%
10/30/2008 10:17	71.08	42.40	74.53	40.73	73.73	42.72
10/30/2008 10:18	71.08	42.40	74.53	40.72	73.84	42.70
10/30/2008 10:19	71.08	42.40	74.53	40.70	73.84	42.70
10/30/2008 10:20	71.08	42.40	74.53	40.70	73.84	42.70
10/30/2008 10:21	71.08	42.40	74.53	40.70	73.84	42.70
10/30/2008 10:22	71.08	42.47	74.53	40.60	73.84	42.70
10/30/2008 10:23	71.08	42.57	74.88	40.45	73.84	42.70
10/30/2008 10:24	71.08	42.70	75.22	40.40	73.84	42.70
10/30/2008 10:25	71.08	42.70	75.22	40.18	73.84	42.57
10/30/2008 10:26	71.08	42.87	75.22	40.03	73.84	42.37
10/30/2008 10:27	71.08	43.13	75.22	39.87	73.84	42.17
10/30/2008 10:28	71.08	42.83	75.22	39.80	73.84	42.10
10/30/2008 10:29	71.08	42.80	75.22	40.00	73.84	42.20
10/30/2008 10:30	71.08	42.72	75.22	40.03	73.84	42.25
10/30/2008 10:31	71.08	42.70	75.22	40.10	73.84	42.40
10/30/2008 10:32	71.08	42.70	75.22	40.05	74.30	42.33
10/30/2008 10:33	71.08	42.72	75.22	40.02	74.19	42.35
10/30/2008 10:34	71.08	42.80	75.22	40.00	74.53	42.25
10/30/2008 10:35	71.08	42.80	75.22	39.83	74.53	42.07
10/30/2008 10:36	71.08	42.90	75.69	39.60	74.53	41.93
10/30/2008 10:37	71.08	42.90	75.80	39.35	74.53	41.70
10/30/2008 10:38	70.85	43.00	75.45	39.33	74.53	41.70
10/30/2008 10:39	70.51	43.18	75.22	39.50	74.53	41.70
10/30/2008 10:40	70.74	43.15	75.80	39.42	74.53	41.70
10/30/2008 10:41	70.51	43.18	75.34	39.52	74.53	41.70
10/30/2008 10:42	70.39	43.30	75.80	39.45	74.53	41.70
10/30/2008 10:43	70.39	43.30	75.92	39.60	74.53	41.83
10/30/2008 10:44	70.39	43.30	75.92	39.60	74.53	41.87
10/30/2008 10:45	70.39	43.30	75.92	39.60	74.53	41.80

Continued on next page

	Panel I		Panel II		Left Side		Right Side	
Date Time	Temperature F	RH %	Temperature F	RH %	Temperature F	RH %	Temperature F	RH %
3/20/2009 10:47	70.39	43.81	70.47	43.06	72.90	44.82	73.51	46.73
3/20/2009 10:54	70.39	44.07	70.70	43.16	73.51	43.79	73.84	44.27
3/20/2009 11:00	70.39	44.07	71.08	43.02	73.84	43.36	73.84	44.05
3/20/2009 11:06	70.70	43.82	71.08	42.84	73.84	42.86	74.30	43.55
3/20/2009 11:12	71.08	43.58	71.41	42.60	74.09	42.51	74.53	43.21
3/20/2009 11:18	71.25	43.30	71.77	42.32	74.45	42.31	74.53	43.08
3/20/2009 11:24	71.77	43.03	71.77	42.05	74.53	42.39	74.53	43.15
3/20/2009 11:30	71.77	42.80	72.33	41.73	74.53	42.51	74.53	43.31
3/20/2009 11:36	71.77	43.11	72.35	41.69	72.75	41.49	72.90	42.32
3/20/2009 11:43	70.64	45.39	70.95	43.66	69.29	45.66	68.96	46.88
3/20/2009 11:49	68.96	48.84	69.31	46.57	68.73	50.92	68.24	53.95
3/20/2009 11:55	68.87	52.91	69.33	50.60	71.52	49.93	71.92	51.54
3/20/2009 12:01	69.19	52.22	70.14	49.92	72.77	46.60	72.90	47.63
3/20/2009 12:07	69.88	50.90	70.95	48.50	73.73	44.69	73.82	45.65
3/20/2009 12:13	70.60	49.61	71.67	47.14	74.38	43.14	74.49	44.07
3/20/2009 12:19	71.25	48.26	72.35	45.71	74.53	42.16	74.65	43.07
3/20/2009 12:25	71.77	46.94	73.02	44.37	74.93	41.45	74.99	42.38

