

6-30-2016

Hexamethylene Diisocyanate Homopolymer and Monomer Exposure Assessment and Characterization at an Automobile Manufacturer in the United States

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Hexamethylene Diisocyanate Homopolymer and Monomer Exposure Assessment and
Characterization at an Automobile Manufacturer in the United States

by

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A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Public Health
Department of Environmental and Occupational Health
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Date of Approval:
April 19, 2016

Keywords: industrial, hygiene, clear, coat, urethane

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Acknowledgments

I would like to take this moment to thank my family for always supporting me; they have helped me push myself far beyond my potential. Also, I would like to thank my wife for truly being my partner, and helping me cross the finish line. To my friends and classmates: Thank you for your intelligence, support, and for challenging me to always better myself.

The faculty and staff at the University of South Florida always made me feel at home, and helped me develop myself to become an occupational and environmental health professional. Thank you to Dr. Steve Mlynarek for keeping me honest, being a true mentor, and pushing me to reach higher.

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List of Abbreviations and Acronyms

| | |
|---------|--|
| ACGIH | American Conference of Governmental Industrial Hygienists |
| DBA | Di-n-butylamine |
| DOT | Department of Transportation |
| GFF | Glass Fiber Filter |
| HDI | Hexamethylene Diisocyanates |
| HPLC-MS | High Performance Liquid Chromatography – Mass Spectrometry |
| MAMA | 9-N-methylaminomethyl anthracene |
| MDI | Diphenyl Methane Diisocyanates |
| MOPIP | 1,2-methoxyphenyl piperazine |
| NIOSH | National Institute for Occupational Safety and Health |
| OSHA | Occupational Safety and Health Administration |
| PEL | Permissible Exposure Limit |
| PPM | Parts Per Million |
| PPB | Parts Per Billion |
| REL | Recommended Exposure Limit |
| TDI | Toluene Diisocyanates |
| TLV | Threshold Limit Value |
| TWA | Time Weighted Average |

Abstract

A variety of paint products are used for their aesthetic and anti-corrosive properties. Isocyanates are consistently found in automobile paint products, particularly in clear coat polyurethane products. Clear coat is typically sprayed via pressurized air by means of an auto-spray robot. In clear coat repair situations, manual, air-powered spray guns are used, and manual spray Operators administer the clear coat material. The isocyanates are a primary anti-corrosive agent in polyurethane products. The Occupational Safety and Health Administration (OSHA) has not established a Permissible Exposure Limit (PEL). The National Institute for Occupational Safety and Health (NIOSH) and American Conference of Governmental Industrial Hygienists (ACGIH) have set Recommended Exposure Limit (REL) and Threshold Limit Value (TLV), respectively. NIOSH recommends a 0.005 parts per million (ppm), 10-hour Time Weighted Average (TWA), and a ceiling exposure of 0.020 ppm in a 10 minute period. Similarly, ACGIH recommends a 0.005 ppm, 8 hour TWA.

Automobile manufacturers use clear coats in a variety of ways. Some may use clear coats with blocked isocyanates, or isocyanates that are completely reacted, and others may use clear coat products that allow isocyanates to be liberated during an application, baking, and curing process. The research objective of this study was to characterize exposure, focusing on a single manufacturer's use of isocyanate-containing clear coats in their Paint Department. A newly evaluated medium (ISO 17734) using di-n-butylamine as a derivative agent, in a denuder tube, was selected instead of NIOSH methods 5521, 5522, and 5525. The ISO evaluated medium was

selected to reduce secondary hazard exposure to toluene in impingers. Second, a medium developed by SKC, Inc., called ISO-CHEK®, was not selected because of the short collection time, sensitivity of the medium after collection, and storage and shipping requirements for analysis.

Sampling took place over two days, one day for manual spray operations with 2 personal samples from Operators, and 4 area samples collected, and the second day for auto-sprayer Inspectors with 4 personal samples collected. The samples were then analyzed for hexamethylene diisocyanates (HDI) monomer and homopolymer species. The 0.005 ppm, 10 hour TWA; the 0.020 ppm ceiling limit (10 minutes); and the 0.005 ppm 8-hour TWA TLV were not exceeded on either day of sampling. Neither the area nor the personal samples exceeded the 10 hour TWA, ceiling limit, or TLV. In fact, the results had to be recalculated in to parts per billion (ppb). The average exposure for manual spray Operators was 0.052 ppb for the homopolymer, and 0.024 ppb for the monomer species. For auto-spray Inspectors, the average was 0.053 ppb for the homopolymer component and 0.021 ppb for the monomer species. Though the average isocyanate concentration was similar for both Operators and Inspectors, the averages are still below REL and TLV recommendations. These data provided preliminary information regarding the exposure to isocyanates from clear coat use, and also provide context for future evaluation of isocyanate use at this automobile manufacturer. The low concentration of isocyanates could indicate working ventilation systems, liberation of isocyanate species to non-hazardous forms, or low volatilization of isocyanates from the clear coat.

Introduction

In North America, there are more than 15 automobile companies with manufacturing plants across Canada, and the United States of America. In the United States alone, there are approximately 50 automobile manufacturing plants, mostly on the East and West coasts, and the Southeastern United States. A common constant in design, manufacturing, and point of sale are the quality and color of paint used on vehicles. Paint products in manufacturing are used to not only create an aesthetic appeal to products, but to reduce the chance of corrosion. Applications of clear coat, topcoat paint, and other polyurethane based top coats are used to prevent corrosion via their organic nature. This anti-corrosive property is primarily accomplished by including organic groups called isocyanates. Isocyanates are low molecular weight chemicals which contain one or more $-N=C=O$ functional group. This functional group is typically attached to an aliphatic or aromatic molecule. Isocyanates are also highly reactive molecules, and are classified based on the number of $-N=C=O$ groups that are found in the molecule. The classifications are known as diisocyanate monomers (two $-N=C=O$ groups) or polyisocyanates (three or more NCO groups) (Deft, 2011). There is also a third classification group known as oligomeric isocyanates, which are made up of low molecular weight groups with 10 or less $-N=C=O$ groups. Due to the attributed characteristics of adding flexibility, abrasion and impact resistance, and durability, isocyanate monomers and oligomers are essential to the topcoat material, and application in manufacturing (Liu et al., 2007).

The exposure to isocyanates in manufacturing environments can cause potentially serious medical maladies such as asthma, contact dermatitis, and hypersensitivity pneumonitis. The most common health outcome that is coupled with isocyanate exposure is sensitization leading to occupational asthma. Entry into the body is most often through the respiratory system; ventilation and respiratory protection are critical to workplace health in the face of isocyanate exposure (Abadin et al., 1998). Skin exposure, and ensuing skin sensitization, is also a route of isocyanate entry. Exposure via ingestion is much less likely, though isocyanate species may exist on hands, and may enter the body via eating, drinking or smoking if the hands are unwashed after isocyanate interaction (Abadin and Spoo, 1998). Isocyanates are excreted via urine, though the length of time for break down and excretion is uncertain.

Background

Sampling and analytical method selection for isocyanate exposure monitoring proves to be difficult for a variety of reasons. Streicher et al. mention, “isocyanates volatilize quickly and form particles and vapors. Second, not all species are stable, or reactive. This point becomes especially troublesome during isocyanate species collection and measurement” (Streicher et al. 2000). Finally, if the concentrations of isocyanates are low, then low-level detection instruments, sampling media, or methods of analyses are required (Streicher et al., 2000).

Methods of collecting isocyanates for measurement are centered on collecting aerosol particles and vapors. The National Institute for Occupational Safety and health (NIOSH) has developed Methods 5521, 5522, and 5525. The Occupational Safety and Health Administration (OSHA) Method 42 is another federally developed method. ISO-CHEK®, by SKC, Inc., is a privately developed collection method, and is a commonly used method in the manufacturing environment (OSHA, 2012). This is due to ease of use, reduction of toluene risk from NIOSH impinger collection methods, and straightforwardness of laboratory analysis. There are two strengths to ISO CHEK®: the ability to collect two isocyanate species (monomers and homopolymers), and the ability to collect particles and vapors. The ISO-CHEK® method is a two-stage cassette, and consists of an untreated Teflon filter in Stage 1 (which collects particulates), and a glass fiber filter (GFF) in Stage 2. The GFF is a 9-N-methylaminomethyl anthracene (MAMA) treated component that is able to capture vaporized isocyanates. After

sampling is completed, the ISO-CHEK® cassette is field derivatized by removing the Teflon filter, and placing it in a bath of 1,2-methoxyphenyl piperazine (MOPIP) and toluene solution.

The field derivatization, however, “runs the risk of underreporting isocyanate capture” [England et al. 2000]. When the Teflon filter is field derivatized, the collection method may lead to contamination, sampling error, and under collection due to the volatility of isocyanates. Second, ISO-CHEK® only has a 15 minute sampling time, requiring filters or cassettes to be changed at the end of each sampling period. This poses a risk to experimental continuity, and to sample integrity. ISO-CHEK® samples are also time and temperature sensitive. If the filters are not analyzed within 7-10 days, then they may be deemed invalid. Finally, the derivatization solution itself is considered a hazardous material according to Department of Transportation (DOT) regulations (England et al., 2000).

An alternative to ISO-CHEK® is the use of di-n-butylamine (DBA) as a derivative collection agent. This is typically found in denuder-filter samplers. The Supelco ASSET™ EZ4-NCO sampler is one such sampling instrument. The ASSET™ sampler can measure for 8 hours to establish TWA, does not require field derivatization, nor does it require stringent storage methods. DBA, as a derivative agent, has been found by Streicher et al. to reduce underreporting of isocyanate capture. It also poses a lower health risk compared to toluene or MOPIP (Streicher et al., 2000).

Purpose

The purpose of this study was to quantify the exposure to workers at an automobile plant in the Midwest United States, and determine the concentration of two specific species of isocyanates, the hexamethylene diisocyanate monomer and homopolymer. We will use the ASSET™ method, which contains the DBA collection agent, to collect isocyanate samples, and compare them to established exposure limits from NIOSH and ACGIH. Currently, OSHA does not have a limit established for HDI species, and refers to NIOSH, ACGIH and other isocyanate permissible exposure limits.

Literature Review

Contents of Clear Coats

Application of clear coats, as previously indicated, is to protect base coats and other paint features. In decades past, before the use of robots and automatic sprayers, base coat and clear coat application was done manually. Workers skilled in paint spraying would apply clear coat via spray gun. As noted by Whitaker and colleagues, isocyanates are the prime components in many coatings. In coatings containing polyurethanes, “isocyanates are present in catalyst fortifiers” (Whitaker, 2012). It is the clear coat fortifiers that are of highest priority for occupational health, as those tend to contain the highest isocyanate concentration. Typically, application of polyurethane coatings, via air pressure spray methods, generates overspray (Pronk et al., 2006). This overspray can contain partially or completely unreacted isocyanates. Modern paint shops are typically designed to reduce the over spray concentration by way of ventilation exhaust systems, make-up air, or particulate water traps. Upon further analysis of coating and finishing compounds, the $-N=C=O$ bonds of the isocyanate molecule are found in all polyurethane compounds and products. They are especially prevalent in coatings, such as varnishes, paints and clear coats. Typically, as stated by England et al., “they are created by way of reacting phosgene with amines, and have a carbamoyl chloride intermediate” (England et al., 2000). Isocyanates are electrophilic and react with water or alcohol to form urethane bonds. Reaction with two or more hydroxyl groups forms polyurethane, and carbon dioxide is the by-product. The carbon dioxide is typically ventilated in the reaction, or blown off. Isocyanates are highly volatile, unstable, and

vaporize quickly (Streicher et al., 2000). In fact, isocyanates can exist in both aerosol and vapor phases. The size of the aerosol particles ranges from 20 to 50 μm (Whitaker, 2014), and can remain suspended in the local air. Thermal degradation has also shown to release isocyanate particles into the breathing zone (Rosenberg et al., 2002). Rosenberg and colleagues go on to conjecture that “it has been observed that thermal degradation of polyurethane products, from baking, welding, and grinding can release isocyanates.” The majority of the isocyanates detected during thermal degradation were TDI and HDI species. Boutain et al. conjecture that “even at low concentrations, isocyanate aerosols can have significant effects on workers’ health” (Boutain et al., 2000).

Exposure to Isocyanates in Industrial Settings

From Creely et al, “this over spray is one of the main pathways for isocyanate inhalation and dermal exposure” (Creely, 2006). Creely goes on to state that the principle isocyanate species are hexamethylene diisocyanates (HDI), toluene diisocyanates (TDI) and diphenyl methane diisocyanates (MDI). Most famously, the Bhopal disaster of December 2nd and 3rd, 1984 released roughly 30 metric tons of methyl isocyanate into the air, along with reacting compounds (Creely, 2006). Isocyanate containing products are being increasingly used in a variety of foams, coatings and sealants. In terms of potential long-term exposures, vehicle and vehicular repair shops use products containing isocyanates most often. Cowie et al. estimate that approximately more than 150,000 thousand workers are exposed to isocyanates on a daily basis, but the exposure concentration is unknown (Cowie et al., 2005). Because isocyanates are being used more often in a variety of products, Cowie et al. note that it is difficult to give a better estimate. DeNola et al. found that when applying polyurethane paints and clear coats, even in well-ventilated areas, there can still be measurable concentrations, though below the permissible

exposure levels. Their study of application of clear coats in a tropical climate also provided evidence that workers in well ventilated work spaces may still require respiratory protection (DeNola et al., 2009). DeNola hypothesizes that polyurethane products may have been affected by the tropical climate, and allowed isocyanates to continue liberating even after application. DeNola also found that thermal abrasion of polyurethane materials allowed for liberation of isocyanate species. This was primarily due to slow volatilization of isocyanates (DeNola et al., 2009). As established by NIOSH and ACGIH, the respective Recommended Exposure Level and Threshold Limit Value are 0.005 ppm.

Exposure Assessments of Isocyanates

A difficulty encountered when conducting isocyanate exposure assessments is varied exposure time. As documented by Woskie et al. when studying automotive repair shops, exposures were determined by size of the repair task, length of clear coat use, volume of repairs and difficulty of the repair (Woskie et al., 2004). Heline goes further into this idea, comparing two different assessment methods: Use of solvent free and solvent liberated isocyanate collection methods.

When preparing for this study, the experimenters deliberated on whether solvent-free or solvent-based collection methods were more reliable when studying isocyanates. After reviewing the Heline literature, we pursued justifying the use of solvent-free methodologies (Heline, 2014). Papers by Carlton et al., and England et al. showed differences between solvent-based and solvent-free, namely, that solvent-based isocyanate collection typically under estimated the overall isocyanate concentrations. Investigating further, it is conjectured that the process of transferring and waiting for laboratory analysis cause some of the isocyanate species to volatilize or dissipate (Carlton et al., 2000)(England et al., 2000). Moreover, the analysis must be

completed in 7 to 10 days (Omega Specialty Company), to avoid loss of isocyanate species. ISO-CHEK® is typically the preferred method of isocyanate capture. In the ISO-CHEK® manual (Omega Specialty Company), it states that it uses a two stage filter mechanism; one stage for vapors, and the other for aerosols. The first stage contains a Teflon (untreated) filter for aerosol collection, and the second stage is a glass fiber filter, which has been impregnated with 9-(N-methylaminomethyl) anthracene (MAMA). The second stage is designed to capture isocyanate vapors. The first stage filter is placed into 1-(2-methoxyphenyl) piperazine (MOPIP) in a toluene solution to derive the aerosols. Another difficulty of solvent-based analysis is the time restriction of the ISO-CHEK® method. The sampling media must be changed every 15 minutes due to rapid impregnation, and this leads to protocol and sampling discontinuity. The final factor in the ISO-CHEK® process is the MOPIP solution. The Department of Transportation has deemed MOPIP a hazardous material (DOT regulations, 2012). In comparison, The ASSET™ sampling media only has a two-stage denuder and filter mechanism. The denuder (first stage) is a di-n-butylamine (DBA)-impregnated glass fiber filter (GFF), contained in a polypropylene cylinder. The first stage captures isocyanate vapors. A DBA-impregnated GFF is in the second stage, which captures aerosol phase isocyanates (ISO, 2006E). “The DBA reagent is stable in an environment of antagonistic or interfering compounds, and promotes fast rates of reaction” (Karlsson et al., 1998; Marand et al., 2005; Karlsson et al., 2005). Until recently, quantification of isocyanates was limited to monomeric species because of the lack of an oligomeric standard for analysis. Recently, ISO Guide 34:2009 and ISO 17025:2005 was released, covering analysis of HDI oligomers as captured by ASSET™. In addition to the ability to capture both monomeric and oligomeric species, ASSET™ can be used to sample for 8 hours or more. This eliminates disruptions in isocyanate capture, and limited disruption of productivity of the worker that the

sampler is placed on. Finally, the ASSET™ sampler does not require field derivatization, does not have storage restriction or requirements, nor is it limited by DOT shipping restrictions (Sigma-Aldrich, 2013). To limit the risks and potential negative health effects, and increase productivity and isocyanate capture, the ASSET™ EZ4 NCO sampling medium was selected for this study. This decision took into consideration the use of HDI containing polyurethane clear coats. Table I, adapted and modified from Heline (Heline, 2014), shows the different media and analytical methods for HDI concentration collection and measurement.

Table I
Standard Methods of Determining HDI Concentration from Air Samples

| | ASSET™ | ISO-CHEK® | NIOSH 5521 | NIOSH 5522 | NIOSH 5525 | OSHA 42 |
|---|------------------------|---|--------------------------|---|--|---|
| Analyte | HDI | HDI | HDI | HDI | HDI | |
| | Monomer | Monomer | Monomer | Monomer | Monomer | HDI |
| | HDI | HDI | HDI | HDI | HDI | Monomer |
| Sampler | Polymers | Polymers | Polymers | Polymers | Polymers | |
| | 13-mm filter & denuder | 37-mm closed-face double filter cassette | Impinger | Impinger | Filter, Impinger, or Impinger & filter | 37-mm single filter open-faced cassette |
| Sample Media | GFF & Denuder w/DBA | PTFE Filter Field derivatized w/MOPIP, GFF w/MAMA | MOPIP in toluene | Tryptamine in DMSO | GFF w/MAP in 37-mm cassette or IOM sampler, or MAP in butyl benzoate | GFF w/1-2PP |
| | | | | | | |
| Flow Rate (lpm) | 0.2 | 1 | 1 | 1 - 2 | 1 - 2 | 1 |
| Analysis | HPLC | HPLC | HPLC | HPLC | HPLC | HPLC |
| Detection | MS or MS/MS | UP/PDA | UV/PDA, EC | FL/EC | UV/FL | UV, FL |
| | | | | | | |
| Standard Method Publication Year | 2006 Monomer | 2012 Monomer 2006 Polymer | 1994 | 1998 | 2003 | 1989 |
| Limit of Quantification* | 0.2 ug/m ³ | 0.6 ug/m ³ | 0.1 ug/m ³ | 0.1 ug/m ³ | 0.1 ug/m ³ | 0.6 ug/m ³ |
| Evaluation Standard | ISO 17734 | ASTM 6561 ASTM 6562 | Unrated NIOSH Evaluation | Evaluation, recommend ed for area sampling only | Partial NIOSH Evaluation | Partial NIOSH Evaluation |
| | | | | | | |

Notes: GFF = Glass Fiber Filter; DBA = di-*n*-butylamine; PTFE = polytetrafluoroethylene; MOPIP = 1-(2-methoxyphenyl)piperazine; MAMA = 9-(N-methylamiomethyl)anthracene; DMSO = dimethyl sulfoxide; MAP = 1-(9-anthracenylmethyl)piperazine; IOM = Institute of Medicine; 1-2PP = 1-(2-pyridyl)piperazine; HPLC = High Performance Liquid Chromatography; MS = Mass Spectrometry; MS/MS = Tandem Mass Spectrometry; UV = ultraviolet; PDA = photodiode array; EC = electrochemical; FL = fluorescence.