E.13. PTFE Filters Loading Data (Chapter 6)

Date	Port #	Panel	Pre Weight mg	Post Weight mg	Mass Loading
5/29/2008	18c	I	88.97	115.91	26.94
	19c	I	78.31	109.73	31.42
	20c	I	86.04	112.46	26.42
	21c	I	84.33	110.45	26.12
	22c	I	88.77	119.09	30.32
	23c	I	91.84	121.31	29.47
	24c	I	86.28	110.82	24.54
	25c	I	84.95	106.05	21.1
	26c	I	89.26	119.42	30.16
	27c	I	84.34	119.65	35.31
	28c	I	80.25	118.76	38.51
	29c	I	78.94	110.78	31.84
	30c	II	90.73	126.73	36
	31c	II	84.98	125.58	40.6
	32c	II	78.76	123.48	44.72
	33c	II	89.35	132.43	43.08
	34c	II	82.96	125.34	42.38
	35c	II	84.74	127.78	43.04
	36c	II	88.15	132.96	44.81
	37c	II	83.6	120.99	37.39
	38c	II	89.94	133.78	43.84
	39c	II	88.51	138.33	49.82
	40c	II	79.22	123.68	44.46
	41c	II	87.42	128.11	40.69

Continued on next page

Date	Port #	Panel	Pre Weight mg	Post Weight mg	Mass Loading
5/30/2008	18d	I	83.99	112.58	28.59
	19d	I	81.77	112.17	30.4
	20d	I	80.99	112.83	31.84
	21d	I	80.25	107.48	27.23
	22d	I	89.59	115.92	26.33
	23d	I	90.27	118.33	28.06
	24d	I	86.41	111.61	25.2
	25d	I	80.48	106.39	25.91
	26d	I	82.21	111.5	29.29
	27d	I	80.83	116.99	36.16
	28d	I	83.26	117.57	34.31
	29d	I	82.9	113.68	30.78
	30d	II	82.39	112.71	30.32
	31d	II	85.75	118	32.25
	32d	II	83.52	115.38	31.86
	33d	II	82.74	114.69	31.95
	34d	II	81.32	111.23	29.91
	35d	II	81.38	114.55	33.17
	36d	II	80.62	114.06	33.44
	37d	II	86.33	114.22	27.89
	38d	II			
	39d	II	92.79	128.5	35.71
	40d	II	86.71	126.57	39.86
	41d	II	87.72	124.06	36.34

Continued on next page

Date	Port #	Panel	Pre Weight mg	Post Weight mg	Mass Loading
10/13/2008	18e	I	79.63	105.36	25.73
	19e	I	79.68	106.76	27.08
	20e	I	82.7	108.86	26.16
	21e	I	81.46	104.84	23.38
	22e	I	81.58	114.76	33.18
	23e	I	81.3	115.99	34.69
	24e	I	81.44	112.57	31.13
	25e	I	85.79	112.56	26.77
	26e	I	84.01	113.41	29.4
	27e	I	80.76	109.98	29.22
	28e	I	80.05	107.47	27.42
	29e	I	357.17	380.96	23.79
	30e	II	79.95	110.82	30.87
	31e	II	79.78	110.96	31.18
	32e	II	81.48	109.15	27.67
	33e	II	81.84	106.12	24.28
	34e	II	81.45	109.47	28.02
	35e	II	78.3	107.71	29.41
	36e	II	81.6	111.57	29.97
	37e	II	78.91	103.45	24.54
	38e	II	80.01	104.08	24.07
	39e	II	80.44	105.96	25.52
	40e	II	85.4	110.02	24.62
	41e	II	363.75	385.04	21.29

Continued on next page

Date	Port #	Panel	Pre Weight mg	Post Weight mg	Mass Loading
10/28/2008	18f	I	349.18	384.3	35.12
	19f	I	353.53	389.55	36.02
	20f	I	476.16	509.85	33.69
	21f	I	357.16	388.05	30.89
	22f	I	357.46	394.51	37.05
	23f	I	343.04	378.23	35.19
	24f	I	338.21	369.32	31.11
	25f	I	344.41	368.59	24.18
	26f	I	339.22	378.86	39.64
	27f	I	344.35	385.61	41.26
	28f	I	352.37	388.45	36.08
	29f	I	357.51	387.92	30.41
	30f	II	353.95	392.2	38.25
	31f	II	365.48	405.78	40.3
	32f	II	348.1	384.19	36.09
	33f	II	335.44	368.63	33.19
	34f	II	339.75	376.06	36.31
	35f	II	330.72	367.65	36.93
	36f	II	363.27	398.45	35.18
	37f	II	344.56	377.88	33.32
	38f	II	336.46	367.45	30.99
	39f	II	343.37	375.64	32.27
	40f	II	341.84	372.58	30.74
	41f	II	353.1	383.17	30.07

Continued on next page

Date	Port #	Panel	Pre Weight mg	Post Weight mg	Mass Loading
10/29/2008	18g	I	360.41	385.63	25.22
	19g	I	349.64	378.88	29.24
	20g	I	356.44	392.08	35.64
	21g	I	362.99	398.23	35.24
	22g	I	339.9	380.17	40.27
	23g	I	356.55	397.76	41.21
	24g	I	357.33	400.54	43.21
	25g	I	359.98	406.23	46.25
	26g	I	364.57	401.42	36.85
	27g	I	362.31	404.03	41.72
	28g	I	357.14	399.46	42.32
	29g	I	346.12	392.1	45.98
	30g	II	362.61	410.72	48.11
	31g	II	348.61	392.13	43.52
	32g	II	354.41	398.16	43.75
	33g	II	349.73	388.99	39.26
	34g	II	345.3	392.16	46.86
	35g	II	354.98		
	36g	II	356.99		
	37g	II	347.72	384.15	36.43
	38g	II	345.16	377.81	32.65
	39g	II	362.64	398.22	35.58
	40g	II	351.96	382.21	30.25
	41g	II	327.87	356.64	28.77

Continued on next page

Date	Port #	Panel	Pre Weight mg	Post Weight mg	Mass Loading
10/30/2008	18h	I	338.59	361.77	23.18
	19h	I	339.79	367.41	27.62
	20h	I	345.12	373.79	28.67
	21h	I	336.87	367.03	30.16
	22h	I	352.6	386.35	33.75
	23h	I	347.89	383.38	35.49
	24h	I	342.49	377.13	34.64
	25h	I	353.35	389.91	36.56
	26h	I	356.75	386.46	29.71
	27h	I	344.82	378.86	34.04
	28h	I	341.3	376.31	35.01
	29h	I	357.56	391.32	33.76
	30h	II	350.33	371.44	21.11
	31h	II	350.13	375.46	25.33
	32h	II	344.58	370.37	25.79
	33h	II	350.53	376.75	26.22
	34h	II	348.45	379.75	31.3
	35h	II	351.71	384.09	32.38
	36h	II	357.16	389.89	32.73
	37h	II	338.69	373.51	34.82
	38h	II	354.83	380.15	25.32
	39h	II	359.78	392.38	32.6
	40h	II	328.17	359.06	30.89
	41h	II	354.11	387.99	33.88

Continued on next page

Date	**Port #**	**Panel**	**Pre Weight** **mg**	**Post Weight** **mg**	**Mass Loading**
3/20/2009	18i	I	357.56	396.71	39.15
	19i	I	360.5	405.03	44.53
	20i	I	355.62	394.51	38.89
	21i	I	337.47	373.81	36.34
	22i	I	326.52	368.53	42.01
	23i	I	345.7	390.2	44.5
	24i	I	354.72	398.37	43.65
	25i	I	354.43	392.42	37.99
	26i*	I	360.61	NA	NA
	27i	I	363.55	396	32.45
	28i	I	345.46	379.41	33.95
	29i	I	375.94	408.84	32.9
	42i	I	356.89	387.47	30.58
	30i	II	356.13	401.84	45.71
	31i	II	348.33	393.96	45.63
	32i	II	354.18	398.12	43.94
	33i	II	354.02	388.99	34.97
	34i	II	331.89	376.57	44.68
	35i	II	348.13	394.7	46.57
	36i	II	332.75	376.06	43.31
	37i	II	349.53	388.25	38.72
	38i	II	356.87	394.56	37.69
	39i	II	374	407.17	33.17
	40i	II	349.1	381.38	32.28
	41i*	II	359	389.46	30.46