*Adapted and Modified from Heline, T. (2014). Field Evaluation of Solvent-Free Sampling with Di-N-Butylamine for the Determination of Airborne Monomeric and Oligomeric 1,6-Hexamethylene Diisocyanate. Air Force Institute of Technology. AFIT-ENV-14-M-29

Methods

The study, conducted in a Midwestern US automobile plant, assessed isocyanate exposure to Operators and Inspectors in the paint department; both groups are in the presence of clear coat application. Operators are responsible for clear coat test spraying, and completing repairs on finished products. Inspectors examine parts that have clear coat sprayed on them via automatic sprayers (robots), and may manual spray parts as needed. The HDI personal and area samples were collected using the ASSET™ EZ4 NCO denuder tube method, at 0.2 liters per minute, due to its ability to capture both HDI monomers and polymers, and low limit of quantification. We collected a total of six personal samples, and four area samples in the paint department. The six personal samples were collected from two Operators and four Inspectors. Four area samples were taken to assess the presence of isocyanates in the environment. In each process, only one person at a time was in contact with the clear coat. The various assessment settings and operations are described below in further detail.

During the sampling, all persons spraying wore personal protective equipment, which included a P100 filtered, full-face mask; a paint suit, nitrile gloves, a rubber chemical apron, and steel-toed safety shoes.

Personal Sampling

I. Manual Clear Coat Spray Operator in Test Lab

One personal sample was collected in the Test Lab. Personal sampling in the Test Lab took place during the formulation of clear coat, and the spraying of five sample panels with a typical clear coat formulation. The Test Lab is used to ensure the formulation of the clear coat is correct and within company standards. The Test Lab consists of two areas: a formulation area, and a testing area. The Test Lab Operator manually mixed the components of the clear coat in the formulation area. The components were a series of clear coat urethane products and catalyzing agents. After formulation was completed, the clear coat was mixed by mechanical shaking and stirring, heated to 130° F to catalyze, then loaded into a spray canister. The spray canister was moved to the testing area, attached to a compressed air sprayer, and the five sample panels were sprayed. The testing area has a waterfall vacuum trap. When the waterfall was running, it created a vacuum, drawing in spray particulates, and trapped them in the water. The waterfall and captured particulates are then fed into a sluiceway and sludge pit for material recovery and recycling. The room had an overall negative pressure, with some air being drawn in from the outside. The air from the outside was filtered via HEPA filters. Isocyanate sampling was conducted during formulation and spraying tasks. Each panel was sprayed with a sweeping motion to completely cover the panel with an even amount of clear coat.

II. Final Repair Clear Coat Spray Operator

The personal sample was taken during a clear coat spray repair method, which consisted of spraying clear coat to repair damage to a component. The Final Repair area is an open, and well-lit repair stage. Parts and automobile bodies are moved into the repair stage for the Operator

to repair. The ventilation system works via a downdraft makeup air system, pushing particulates and vapors into a water trap, which is pushed out to a reclamation and recycling area. The Operator taped off the car body area to be repaired, and removed any scuffs, dirt or other contaminants from the car body. Then, the Operator attached a clear coat canister to a supplied compressed air sprayer, and sprayed clear coat until the repair area was evenly covered. Once the components were repaired, and the clear coat had been sprayed, they were placed in an infrared baking oven to cure the clear coat. The clear coat spray duration was dependent on the size of a clear coat repair. The clear coat spray task may have required five or more minutes of spraying, depending on the size and quantity of repairs on each damaged component.

III. Inspector Exposure to Automatic Clear Coat Application on Components

Four personal samples were collected to determine Inspector exposure from clear coat application to components. The Inspectors were responsible for ensuring automatic clear coat application and part quality. Not only did they interact with sprayed components, they also maintained and repaired clear coat spraying robots. The robots were situated in contained booths with make-up air flowing downward. The make-up air was meant to capture clear coat particulates and deposit them in a water trap below the floor of the clear coat booth. During production, the spraying robots were stopped, at which time they were cleaned to ensure consistent clear coat application. The parts were sprayed automatically, and then pass through a staging area before entering a baking oven. In this staging area, the Inspectors walked into the booth, and assessed the parts for quality control, and clear coat application consistency. Their task required at least 10 to 15 minutes inside the booth staging area for the previously detailed tasks. Occasionally, Inspectors must manually apply clear coat in certain situations, such as a

robot malfunction or inconsistent clear coat application. During the time of this study, the Inspectors conducted no manual application. These Inspectors handled the components needed to formulate the clear coat, including mixing, and testing the mix. The mixing and testing was conducted via a mostly hands-free method; materials are piped in to mixing containers, and then pumped to the auto-spray robots. Their work location was typically in labs, mixing rooms, and occasionally the production line, if necessary. Inspectors ensured quality control of the clear coat by mixing and testing components in a similar fashion as the test lab. The process of clear coat mixing and formulation has variable timing; it is dependent on volume of production and production component needs. The data for the airflow in the automatic clear coat spray areas were not available during this assessment. This area also used forced make up air into a water trap, capturing aerosol and vapor molecules and pushing them to the reclamation and recycling area.

Area Sampling

A total of four area samples were collected during clear coat repair: One sample was collected during the clear coat repair procedure, and three more area samples were collected during the post-repair infrared baking process. Area samples were collected to determine if there were existing isocyanates in the environment after manual clear coat spraying was conducted, and to determine how much isocyanate concentration was present during the baking process. Once the samples were collected, we then sent them via chain of custody to a qualified laboratory for analysis. Refer to the appendix for complete laboratory analysis, and qualifications.

Isocyanate Analysis by Supelco Method, Extraction and Analysis of ASSET™ EZ4-NCO Sampler, as adapted from ISO 17734-1

The ASSET™ EZ4-NCO Sampler is extracted via the ISO 17734-1 method. The filter media from the denuder is extracted into 3 ml of aqueous 1 mM H₂SO₄, 3 ml of methanol, and 5.5 ml of toluene. This required a four-step process, including shaking, sonicating, a second shaking, and finally, a centrifuge. After the centrifuge process, the toluene layer comes to the top, and was removed. Another 5.5 ml aliquot of toluene was added to the original sample, but evaporated via nitrogen vaporization. The sample is then dissolved in 1 ml of acetonitrile for analysis (Supelco Analytical, 2013). To measure isocyanate concentration, they are analyzed via High Performance Liquid Chromatography – Mass Spectrometry (HPLC-MS).

Results

Tables II - XVI show the results from the study. Tables II and III show the combined HDI data from the manual spray operation and auto-spray inspection personal sampling.

Table II - Combined HDI Concentration - Personal Sample - Operator

| Sample Type | Sample Time (min) | Sample (ppb) | *8 Hour TWA (ppb) | **Task TWA (ppb) |
|-------------------|-------------------|--------------|-------------------|------------------|
| Operator 1 | 37 | 1.51 | 0.117 | 1.38 |
| Operator 2 | 15 | 1.06 | 0.033 | |
| Average | 26 | 1.29 | 0.075 | |

*Projected 8 hour Time Weighted Average – $(X_1T_1 + X_2T_2 + \dots + X_nT_n) / 8 \text{ hrs}$

**Projected Task Time Weighted Average – $(X_1T_1 + X_2T_2 + \dots + X_nT_n) / T_1 + T_2 + \dots + T_n$

Table III - Combined HDI Concentration - Personal Sample - Inspector

| Sample Type | Sample Time (min) | Sample (ppb) | *8 Hour TWA (ppb) | **Task TWA (ppb) |
|--------------------|-------------------|--------------|-------------------|------------------|
| Inspector 1 | 263 | 0.076 | 0.041 | 0.168 |
| Inspector 2 | 152 | 0.13 | 0.041 | |
| Inspector 3 | 226 | 0.38 | 0.18 | |
| Inspector 4 | 187 | 0.078 | 0.030 | |
| Average | 207 | 0.17 | 0.072 | |

*Projected 8 hour Time Weighted Average – $(X_1T_1 + X_2T_2 + \dots + X_nT_n) / 8 \text{ hrs}$

**Projected Task Time Weighted Average – $(X_1T_1 + X_2T_2 + \dots + X_nT_n) / T_1 + T_2 + \dots + T_n$

Tables IV and V show the homopolymer and monomer concentrations collected from the Operator personal sampling.

| Table IV - HDI Homopolymer Sample Concentration - Personal Sample - Operator | | | | |
|---|--------------------------|---------------------|--------------------------|-------------------------|
| Sample Type | Sample Time (min) | Sample (ppb) | *8 Hour TWA (ppb) | **Task TWA (ppb) |
| Operator 1 | 37 | 1.22 | 0.094 | 0.96 |
| Operator 2 | 15 | 0.33 | 0.010 | |
| Average | 26 | 0.78 | 0.052 | |

*Projected 8 hour Time Weighted Average – $(X_1T_1 + X_2T_2 + \dots + X_nT_n) / 8 \text{ hrs}$

**Projected Task Time Weighted Average – $(X_1T_1 + X_2T_2 + \dots + X_nT_n) / T_1 + T_2 + \dots + T_n$

| Table V - HDI Monomer Sample Concentration - Personal Sample - Operator | | | | |
|--|--------------------------|---------------------|--------------------------|-------------------------|
| Sample Type | Sample Time (min) | Sample (ppb) | *8 Hour TWA (ppb) | **Task TWA (ppb) |
| Operator 1 | 37 | 0.29 | 0.0224 | 0.42 |
| Operator 2 | 15 | 0.73 | 0.0228 | |
| Average | 26 | 0.51 | 0.024 | |

*Projected 8 hour Time Weighted Average – $(X_1T_1 + X_2T_2 + \dots + X_nT_n) / 8 \text{ hrs}$

**Projected Task Time Weighted Average – $(X_1T_1 + X_2T_2 + \dots + X_nT_n) / T_1 + T_2 + \dots + T_n$

Tables VI and VII show the breakdown between homopolymer and monomer concentrations collected from Inspector personal sampling.

| Table VI - HDI Homopolymer Concentration - Personal Sample - Inspector | | | | |
|---|--------------------------|---------------------|--------------------------|-------------------------|
| Sample Type | Sample Time (min) | Sample (ppb) | *8 Hour TWA (ppb) | **Task TWA (ppb) |
| Inspector 1 | 263 | 0.035 | 0.019 | 0.12 |
| Inspector 2 | 152 | 0.078 | 0.025 | |
| Inspector 3 | 226 | 0.33 | 0.16 | |
| Inspector 4 | 187 | 0.020 | 0.0076 | |
| Average | 207 | 0.12 | 0.053 | |

*Projected 8 hour Time Weighted Average – $(X_1T_1 + X_2T_2 + \dots + X_nT_n) / 8 \text{ hrs}$

**Projected Task Time Weighted Average – $(X_1T_1 + X_2T_2 + \dots + X_nT_n) / T_1 + T_2 + \dots + T_n$

| Table VII - HDI Monomer Concentration - Personal Sample - Inspector | | | | |
|--|--------------------------|---------------------|--------------------------|-------------------------|
| Sample Type | Sample Time (min) | Sample (ppb) | *8 Hour TWA (ppb) | **Task TWA (ppb) |
| Inspector 1 | 263 | 0.041 | 0.023 | 0.05 |
| Inspector 2 | 152 | 0.051 | 0.016 | |
| Inspector 3 | 226 | 0.048 | 0.023 | |
| Inspector 4 | 187 | 0.058 | 0.023 | |
| Average | 207 | 0.050 | 0.021 | |

*Projected 8 hour Time Weighted Average – $(X_1T_1 + X_2T_2 + \dots + X_nT_n) / 8 \text{ hrs}$

**Projected Task Time Weighted Average – $(X_1T_1 + X_2T_2 + \dots + X_nT_n) / T_1 + T_2 + \dots + T_n$

Tables VIII – X show the combined, homopolymer and monomer concentrations collected from area samples in the Final Repair Area.

| Table VIII - Combined HDI Concentration - Area Sample | | | | |
|--|--------------------------|---------------------|--------------------------|-------------------------|
| Sample Type | Sample Time (min) | Sample (ppb) | *8 Hour TWA (ppb) | **Task TWA (ppb) |
| Area Sample 1 | 21 | 0.94 | 0.041 | 2.14 |
| Area Sample 2 | 15 | 0.97 | 0.030 | |
| Area Sample 3 | 40 | 0.36 | 0.030 | |
| Area Sample 4 | 37 | 0.39 | 0.030 | |
| Average | 28.25 | 0.67 | 0.033 | |

*Projected 8 hour Time Weighted Average – $(X_1 T_1 + X_2 T_2 + \dots + X_n T_n) / 8 \text{ hrs}$

**Projected Task Time Weighted Average – $(X_1 T_1 + X_2 T_2 + \dots + X_n T_n) / T_1 + T_2 + \dots + T_n$

| Table IX - HDI Homopolymer Sample Concentration - Area Sample | | | | |
|--|--------------------------|---------------------|--------------------------|-------------------------|
| Sample Type | Sample Time (min) | Sample (ppb) | *8 Hour TWA (ppb) | **Task TWA (ppb) |
| Area Sample 1 | 21 | 0.18 | 0.0077 | 0.13 |
| Area Sample 2 | 15 | 0.24 | 0.0076 | |
| Area Sample 3 | 40 | 0.09 | 0.0077 | |
| Area Sample 4 | 37 | 0.10 | 0.0075 | |
| Average | 28.25 | 0.15 | 0.008 | |

*Projected 8 hour Time Weighted Average – $(X_1 T_1 + X_2 T_2 + \dots + X_n T_n) / 8 \text{ hrs}$

**Projected Task Time Weighted Average – $(X_1 T_1 + X_2 T_2 + \dots + X_n T_n) / T_1 + T_2 + \dots + T_n$

| Table X - HDI Monomer Sample Concentration - Area Sample | | | | |
|---|--------------------------|---------------------|--------------------------|-------------------------|
| Sample Type | Sample Time (min) | Sample (ppb) | *8 Hour TWA (ppb) | **Task TWA (ppb) |
| Area Sample 1 | 21 | 0.76 | 0.0333 | 0.43 |
| Area Sample 2 | 15 | 0.73 | 0.0228 | |
| Area Sample 3 | 40 | 0.27 | 0.0225 | |
| Area Sample 4 | 37 | 0.29 | 0.0224 | |
| Average | 28.25 | 0.51 | 0.025 | |

*Projected 8 hour Time Weighted Average – $(X_1 T_1 + X_2 T_2 + \dots + X_n T_n) / 8 \text{ hrs}$

**Projected Task Time Weighted Average – $(X_1 T_1 + X_2 T_2 + \dots + X_n T_n) / T_1 + T_2 + \dots + T_n$

Tables XI – XIII show the descriptive statistics for the personal and area samples.

| Table XI - Descriptive Statistics for Personal Sampling Data HDI Homopolymer and Monomer - Auto-Spray Inspectors | | |
|---|--------------------|----------------|
| Statistic | Homopolymer | Monomer |
| Count | 4 | 4 |
| Mean (ppb) | 0.12 | 0.050 |
| Standard Deviation (ppb) | 0.14 | 0.0070 |

| Table XII - Descriptive Statistics for Personal Sampling Data HDI Homopolymer and Monomer – Test and Repair Operators | | |
|--|--------------------|----------------|
| Statistic | Homopolymer | Monomer |
| Count | 2 | 2 |
| Mean (ppb) | 0.78 | 0.51 |
| Standard Deviation (ppb) | 0.63 | 0.31 |

| Table XIII - Descriptive Statistics for Sampling Data HDI Homopolymer and Monomer – Area Samples | | |
|---|--------------------|----------------|
| Statistic | Homopolymer | Monomer |
| Count | 4 | 4 |
| Mean (ppb) | 0.15 | 0.51 |
| Standard Deviation (ppb) | 0.071 | 0.005 |

Tables XIV – XV shows the descriptive statistics for the Projected 8 hour TWA for the personal sampling data from Operators and Inspectors.

| Table XIV - Descriptive Statistics for Sampling Data HDI Homopolymer and Monomer – Test and Repair Operators Projected 8 hour TWA | | |
|--|--------------------|----------------|
| Statistic | Homopolymer | Monomer |
| Count | 2 | 2 |
| Mean (ppb) | 0.052 | 0.023 |
| Standard Deviation (ppb) | 0.059 | 0.00028 |

| Table XV - Descriptive Statistics for Sampling Data HDI Homopolymer and Monomer – Auto-Spray Inspectors Projected 8 hour TWA | | |
|---|--------------------|----------------|
| Statistic | Homopolymer | Monomer |
| Count | 4 | 4 |
| Mean (ppb) | 0.053 | 0.021 |
| Standard Deviation (ppb) | 0.072 | 0.0035 |

Discussion

On June 20, 2013, OSHA issued a memorandum through its National Emphasis Program, stating the shift in focus to isocyanates. The document raises awareness on the use of isocyanates in industry, the effects of exposure and associated disease outcomes, and a targeted approach to limiting exposure (OSHA, 2013). The NIOSH approach to identifying and analyzing isocyanates is first noted in 1973, with the publication of a “Criteria for Recommended Standard: Occupational Exposure to Diisocyanates”. In the document, NIOSH recommends control methods, and a standard based on impinger collection, and laboratory analysis of diisocyanate species. The 1973 recommendation was to limit exposure to a “ceiling concentration of 20 ppb and a TWA of 5 ppb” (NIOSH, 1978). NIOSH periodically updates its recommendation based on current research. Currently, Streicher et al. are developing analytical methods of measuring chemical bonds between polymeric isocyanates so that a standard may be developed for polymeric isocyanate species, and a refined standard may be developed for monomeric species. (Streicher et al., 2000). OSHA does not yet have an established limit for HDI species, though it refers to other isocyanate exposure limits, and those established by NIOSH and ACGIH.

Overall, this study analyzed HDI concentrations during clear coat spraying operations in automobile manufacturing. We further investigated the concentrations of two species of HDI: Homopolymeric and monomeric forms. At a basic level, monomers can be chemically bonded together, and can form homopolymers. In Tables II - VII of the collected data, we see that the personal isocyanate exposures are below both the ACGIH TLV and NIOSH REL exposure limits

of 0.005 ppm. Area sample concentration, as reported in Tables VIII – X, show that environmental exposure to HDI was also below accepted limits. In fact, the researcher made the decision to report collected concentrations in parts per billion (ppb) to present more meaningful numbers, rather than report numbers in scientific notation. The reasons for the low concentration collection can be attributed to many reasons. First, the areas assessed all had active ventilation systems. The systems were designed to push particulates and aerosols into a water trap (situated beneath a grate covered floor), which was then collected and expelled into a reclamation area. Ventilation is designed to remove any unreacted isocyanate particles from the work area. As mentioned previously, isocyanates liberate quickly due to a low vapor pressure. Coupled with the ventilation system, there theoretically should not be much vapor capture. Findings by Streicher et al. support that low isocyanate concentrations occur due to rapid volatilization, and that “perhaps low-level measurement instruments could have been selected” (Streicher et al., 2000). In Table I, the NIOSH methods tend to have lower detection levels, however, the NIOSH methods typically involve methods that include the use of toxic chemicals, and increase the chance of exposure to the investigator. Streicher et al wrote “contained cassettes or tubes were more practical” (Streicher et al. 2000).

Creely et al. conjecture that overspray is a main pathway for isocyanate exposure, though the model used in that study indicated for non-automotive polyurethane products (Creely, 2006). In the non-automotive settings that were studied, ventilation systems were not used often due to the nature of the work (urethane insulation foam spraying, large transportation vehicle production). To compare the outcome in this study to the method used by Deft, the monomer and homopolymer species were combined and analyzed in Tables II and III. When combined, the isocyanate concentration was still below the NIOSH and ACGIH exposure limits. Deft initially

did this to include the polymerized species in isocyanates (Deft, 2011). Tables IV-VII show a breakdown between monomer and homopolymer species from personal sampling; the concentrations collected are still below the NIOSH and ACGIH limits. In Tables VIII – X, the area samples are all below exposure limits, although HDI monomer concentrations are higher than homopolymer concentrations. Monomer concentrations could be higher than homopolymer concentrations due to bond breaking in the homopolymer. The weak chemical bonds break between each monomer element, causing the homopolymer to return to its monomeric form, thus creating a secondary source for monomers.

In the projected 8-hour TWA data, the auto-spray Inspectors show to have a higher exposure than the manual sprayers, but are still well below exposure limits. When analyzing the environment in which the area samples were taken, heating elements were present, posing a possible reason as to why there was decreased homopolymer collection, and similar monomer collection from each sample. As the name implies, homopolymer signifies a polymer made up of the same or similar molecules, all held together by a chemical bond. When comparing Operator 1 and 2, Operator 1 has more exposure (by as much as a factor of 3.7) to HDI homopolymer than Operator 2. Operator 1, which was the test lab manual spray operation, was conducted in a smaller space with the waterfall trap mechanism. A smaller volume room could have been conducive to a higher concentration of homopolymer component collection, thus a higher concentration of HDI homopolymer being present when spraying clear coat.