***Filter 26 was replaced by filter 41 during field experiment**

E.14. Permeation Data - SWYPE Calibration by RGB Analysis (Chapter 6)

Load	**Red**			**Green**			**Blue**		
µg hardener	**mean**	**SD**	**median**	**mean**	**SD**	**median**	**mean**	**SD**	**median**
0	249.41	7.03	251	229.86	6.94	231	171.04	14.57	172
0	246.51	7.6	248	225.06	6.91	226	164.06	14.24	165
0	248.92	7.66	250	228.42	7.33	229	165.88	11.63	167
0	247.89	8.4	249	227.37	7.84	229	168.16	1.14	169
0	249.54	5.56	250	228.4	5.78	229	163.91	12.93	165
0	245.6	9.69	247	223.25	8.9	224	158.7	13.41	160
42	244.49	10.15	247	202.33	27.17	213	157.8	21.9	163
42	245.6	9.19	247	198.45	32.93	214	151.65	39.43	169
52.5	241.24	9.08	243	182.29	24.74	181	138.81	22.61	140
52.5	239.47	9.37	241	173.91	28.55	171	133.41	27.76	135
84	239.31	9.83	241	176.86	35.49	172	135.21	34.02	135
84	242.93	9.32	244	178.77	30.22	170	133.97	30.22	131
105	239.88	8.9	241	166.96	34.32	160	118.2	40.21	112
105	240.88	12.33	244	172.25	29.2	168	124.45	36.55	126

Continued on next page

E.15. SWYPE Permeation Results for Screening Experiments (Chapter 6)

Date	Original File*	Cell	Glove	Panel	Paint Formulation	Observed Color Scale
5/29/2008	Scan08529-0001	blank				
	Scan08529-0002	1c	Latex	I	A & I	1
	Scan08529-0002	3c	Nitrile	I	A & I	0.5
	Scan08529-0002	6c	Latex	I	A & I	1
	Scan08529-0002	8c	Nitrile	I	A & I	0.5
	Scan08529-0003	10c	Nitrile	II	B & I	0.5
	Scan08529-0003	12	Nitrile	II	B & I	0.5
	Scan08529-0003	15c	Latex	II	B & I	1
	Scan08529-0003	16c	Latex	II	B & I	1
5/30/2008	Scan08530-0001	blank				
	Scan08530-0002	1d	Nitrile	I	A & I	
	Scan08530-0002	3d	Latex	I	A & I	1
	Scan08530-0002	6d	Latex	I	A & I	1
	Scan08530-0002	7d	Nitrile	I	A & I	0.5
	Scan08530-0003	12d	Latex	II	B & I	1
	Scan08530-0003	13d	Nitrile	II	B & I	0.5
	Scan08530-0003	15d	Latex	II	B & I	1
	Scan08530-0003	16d	Latex	II	B & I	1