Alternatively, the homopolymer may not have broken down into the more basic monomer form. The sample collection time difference between Operators 1 and 2 was due to process time. Operator 1 was in a spray test lab, which is a less time-controlled environment, but the process task is similar to that of Operator 2. Operator 2 is in a more time-controlled process, with focus

being on completing jobs tasks, ensuring quality, and completing as many tasks as possible in a typical 8-hour shift. As per the requirements of the ASSET™ EZ4-NCO Sampler, we let the sample collection run for 15 minutes. Operator 2 has a higher exposure, and this could be due to the process time combined with the amount of clear coat used to complete the repair task. It should be noted the projected 8-hour TWA for both Operators.

On the second day of sampling, the focus was on Inspectors in the auto-spray processes. As with the Operators and the manual spray areas, the Inspectors were below exposure levels to HDI monomers and homopolymers. Of the recorded exposures, Inspector 4 had an increased exposure to combined HDI (Table III) and HDI monomers (Table VII), although these were still below REL and TLV for HDI. Inspector 2 had higher exposure to homopolymer species (Table VI). We can conjecture that Inspector 4 may have spent more time in the post auto-spray inspection zone, or there was a higher volume of production requiring more clear coat application. In a similar study and method, Woskie and colleagues studied variance in exposure time, where similar criteria (repair time, length of clear coat use, and volume of repairs) were studied, and similar difficulties were encountered (Woskie et al., 2004). No clear solution is apparent. The development of a passive badge, or strict adherence to an 8-hour TWA, is a potential solution.

Tables XI – XV show the statistical analysis for the data, which are separated into personal (Operator, Inspector) and area sampling, and shows the difference between homopolymeric and monomeric HDI. From Tables XI and XII, we see that the average exposure was higher for the manual sprayers than the auto-spray Inspectors (between 2 to 40 times greater), though both are still well below the NIOSH and ACGIH recommended standards. In

addition, the standard deviations show high variation between the values, though the standard deviations are close to zero.

Table XVI shows the percent error of the collected data compared to NIOSH REL and ACGIH TLV for HDI, and this shows a high rate of error for the data. The percent error could show the inaccuracy of the data and collection method, or simply depict the difference between the actual and predicted values.

Statistical analysis could be enriched if this study compared two collection methods, as Heline and Carlton et al. had done. (Heline, 2014, Carlton et al., 2000). A comparison of over and under estimation could have provided another facet to understanding isocyanate collection, volatilization, and analysis. With a small sample size, statistically significant and meaningful data were difficult to collect, much less analyze. Another aspect of the area sampling that could be investigated further is the change in isocyanate volatilization between areas where heating lamps are in use and areas where no heating lamps are present. Furthermore, this study did not measure other isocyanate species, namely methylene diphenyl diisocyanate (MDI), or toluene diisocyanate (TDI). Characterizing these isocyanate species would provide a more complete picture of isocyanate exposure, or lack thereof. Another step in a future study would be to compare the ASSET™ method with the ISO-CHEK® media. This would explore the difference in lower concentration isocyanate collection between the two methods.

In terms of health outcomes at low levels (in ppb) of exposure, Pronk et al. found little in terms of health and even ruled out sensitization (Pronk et al., 2006). Pronk further explains that most of the health outcomes found in auto body repair activity were mainly found in those who smoked, and conjectured that smoking may exacerbate the effect of isocyanate exposure, among other symptoms. In a study by Musk and colleagues, 107 subjects in the urethane plastics

industry showed no symptoms or negative health outcomes after exposure to isocyanate at 0.001 ppm (Musk et al., 1982). It should be noted that Musk and colleagues investigated TDI and MDI species of isocyanates. The study by Musk et al. also showed that smoking while working with isocyanates showed a positive correlation that resulted with negative health outcomes, including respiratory disease, and asthma. Again, smoking would be the “major indicator for negative health outcomes instead of isocyanates” (Musk et al., 1982).

Future health outcome evaluation could be investigated in a similar fashion to that of Rosenberg and colleagues, in which biomarkers associated with isocyanate clearance were assessed as they were passed through urine (Rosenberg et al., 2002). Additionally, conducting longitudinal Forced Expiratory Volume (FEV) tests, such as those conducted by Musk et al., during spirometry exams could show whether a correlation exists for low level exposures in the parts per billion (Musk et al., 1982).

The primary weakness of this study was the small sample size. With a small sample size, it was difficult to have meaningful statistical analysis, and make comparisons to larger datasets. A larger study, over a longer period of time, would have provided a more thorough view of the exposure, with statistical strength. Another weakness of may have been the collection method itself. Using the ASSET™ method and the ISO-CHEK® media would have provided a means for comparative analysis between two collection protocols, and determine if there was a difference in the measured concentration when the exposure was the same.

Conclusion

This study quantified the worker exposure to isocyanate species in automobile clear coat application. At an automobile plant in the Midwest United States, and using the ASSET™ method to collect isocyanate samples, we collected hexamethylene diisocyanate monomers and homopolymers. We conclude that the current exposure to Inspectors and Operators is minimal, and below current ACGIH and NIOSH exposure levels by a factor of 1000; reported concentrations were converted to parts per billion to report significant data. The projected 8-hour time weighted average was below the NIOSH and ACGIH 0.005 ppm TWA limit, as well as the 0.02 ppm - 10 minute ceiling limit. Area sampling also showed that there were negligible concentrations of isocyanates in terms of environmental exposure.

Future studies should include increased personal sampling size, in conjunction with a biomarker analysis, to determine if isocyanate exposure is consistent between manual spraying, and automatic spraying methods.

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Appendix 1:
List of Equipment and Instrumentation

GilAir*

Personal Sampling Pumps (0.2 LPM)

*Calibrated by manufacturer in January 2015

DryCal DC Lite Primary Flow Meter*

*Calibrated by manufacturer in November 2014

Supelco ASSET™ EZ4-NCO sampler

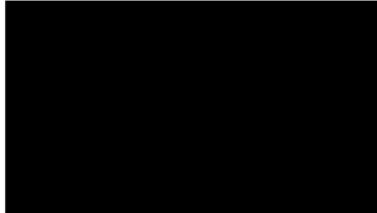
Tygon Tubing

Appendix 2:
Analytical Results, Laboratory Accreditation, and Supporting Documents

The following documents are the analytical results, analytical laboratory accreditation, and supporting documents for the study. Names, addresses and other contact information may have been redacted to protect privacy and proprietary information.



June 30, 2015



Bureau Veritas Work Order No. 15060624

Reference:



Bureau Veritas North America, Inc. received 7 samples on June 10, 2015 for the analyses presented in the following report.

Enclosed is a copy of the Chain-of-Custody record, acknowledging receipt of these samples. Please note that any unused portion of the samples will be discarded 30 days after the date of this report, unless you have requested otherwise.

This material is confidential and is intended solely for the person to whom it is addressed. If this is received in error, please contact the number provided below.

We appreciate the opportunity to assist you. If you have any questions concerning this report, please contact a Client Services Representative at (800) 806-5887.

Sincerely,

Scott Caillouette

Client Services Representative

Electronic signature authorized through password protection

Bureau Veritas North America, Inc.

Health, Safety, and Environmental Services

22345 Roethel Drive

Novi, MI 48375

Main: (248) 344.1770

Fax: (248) 344.2655

www.us.bureauveritas.com



CASE NARRATIVE

Date: 30-Jun-15

CLIENT: [REDACTED]

Project:

Work Order No 15060624

The results of this report relate only to the samples listed in the body of this report.

Unless otherwise noted below, the following statements apply: 1) all samples were received in acceptable condition, 2) all quality control results associated with this sample set were within acceptable limits and/or do not adversely affect the reported results, and 3) the industrial hygiene results have not been blank corrected.



ANALYTICAL RESULTS

Date: 30-Jun-15

Client: [REDACTED]

Project: [REDACTED]

Work Order No: 15060624

Sample Identification: BLANK

Lab Number: 001A

Date Sampled: 6/8/2015

Sample Type: Asset EZ4-NCO

Date Received: 6/10/2015

Analyst: KAR

Air Volume (L): NA

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|---------------|--------------------|----------------------|-------|-------------------------|---------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Polymeric HDI | <15 | -- | -- | 15 | ISO 17734 Mod | 06/26/2015 |

Sample Identification: MAP-15-A-0017

Lab Number: 002A

Date Sampled: 6/8/2015

Sample Type: Asset EZ4-NCO

Date Received: 6/10/2015

Analyst: KAR

Air Volume (L): 7.4111

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|---------------|--------------------|----------------------|-------|-------------------------|---------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Polymeric HDI | 190 | 0.025 | -- | 15 | ISO 17734 Mod | 06/26/2015 |

Sample Identification: MAP-15-A-0018

Lab Number: 003A

Date Sampled: 6/8/2015

Sample Type: Asset EZ4-NCO

Date Received: 6/10/2015

Analyst: KAR

Air Volume (L): 4.2042

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|---------------|--------------------|----------------------|-------|-------------------------|---------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Polymeric HDI | <15 | <0.0036 | -- | 15 | ISO 17734 Mod | 06/26/2015 |



ANALYTICAL RESULTS

Date: 30-Jun-15

Client: [REDACTED]

Project: [REDACTED] Work Order No: 15060624

Sample Identification: MAP-15-A-0019

Lab Number: 004A Date Sampled: 6/8/2015

Sample Type: Asset EZ4-NCO Date Received: 6/10/2015

Analyst: KAR Air Volume (L): 3.0045

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|---------------|--------------------|----------------------|-------|-------------------------|---------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Polymeric HDI | 20 | 0.0067 | -- | 15 | ISO 17734 Mod | 06/26/2015 |

Sample Identification: MAP-15-A-0020

Lab Number: 005A Date Sampled: 6/8/2015

Sample Type: Asset EZ4-NCO Date Received: 6/10/2015

Analyst: KAR Air Volume (L): 3.003

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|---------------|--------------------|----------------------|-------|-------------------------|---------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Polymeric HDI | <15 | <0.0050 | -- | 15 | ISO 17734 Mod | 06/26/2015 |

Sample Identification: MAP-15-A-0021

Lab Number: 006A Date Sampled: 6/8/2015

Sample Type: Asset EZ4-NCO Date Received: 6/10/2015

Analyst: KAR Air Volume (L): 8.012

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|---------------|--------------------|----------------------|-------|-------------------------|---------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Polymeric HDI | <15 | <0.0019 | -- | 15 | ISO 17734 Mod | 06/26/2015 |



ANALYTICAL RESULTS

Date: 30-Jun-15

Client: [REDACTED]
Project: [REDACTED] Work Order No: 15060624

Sample Identification: MAP-15-A-0022

Lab Number: 007A Date Sampled: 6/8/2015

Sample Type: Asset EZ4-NCO Date Received: 6/10/2015

Analyst: KAR Air Volume (L): 7.4074

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|---------------|--------------------|----------------------|-------|-------------------------|---------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Polymeric HDI | <15 | <0.0020 | -- | 15 | ISO 17734 Mod | 06/26/2015 |

General Notes:

<: Less than the indicated reporting limit (RL).

--: Information not available or not applicable.

Back sections (if applicable) were checked and showed no significant breakthrough unless otherwise noted.

Air Sampling Data Collection Form

Location: [REDACTED]

Department: Paint

SEG Name: [REDACTED]

SEG Number: MAP-189

General Activities: 2K testing - PA test lab

Sample Date: 6/8/15

- Quality spray / MIX

Associate / #:

Pump #:

Calibration Standard:

17192

7270 / 1/13/16

| Pump | Measurement description | Result | Method Standard | | | |
|---|------------------------------|---------------|-----------------|--|--|--|
| Pump on, verify flow using calibration standard, adjust | Pre-use calibration [L/min] | 0.2005 | | Note: Consult the air sampling pump manual for calibration instructions. | | |
| Pump on, verify flow using calibration standard | Post-use calibration [L/min] | 0.2001 | | | | |
| Battery Indicator | Battery Check | OK | | | | |
| | Average Flow Rate [L/min] | 0.2003 | +/- 5% OK | (Pre + Post Calibration) / 2 | | |
| | Sample Number | MAP-15-A-0017 | | | | |
| Pump on | Start time | 1:24 PM | | | | |
| Pump off | Stop time | 2:02 PM | | | | |
| | Run time [Min] | 37 min | | | | |
| | Sample Volume [L] | 7.4111 | | | | |
| Cross out if not used | | | | | | |

Sample collected by (print): Karthik Sivaraman

Modified for Hygieia
1/23/04

Respiratory Protection used?

TYPE / FILTER:

See comments

Sample device placement:

/ R

| Chemicals for Analysis | | Countermeasure |
|------------------------|----------------------------------|--|
| | Ventilation (type / performance) | <u>mixing</u> |
| | Eye / Face Protection | <u>Face shield, safety glass</u> |
| | Skin | <u>Paintant, apron, gloves (nitrile)</u> |
| | Foot | <u>Steel toe safety shoe</u> |
| | Protective Apparel | <u>Apron</u> |

| | | | |
|----------|--|-----------------------|--|
| Comments | Inlet filters were replaced 1.5 wks ago (last wk in May) | | Spray PPE |
| | No resp protection used for mixing, full face resp used for spray. | | Full face Respirator |
| | Spray time: 657sec; 59sec; 39sec; 45sec, stepped out to put mask on @ 1:36p, took mask off @ 1:55 stepped out 2pm. | | <u>Paintant, apron, nitrile gloves, steel toe,</u> |
| | PRODUCTION RECORD: | | |
| | Representative Conditions? Y / N | Blank sample #: 14030 | Entered into IH database? Y / N |
| | Record Code: S-7790-740-006-000 | | |

Air Sampling Data Collection Form

Location:

Department:

Paint

SEG Name:

SEG Number:

Final Repair

General Activities:

Sample Date:

Pump #:

01008

Calibration Standard:

7270 / 11/13/16

| Pump | Measurement description | Result | Method Standard | Note: Consult the air sampling pump manual for calibration instructions. |
|---|------------------------------|-------------------|-----------------|--|
| Pump on, verify flow using calibration standard, adjust | Pre-use calibration [L/min] | 0.2003 | | |
| Pump on, verify flow using calibration standard | Post-use calibration [L/min] | 0.2001 | | |
| Battery Indicator | Battery Check | OK | OK | |
| Run time Sample volume = Avg. Flow Rate X Run time | Average Flow Rate [L/min] | 0.2002 | +/- 5% OK | (Pre + Post Calibration) / 2 |
| | Sample Number | MAP-15-A-0618 | | |
| | Pump on | Start time | 3:37 PM | |
| | Pump off | Stop time | 3:58 PM | |
| | | Run time [Min] | 21 min | |
| | | Sample Volume [L] | 4.2042 | |
| | | | | Cross out if not used |

Sample collected by (print): Karthik Sivaraman

Modified for Hygieia
1/23/04

Respiratory Protection used?

Y / N TYPE / FILTER:

Sample device placement:

L/R

| Chemicals for Analysis | Countermeasure | |
|------------------------|----------------------------------|--|
| | Ventilation (type / performance) | |
| | Eye / Face Protection | |
| | Skin | |
| | Foot | |
| | Protective Apparel | |

IR oven 70°f - 290°f

Area sample

7.53 ac spray.

Comments

PRODUCTION RECORD:

Representative Conditions? Y / N

Blank sample #: 14030

Entered into IH database? Y / N

Record Code: S-7790-740-006-000

Air Sampling Data Collection Form

Location: [REDACTED] Department: Paint
 SEG Name: Final Repair SEG Number: [REDACTED]
 General Activities: Personal sample (2Kcc) Sample Date: 6/18/15
 Associate / #: [REDACTED]
 Pump #: 17192 Calibration Standard: 7270 / 1/13/16

| Pump | Measurement description | Result | Method Standard | | | |
|---|------------------------------|---------------|-----------------|--|--|--|
| Pump on, verify flow using calibration standard, adjust | Pre-use calibration [L/min] | 0.2065 | | Note: Consult the air sampling pump manual for calibration instructions. | | |
| Pump on, verify flow using calibration standard | Post-use calibration [L/min] | 0.2001 | | | | |
| Battery Indicator | Battery Check | OK | | | | |
| | Average Flow Rate [L/min] | 0.2003 | +/- 5% OK | (Pre + Post Calibration) / 2 | | |
| | Sample Number | MAP-15-A-0019 | | | | |
| Pump on | Start time | 4:16 | | | | |
| Pump off | Stop time | 4:31 | | | | |
| | Run time [Min] | 15 | | | | |
| | Sample Volume [L] | 3.0045 | | | | |
| Cross out if not used | | | | | | |

Sample collected by (print): Karthik Sivaraman

Modified for Hygeia
1/23/04

Respiratory Protection used? N TYPE / FILTER: org. solvent vapor full face particulate pre-filter.

Sample device placement: L R

| Chemicals for Analysis | Countermeasure |
|------------------------|----------------------------------|
| | Ventilation (type / performance) |
| | Eye / Face Protection |
| | Skin |
| | Foot |
| | Protective Apparel |

~~2:44 sec~~ ^{2 min 44 sec} clear coat application.

Comments

PRODUCTION RECORD:

Representative Conditions? Y / N | Blank sample #: 14030 | Entered into IH database? Y / N | Record Code: S-7790-740-006-000

Air Sampling Data Collection Form

Location: [REDACTED] Department: Paint
 SEG Name: Final Repair SEG Number: [REDACTED]
 General Activities: Area Sample Sample Date: 6/8/15
 2K clearcoat Spray Associate #: Area Sample
 Pump #: 01008 Calibration Standard: 7270 / 11/3/16

| Pump | Measurement description | Result | Method Standard | Note: Consult the air sampling pump manual for calibration instructions. |
|---|------------------------------|---------------|-----------------|--|
| Pump on, verify flow using calibration standard, adjust | Pre-use calibration [L/min] | 0.2003 | | |
| Pump on, verify flow using calibration standard | Post-use calibration [L/min] | 0.2001 | | |
| Battery Indicator | Battery Check | OK | OK | |
| | Average Flow Rate [L/min] | 6.2002 | +/- 5% OK | (Pre + Post Calibration) / 2 |
| | Sample Number | MAP-15-A-0020 | | |
| Pump on | Start time | 4:16pm | | |
| Pump off | Stop time | 4:31pm | | |
| | Run time [Min] | 15 | | |
| | Sample Volume [L] | 3.003 | | |
| Cross out if not used | | | | |

Sample collected by (print): Karthik Sivaraman

Modified for Hygeia
1/23/04

Respiratory Protection used? Y / N TYPE / FILTER: _____
Sample device placement: L / R _____

| Comments | Chemicals for Analysis | Countermeasure |
|----------|--|--|
| | | Ventilation (type / performance) <u>Area Sample.</u> |
| | | Eye / Face Protection |
| | | Skin |
| | | Foot |
| | | Protective Apparel |
| | <u>2K Final Repair Spray - Area Sample</u> | |

2min 44sec spray time

PRODUCTION RECORD:

| | | | |
|----------------------------------|-----------------------|---------------------------------|---------------------------------|
| Representative Conditions? Y / N | Blank sample #: 14030 | Entered into IH database? Y / N | Record Code: S-7790-740-006-000 |
|----------------------------------|-----------------------|---------------------------------|---------------------------------|

Air Sampling Data Collection Form

Location: [REDACTED] Department: Paint
 SEG Name: Final Repair SEG Number: [REDACTED]
 General Activities: 2K large repair bake (area sample) Front Sample Date: 6/8/15
 Associate / #: Area
 Pump #: 17192 Calibration Standard: 7270 / 1/13/16

| Pump | Measurement description | Result | Method Standard | | | |
|---|------------------------------|---------------|-----------------|--|--|--|
| Pump on, verify flow using calibration standard, adjust | Pre-use calibration [L/min] | 0.2005 | 0.2001 | Note: Consult the air sampling pump manual for calibration instructions. | | |
| Pump on, verify flow using calibration standard | Post-use calibration [L/min] | 0.2003 | | | | |
| Battery Indicator | Battery Check | OK | | | | |
| | Average Flow Rate [L/min] | 0.2003 | +/- 5% OK | (Pre + Post Calibration) / 2 | | |
| | Sample Number | MAP-15-A-0021 | | | | |
| Pump on | Start time | 4:38 | | | | |
| Pump off | Stop time | 5:15 | | | | |
| | Run time [Min] | 40 | | | | |
| | Sample Volume [L] | 8.012 | | | | |
| Cross out if not used | | | | | | |