*Several SWYPE samples were scanned in the same file

Continued on next page

	Red			Green			Blue			G+B	Load*
Cell	mean	SD	median	mean	SD	median	mean	SD	median	mean	µg hardener
Blank 5/29/08	249.14	5.54	250	230.47	5.53	231	177.54	13.03	178	409	<3
1c	247.76	4.98	248	216.84	6.74	217	169.2	12.19	170	387	8.2
3c	247.74	7.5	249	222.69	7.05	223	165.57	14.75	166	389	6.3
6c	246.48	6.13	247	210.76	7.52	210	166.25	13.06	167	377	17.9
8c	247.06	10.53	249	221.27	9.8	223	160.78	14.2	163	386	9.2
10c	246.94	4.81	247	220.47	5.81	221	158.42	16.72	160	381	14
12c	247.08	6.03	248	220.23	6.51	220	161.69	12.92	163	383	12.1
15c	244.2	7.3	245	209.28	6.89	210	164.06	12.44	165	375	19.8
16c	242.1	8.08	243	208.16	8.77	209	151.32	16.69	153	362	32.1
Blank 5/30/08	249.95	6.25	251	230.82	6.24	232	173.26	13.11	173	405	<3
1d	250.63	6.15	252	223	6.19	223	158.9	14.69	159	382	13.1
3d	248.04	5.27	249	209.21	6.7	209	166.71	11.16	167	376	18.8
6d	246.91	4.52	247	206.19	7.18	206	161.93	10.88	163	369	25.5
7d	250.26	4.5	251	223.45	5.18	224	160.91	13.2	162	386	9.2
12d	246.95	4.86	247	215.92	6.23	216	163.52	12.5	165	381	14
13d	246.39	7.14	248	223.62	7.06	224	162.82	16.5	164	388	7.3
15d	248.52	4.84	249	213.24	5.78	213	154.07	14.36	155	368	26.5
16d	247.35	5.16	248	213.14	6.75	214	156.98	13.92	159	373	21.7
										LOQ	3

*Calculated using RGB calibration

Continued on next page

E.16. PPZ Coated Filter Permeation Results for Screening Experiments Analyzed by Modified OHSA42/PV2034 (Chapter 6)

Date	Cell	Panel	Material	Thickness mil	Paint Formulation	HDI µg/sample	IPDI µg/sample	Oligomers µg/sample
5/29/2008	2c	I	Nitrile	4.5	A & I	<0.05	<0.05	<0.5
	4c	I	Nitrile	5	A & I	<0.05	<0.05	<0.5
	5c	I	Latex	4.2	A & I	0.26	<0.05	<0.5
	7c	I	Latex	4.2	A & I	0.52	0.12	<0.5
	9c	II	Latex	4.2	B & I	0.26	0.12	<0.5
	11c	II	Latex	4.1	B & I	0.47	0.13	<0.5
	13c	II	Nitrile	4.8	B & I	<0.05	<0.05	<0.5
	14c	II	Nitrile	4.8	B & I	<0.05	<0.05	<0.5
5/30/2008	2d	I	Latex	4	A & I	0.28	<0.05	<0.5
	4d	I	Nitrile	5	A & I	<0.05	<0.05	<0.5
	5d	I	Nitrile	4.8	A & I	<0.05	<0.05	<0.5
	8d	I	Latex	4.1	A & I	0.14	<0.05	<0.5
	9d	II	Nitrile	5	B & I	<0.05	<0.05	<0.5
	10d	II	Latex	4	B & I	0.24	<0.05	<0.5
	11d	II	Nitrile	4.5	B & I	0.24	<0.05	<0.5
	14d	II	Nitrile	4.5	B & I	<0.05	<0.05	<0.5
					LOQ	<0.05	<0.05	<0.5

Continued on next page

Date	Panel	Cell	Material	Thickness mil	Paint Formulation	HDI µg/sample	IPDI µg/sample	Oligomers µg/sample
10/30/2008	I	1h	Nitrile	5	B & II	<0.05	0.060	<0.05
	I	2h	Latex	14	B & II	<0.05	<0.05	<0.05
	I	3h	Latex	4.5	B & II	0.2	0.1	<0.05
	I	4h	Nitrile	5	B & II	0.080	0.051	<0.05
	I	5h	Nitrile	7.9	B & II	<0.05	<0.05	<0.05
	I	6h	Latex	4	B & II	<0.05	0.2	<0.05
	I	7h	Nitrile	8	B & II	<0.05	<0.05	<0.05
	I	8h	Latex	13.5	B & II	<0.05	<0.05	<0.05
	II*	9h	Nitrile	7.5	A & I	<0.05	<0.05	<0.05
	II	12h	Latex	4	A & I	0.2	0.1	<0.05
	II	13h	Nitrile	5	A & I	<0.05	<0.05	<0.05
	II	14h	Nitrile	8	A & I	<0.05	<0.05	<0.05
	II	15h	Latex	14	A & I	<0.05	<0.05	<0.05
	II	16h	Latex	14.2	A & I	<0.05	<0.05	<0.05
			blank		None	<0.05	<0.05	<0.05
					LOQ	<0.05	<0.05	<0.05