Sample collected by (print): Karthik Sivaraman

Modified for Hygieia
1/23/04

Respiratory Protection used? Y / N TYPE / FILTER: area sample
Sample device placement: L / R

| Comments | Chemicals for Analysis | Countermeasure |
|----------|------------------------|---|
| | | Ventilation (type / performance) <u>area sample</u> . |
| | | Eye / Face Protection |
| | | Skin |
| | | Foot |
| | | Protective Apparel |
| | | |

| | | | |
|----------------------------------|--|---------------------------------|---------------------------------|
| Comments | 2K large repair bake (area) Front more odorous bake out Noticeable smell | | |
| | | | |
| PRODUCTION RECORD: | | | |
| Representative Conditions? Y / N | Blank sample #: 14030 | Entered into IH database? Y / N | Record Code: S-7790-740-006-000 |

Air Sampling Data Collection Form

Location: ████████ Department: Paint
 SEG Name: Final Repair SEG Number: ████████
 General Activities: 2K large repair bake Sample Date: 6/8/15
(area sample) Back Associate / #: area
 Pump #: 01008 Calibration Standard: 7270 / 1/13/2016

| Pump | Measurement description | Result | Method Standard | Note: Consult the air sampling pump manual for calibration instructions. | | |
|---|------------------------------|----------------------|-----------------|--|--|--|
| Pump on, verify flow using calibration standard, adjust | Pre-use calibration [L/min] | <u>0.2008</u> | | | | |
| Pump on, verify flow using calibration standard | Post-use calibration [L/min] | <u>0.2001</u> | | | | |
| Battery Indicator | Battery Check | <u>OK</u> | OK | | | |
| | Average Flow Rate [L/min] | <u>0.2002</u> | +/- 5% OK | (Pre + Post Calibration) / 2 | | |
| | Sample Number | <u>MAP-15-A-0022</u> | | | | |
| Pump on | Start time | <u>4:38</u> | | | | |
| Pump off | Stop time | <u>5:15</u> | | | | |
| | Run time [Min] | <u>37</u> | | | | |
| | Sample Volume [L] | <u>7.4074</u> | | | | |
| <i>Cross out if not used</i> | | | | | | |

Sample collected by (print): Karthik Sivaraman

Modified for Hygeia
1/23/04

Respiratory Protection used? Y / N TYPE / FILTER: area sample
Sample device placement: L / R

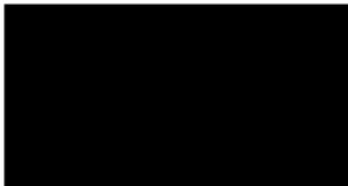
| Comments | Chemicals for Analysis | Countermeasure |
|----------|---|---|
| | | Ventilation (type / performance) <u>area sample</u> |
| | | Eye / Face Protection |
| | | Skin |
| | | Foot |
| | | Protective Apparel |
| | <u>2K large repair bake (area) back.</u> <u>more odorous bake out</u> <u>noticeable smell</u> | |

PRODUCTION RECORD:

Representative Conditions? Y / N Blank sample #: 14030 Entered into IH database? Y / N Record Code: S-7790-740-006-000



July 09, 2015



Bureau Veritas Work Order No. 15060624

Reference:



Bureau Veritas North America, Inc. received 7 samples on June 10, 2015 for the analyses presented in the following report.

This is an additional report. Please see the Case Narrative for details.

This material is confidential and is intended solely for the person to whom it is addressed. If this is received in error, please contact the number provided below.

We appreciate the opportunity to assist you. If you have any questions concerning this report, please contact a Client Services Representative at (800) 806-5887.

Sincerely,

Scott Caillouette
Client Services Representative
Electronic signature authorized through password protection

Bureau Veritas North America, Inc.

Health, Safety, and Environmental Services

22345 Roethel Drive

Novi, MI 48375

Main: (248) 344.1770

Fax: (248) 344.2655

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CASE NARRATIVE

Date: 09-Jul-15

CLIENT: [REDACTED]

Project:

Work Order No 15060624

ADDITIONAL REPORT:

As requested July 6, 2015, we have added monomeric HDI results in this additional report.

The results of this report relate only to the samples listed in the body of this report.

Unless otherwise noted below, the following statements apply: 1) all samples were received in acceptable condition, 2) all quality control results associated with this sample set were within acceptable limits and/or do not adversely affect the reported results, and 3) the industrial hygiene results have not been blank corrected.



ANALYTICAL RESULTS

Date: 09-Jul-15

Client: [REDACTED]

Project:

Work Order No: 15060624

Sample Identification: BLANK

Lab Number: 001A

Date Sampled: 6/8/2015

Sample Type: Asset EZ4-NCO

Date Received: 6/10/2015

Analyst: KAR

Air Volume (L): NA

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|---------------|--------------------|----------------------|-------|-------------------------|---------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Polymeric HDI | <15 | -- | -- | 15 | ISO 17734 Mod | 06/26/2015 |

Sample Identification: BLANK

Lab Number: 001B

Date Sampled: 6/8/2015

Sample Type: Asset EZ4-NCO

Date Received: 6/10/2015

Analyst: KAR

Air Volume (L): NA

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|----------------------------------|--------------------|----------------------|-------|-------------------------|-----------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Hexamethylene diisocyanate (HDI) | <15 | -- | -- | 15 | ISO 17734 Asset | 06/26/2015 |

Sample Identification: MAP-15-A-0017

Lab Number: 002A

Date Sampled: 6/8/2015

Sample Type: Asset EZ4-NCO

Date Received: 6/10/2015

Analyst: KAR

Air Volume (L): 7.4111

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|---------------|--------------------|----------------------|-------|-------------------------|---------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Polymeric HDI | 190 | 0.025 | -- | 15 | ISO 17734 Mod | 06/26/2015 |



ANALYTICAL RESULTS

Date: 09-Jul-15

| | | | | |
|--------------------------------------|---------------|--|--|--------------------------|
| Client: | | | | Work Order No: 15060624 |
| Project: | | | | |
| Sample Identification: MAP-15-A-0017 | | | | |
| Lab Number: | 002B | | | Date Sampled: 6/8/2015 |
| Sample Type: | Asset EZ4-NCO | | | Date Received: 6/10/2015 |
| Analyst: | KAR | | | Air Volume (L): 7.4111 |

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|----------------------------------|--------------------|----------------------|----------|-------------------------|-----------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Hexamethylene diisocyanate (HDI) | <15 | <0.0020 | <0.00029 | 15 | ISO 17734 Asset | 06/26/2015 |

| | | | | | | |
|--------------------------------------|---------------|--|--|--|--------------------------|--|
| Sample Identification: MAP-15-A-0018 | | | | | | |
| Lab Number: | 003A | | | | Date Sampled: 6/8/2015 | |
| Sample Type: | Asset EZ4-NCO | | | | Date Received: 6/10/2015 | |
| Analyst: | KAR | | | | Air Volume (L): 4.2042 | |

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|---------------|--------------------|----------------------|-------|-------------------------|---------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Polymeric HDI | <15 | <0.0036 | -- | 15 | ISO 17734 Mod | 06/26/2015 |

| | | | | | | |
|--------------------------------------|---------------|--|--|--|--------------------------|--|
| Sample Identification: MAP-15-A-0018 | | | | | | |
| Lab Number: | 003B | | | | Date Sampled: 6/8/2015 | |
| Sample Type: | Asset EZ4-NCO | | | | Date Received: 6/10/2015 | |
| Analyst: | KAR | | | | Air Volume (L): 4.2042 | |

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|----------------------------------|--------------------|----------------------|---------|-------------------------|-----------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Hexamethylene diisocyanate (HDI) | 22 | 0.0052 | 0.00076 | 15 | ISO 17734 Asset | 06/26/2015 |



ANALYTICAL RESULTS

Date: 09-Jul-15

Client: [REDACTED]

Project:

Work Order No: 15060624

Sample Identification: MAP-15-A-0019

Lab Number: 004A

Date Sampled: 6/8/2015

Sample Type: Asset EZ4-NCO

Date Received: 6/10/2015

Analyst: KAR

Air Volume (L): 3.0045

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|---------------|--------------------|----------------------|-------|-------------------------|---------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Polymeric HDI | 20 | 0.0067 | -- | 15 | ISO 17734 Mod | 06/26/2015 |

Sample Identification: MAP-15-A-0019

Lab Number: 004B

Date Sampled: 6/8/2015

Sample Type: Asset EZ4-NCO

Date Received: 6/10/2015

Analyst: KAR

Air Volume (L): 3.0045

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|----------------------------------|--------------------|----------------------|----------|-------------------------|-----------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Hexamethylene diisocyanate (HDI) | <15 | <0.0050 | <0.00073 | 15 | ISO 17734 Asset | 06/26/2015 |

Sample Identification: MAP-15-A-0020

Lab Number: 005A

Date Sampled: 6/8/2015

Sample Type: Asset EZ4-NCO

Date Received: 6/10/2015

Analyst: KAR

Air Volume (L): 3.003

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|---------------|--------------------|----------------------|-------|-------------------------|---------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Polymeric HDI | <15 | <0.0050 | -- | 15 | ISO 17734 Mod | 06/26/2015 |



ANALYTICAL RESULTS

Date: 09-Jul-15

Client: [REDACTED]

Project: [REDACTED]

Work Order No: 15060624

Sample Identification: MAP-15-A-0020

Lab Number: 005B

Date Sampled: 6/8/2015

Sample Type: Asset EZ4-NCO

Date Received: 6/10/2015

Analyst: KAR

Air Volume (L): 3.003

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|----------------------------------|--------------------|----------------------|----------|-------------------------|-----------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Hexamethylene diisocyanate (HDI) | <15 | <0.0050 | <0.00073 | 15 | ISO 17734 Asset | 06/26/2015 |