*Cells 10h and 11h are not presented here because they were used for other experiments with charcoal cloth

E.17. Permeation Results for Screening Experiments October 29, 2008 Analyzed by Modified Iso-Chek (Chapter 6)

			Paint				Monomer, µg/sample	
Date	Panel	Thickness	Formulation	Back Material	Material	Cell #	IPDI L0050	HDI L0050
10/29/2008	I	4	B & II	MAMA I796 10/09	Latex	2g	0.072	0.595
10/29/2008	I	4.2	B & II	MAMA I794 10/09	Latex	4g	0.122	1.01
10/29/2008	I	5	B & II	MAMA I792 10/09	Nitrile	5g	< 0.001	0.209
10/29/2008	I	4.4	B & II	MAMA I793 10/09	Latex	6g	0.095	0.823
10/29/2008	II	4.2	A & I	MAMA I811 10/09	Latex	9g	0.049	0.188
10/29/2008	II	5.1	A & I	MAMA I808 10/09	Nitrile	10g	< 0.001	0.189
10/29/2008	II	4	A & I	MAMA I797 10/09	Latex	14g	0.177	1.32
10/29/2008	II	4	A & I	MAMA I813 10/09	Nitrile	15g	0.013	0.12
10/29/2008				MAMA I822 10/09	Field blank	17g	< 0.001	< 0.0001
10/29/2008				MAMA	Field blank	18g	< 0.001	< 0.0001
						LOD	0.004	0.005
						LOQ	0.13	0.11

Continued on next page

Date	Panel	Back Material	Material	Cell #	Oligomer, µg/sample			
					Z4470 BA. IPDI Oligomers	N100 Biu. HDI Biuret	N3300A Iso. HDI Isocyanurate	N3400 Dim. HDI Uretidone
10/29/2008	I	PTFE	Nitrile	1g	0.27	0.18	1.78	0.33
10/29/2008	I	PTFE	Nitrile	3g	0.15	0.12	0.94	0.1
10/29/2008	I	PTFE	Latex	7g	0.06	< 0.001	0.64	0.09
10/29/2008	I	PTFE	Nitrile	8g	0.2	< 0.001	0.45	0.31
10/29/2008	II	PTFE	Latex	11g	0.2	< 0.001	0.3	0.32
10/29/2008	II	PTFE	Nitrile	12g	0.26	0.08	0.23	0.4
10/29/2008	II	PTFE	Nitrile	13g	0.14	< 0.001	0.24	0.26
10/29/2008	II	PTFE	Latex	16g	0.32	< 0.001	0.2	0.29
10/29/2008		PTFE	Field blank	19g	0.38	0.15	0.35	0.39
10/29/2008		PTFE	Field blank	0g	0.28	0.17	0.1	0.3
				LOD	1.7	1.7	1.2	2.8
				LOQ	15.7	1.9	5	4.8

E.18. PPZ Coated Filter Permeation Results for Permeation Rate Experiments Analyzed by Modified OHSA42/PV2034 (Chapter 6)

Date	Panel	Cell	Material	Thickness mil	Paint Formulation	Time	HDI µg/sample	IPDI µg/sample	Oligomers µg/sample
10/13/2008	I	1e	Latex	4	A & I	8	0.1	0.1	<0.5
	I	2e	Nitrile	5	A & I	10:30	<0.05	<0.05	<0.5
	I	3e	Nitrile	5.2	A & I	8	<0.05	<0.05	<0.5
	I	4e	Nitrile	5.1	A & I	29:30	<0.05	<0.05	<0.5
	I	5e	Latex	4	A & I	29:30	0.2	<0.05	<0.5
	I	6e	Latex	4	A & I	29:40	0.1	0.1	<0.5
	I	7e	Latex	4	A & I	10:30	0.1	0.1	<0.5
	I	8e	Nitrile	5	A & I	20:40	<0.05	<0.05	<0.5
	II	9e	Latex	4	B & II	30:40	0.3	0.2	<0.5
	II	10e	Nitrile	5	B & II	5:29	<0.05	<0.05	<0.5
	II	11e	Latex	4.3	B & II	30:40	0.1	<0.05	<0.5
	II	12e	Nitrile	5	B & II	9:30	<0.05	<0.05	<0.5
	II	13e	Nitrile	5	B & II	5:29	<0.05	<0.05	<0.5
	II	14e	Nitrile	4.5	B & II	20:8	<0.05	<0.05	<0.5
	II	15e	Latex	4.2	B & II	9:30	<0.05	0.1	<0.5
	II	16e	Latex	4.1	B & II	20:08	0.1	<0.05	<0.5
			blank		none		<0.05	<0.05	<0.5
						LOQ	<0.05	<0.05	<0.5

Continued on next page

Date	Panel	Cell	Material	Thickness mil	Paint Formulation	Time	HDI µg/sample	IPDI µg/sample	Oligomers µg/sample
10/28/2008	I	1f	Nitrile	5	A & I	11:02	<0.05	<0.05	<0.5
	I	2f	Nitrile	5	A & I	29:50	<0.05	<0.05	<0.5
	I	3f	Latex	3.8	A & I	29:50	0.4	0.2	<0.5
	I	4f	Latex	4	A & I	20:23	0.3	0.1	<0.5
	I	5f	Latex	4	A & I	6:58	0.2	0.1	<0.5
	I	6f	Nitrile	5	A & I	6:58	<0.05	<0.05	<0.5
	I	7f	Latex	4.1	A & I	20:23	0.3	0.1	<0.5
	I	8f	Nitrile	4.9	A & I	11:02	<0.05	<0.05	<0.5
	II	9f	Nitrile	5	B & II	6:13	<0.05	<0.05	<0.5
	II	10f	Nitrile	4.8	B & II	13:04	<0.05	<0.05	<0.5
	II	11f	Latex	3.9	B & II	6:13	0.2	0.1	<0.5
	II	12f	Nitrile	5	B & II	20:45	<0.05	<0.05	<0.5
	II	13f	Latex	4	B & II	30:22	0.4	0.2	<0.5
	II	14f	Nitrile	4.8	B & II	20:45	<0.05	<0.05	<0.5
	II	15f	Latex	3.9	B & II	13:04	0.2	0.1	<0.5
	II	16f	Latex	4.5	B & II	30:22	0.6	0.2	<0.5
			blank		None		<0.05	<0.05	<0.5
						LOQ	<0.05	<0.05	<0.5

Continued on next page

Date	Panel	Cell	Material	Thickness mil	Time min	HDI µg/sample	IPDI µg/sample	Oligomers µg/sample
03/20/2009	I	1i	Nitrile	5	43	0.3	<0.1	<1
	I	2i	Latex	4.5	61	1.3	0.2	<1
	I	3i	Latex	4	50	0.7	<0.1	<1
	I	4i	Latex	4.5	43	0.7	<0.1	<1
	I	5i	Nitrile	5.1	61	<0.1	<0.1	<1
	I	6i	Nitrile	5	91	0.2	<0.1	<1
	I	7i	Latex	4.5	91	1	<0.1	<1
	I	8i	Nitrile	5.1	50	<0.1	<0.1	<1
	II	9i	Latex	4.8	89	1.8	0.2	<1
	II	10i	Latex	4.5	49	1.1	<0.1	<1
	II	11i	Nitrile	5	89	0.2	<0.1	<1
	II	12i	Nitrile	5	60	<0.1	<0.1	<1
	II	13i	Latex	4.1	60	1.1	0.2	<1
	II	14i	Nitrile	5.5	38	<0.1	<0.1	<1
	II	15i	Nitrile	5	49	<0.1	<0.1	<1
	II	16i	Latex	4.5	38	0.8	0.1	<1
			blank			<0.1	<0.1	<1
			blank			<0.1	<0.1	<1
					LOQ	<0.1	<0.1	<1

VITA

Diana Ceballos was born in Medellín, Colombia. At the Universidad Pontificia Bolivariana in Medellín she earned a Bachelor of Sciences in Chemical Engineering. She moved to United States for her graduate studies in Atmospheric Chemistry to earn a Master of Science degree at the University of Nevada, Reno. In 2009, she earned a Doctor of Philosophy at the University of Washington in Environmental and Occupational Hygiene.