Sample Identification: MAP-15-A-0021

Lab Number: 006A

Date Sampled: 6/8/2015

Sample Type: Asset EZ4-NCO

Date Received: 6/10/2015

Analyst: KAR

Air Volume (L): 8.012

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|---------------|--------------------|----------------------|-------|-------------------------|---------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Polymeric HDI | <15 | <0.0019 | -- | 15 | ISO 17734 Mod | 06/26/2015 |

Sample Identification: MAP-15-A-0021

Lab Number: 006B

Date Sampled: 6/8/2015

Sample Type: Asset EZ4-NCO

Date Received: 6/10/2015

Analyst: KAR

Air Volume (L): 8.012

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|----------------------------------|--------------------|----------------------|----------|-------------------------|-----------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Hexamethylene diisocyanate (HDI) | <15 | <0.0019 | <0.00027 | 15 | ISO 17734 Asset | 06/26/2015 |



ANALYTICAL RESULTS

Date: 09-Jul-15

Client: [REDACTED]

Project: [REDACTED]

Work Order No: 15060624

Sample Identification: MAP-15-A-0022

Lab Number: 007A

Date Sampled: 6/8/2015

Sample Type: Asset EZ4-NCO

Date Received: 6/10/2015

Analyst: KAR

Air Volume (L): 7.4074

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|---------------|--------------------|----------------------|-------|-------------------------|---------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Polymeric HDI | <15 | <0.0020 | -- | 15 | ISO 17734 Mod | 06/26/2015 |

Sample Identification: MAP-15-A-0022

Lab Number: 007B

Date Sampled: 6/8/2015

Sample Type: Asset EZ4-NCO

Date Received: 6/10/2015

Analyst: KAR

Air Volume (L): 7.4074

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|----------------------------------|--------------------|----------------------|----------|-------------------------|-----------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Hexamethylene diisocyanate (HDI) | <15 | <0.0020 | <0.00029 | 15 | ISO 17734 Asset | 06/26/2015 |

General Notes:

<: Less than the indicated reporting limit (RL).

--: Information not available or not applicable.

Back sections (if applicable) were checked and showed no significant breakthrough unless otherwise noted.



July 16, 2015



Bureau Veritas Work Order No. 15061573

Reference:



Bureau Veritas North America, Inc. received 5 samples on June 25, 2015 for the analyses presented in the following report.

Enclosed is a copy of the Chain-of-Custody record, acknowledging receipt of these samples. Please note that any unused portion of the samples will be discarded 30 days after the date of this report, unless you have requested otherwise.

This material is confidential and is intended solely for the person to whom it is addressed. If this is received in error, please contact the number provided below.

We appreciate the opportunity to assist you. If you have any questions concerning this report, please contact a Client Services Representative at (800) 806-5887.

Sincerely,

Scott Caillouette

Client Services Representative

Electronic signature authorized through password protection

Bureau Veritas North America, Inc.

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CASE NARRATIVE

Date: 16-Jul-15

CLIENT: [REDACTED]

Project:

Work Order No 15061573

The results of this report relate only to the samples listed in the body of this report.

Unless otherwise noted below, the following statements apply: 1) all samples were received in acceptable condition, 2) all quality control results associated with this sample set were within acceptable limits and/or do not adversely affect the reported results, and 3) the industrial hygiene results have not been blank corrected.



ANALYTICAL RESULTS

Date: 16-Jul-15

Client: [REDACTED]

Project:

Work Order No: 15061573

Sample Identification: BLANK

Lab Number: 001A

Date Sampled: 6/24/2015

Sample Type: Asset EZ4-NCO

Date Received: 6/25/2015

Analyst: KAR

Air Volume (L): NA

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|----------------------------------|--------------------|----------------------|-------|----------------------|-----------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Hexamethylene diisocyanate (HDI) | <15 | -- | -- | 15 | ISO 17734 Asset | 07/09/2015 |
| Polymeric HDI | <15 | -- | -- | 15 | ISO 17734 Mod | 07/09/2015 |

Sample Identification: MAP-15-A-0029

Lab Number: 002A

Date Sampled: 6/24/2015

Sample Type: Asset EZ4-NCO

Date Received: 6/25/2015

Analyst: KAR

Air Volume (L): 52.68

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|----------------------------------|--------------------|----------------------|-----------|----------------------|-----------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Hexamethylene diisocyanate (HDI) | <15 | <0.00028 | <0.000041 | 15 | ISO 17734 Asset | 07/09/2015 |
| Polymeric HDI | 38 | 0.00071 | -- | 15 | ISO 17734 Mod | 07/09/2015 |

Sample Identification: MAP-15-A-0030

Lab Number: 003A

Date Sampled: 6/24/2015

Sample Type: Asset EZ4-NCO

Date Received: 6/25/2015

Analyst: KAR

Air Volume (L): 47.95

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|----------------------------------|--------------------|----------------------|----------|----------------------|-----------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Hexamethylene diisocyanate (HDI) | 17 | 0.00035 | 0.000051 | 15 | ISO 17734 Asset | 07/09/2015 |
| Polymeric HDI | 75 | 0.0016 | -- | 15 | ISO 17734 Mod | 07/09/2015 |



ANALYTICAL RESULTS

Date: 16-Jul-15

Client: [REDACTED]

Project: [REDACTED]

Work Order No: 15061573

Sample Identification: MAP-15-A-0031

Lab Number: 004A

Date Sampled: 6/24/2015

Sample Type: Asset EZ4-NCO

Date Received: 6/25/2015

Analyst: KAR

Air Volume (L): 45.58

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|----------------------------------|--------------------|----------------------|-----------|----------------------|-----------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Hexamethylene diisocyanate (HDI) | <15 | <0.00033 | <0.000048 | 15 | ISO 17734 Asset | 07/09/2015 |
| Polymeric HDI | <15 | <0.00033 | -- | 15 | ISO 17734 Mod | 07/09/2015 |

Sample Identification: MAP-15-A-0032

Lab Number: 005A

Date Sampled: 6/24/2015

Sample Type: Asset EZ4-NCO

Date Received: 6/25/2015

Analyst: KAR

Air Volume (L): 37.46

| Analyte | Analytical Results | | | Reporting Limit (ng) | Test Method | Date Analyzed |
|----------------------------------|--------------------|----------------------|-----------|----------------------|-----------------|---------------|
| | (ng) | (mg/m ³) | (ppm) | | | |
| Hexamethylene diisocyanate (HDI) | <15 | <0.00040 | <0.000058 | 15 | ISO 17734 Asset | 07/09/2015 |
| Polymeric HDI | <15 | <0.00040 | -- | 15 | ISO 17734 Mod | 07/09/2015 |

General Notes:

<: Less than the indicated reporting limit (RL).

--: Information not available or not applicable.

Back sections (if applicable) were checked and showed no significant breakthrough unless otherwise noted.

Air Sampling Data Collection Form

Location: XXXXXXXXXX Department: Paint
 SEG Name: BPA - BC/CC Operators SEG Number: XXXXXXXXXX
 General Activities: ISOcyanate sampling Sample Date: 6/24/15
 Pump #: 01008 Associate / #: XXXXXXXXXX
 Calibration Standard: 132008 / Defendair S10

| Pump | Measurement description | Result | Method Standard | Note: Consult the air sampling pump manual for calibration instructions. | | | | | |
|---|------------------------------|---------------------------|-----------------|--|--|--|--|--|--|
| Pump on, verify flow using calibration standard, adjust | Pre-use calibration [L/min] | 0.2012 | Asset | | | | | | |
| Pump on, verify flow using calibration standard | Post-use calibration [L/min] | 0.1994 | | | | | | | |
| Battery Indicator | Battery Check | 0.2003 OK | | | | | | | |
| | | Average Flow Rate [L/min] | 0.2005 | +/- 5% OK | | | | | |
| | | Sample Number | MAP-15-A-0029. | | | | | | |
| Pump on | Start time | 0354 | 25 | | | | | | |
| Pump off | Stop time | 1053 | 1058 | | | | | | |
| | | Run time [Min] | 263 | | | | | | |
| | | Sample Volume [L] | 52.68. | | | | | | |
| Cross out if not used | | | | | | | | | |

Sample collected by (print): Monica Marsh /Karthik Sivaraman

Modified for Hygieia
1/23/04

Respiratory Protection used? Y / N TYPE / FILTER: _____

Sample device placement: L / R _____

| Chemicals for Analysis | Countermeasure |
|------------------------|----------------------------------|
| | Ventilation (type / performance) |
| | Eye / Face Protection |
| | Skin |
| | Foot |
| | Protective Apparel |

| | | | | |
|----------------------------------|--|---------------------------------|---------------------------------|--|
| Comments | <u>Non-smoker / lunch 11AM</u> <u>Break @ 9:15 - 9:28, no shut off required.</u> <u>Started @ 10:53A</u> <u>ended @ 10:58</u> | | | |
| | | | | |
| PRODUCTION RECORD: | | | | |
| Representative Conditions? Y / N | Blank sample #: _____ | Entered into IH database? Y / N | Record Code: S-7790-740-006-000 | |

Air Sampling Data Collection Form

Location: [REDACTED]

Department: Paint

SEG Name: BPA- BC/CC Operator

SEG Number: [REDACTED]

General Activities: Isocyanate sampling

Sample Date: 6/24/15

Pump #:

3011

Associate / #:

Calibration Standard:

132006 / Default S10

| Pump | Measurement description | Result | Method Standard | Note: Consult the air sampling pump manual for calibration instructions. | | | | | |
|---|------------------------------|----------------------|-----------------|--|--|--|--|--|--|
| Pump on, verify flow using calibration standard, adjust | Pre-use calibration [L/min] | <u>0.2003</u> | As set | | | | | | |
| Pump on, verify flow using calibration standard | Post-use calibration [L/min] | <u>0.1993</u> | | | | | | | |
| Battery Indicator | Battery Check | <u>0.1998 OK</u> | OK | | | | | | |
| | Average Flow Rate [L/min] | <u>0.1998</u> | +/- 5% OK | (Pre + Post Calibration) / 2 | | | | | |
| | Sample Number | <u>MAP-15-A-0030</u> | <u>Break</u> | | | | | | |
| Pump on | Start time | <u>638A</u> | <u>925A</u> | | | | | | |
| Pump off | Stop time | <u>910A</u> | <u>1053A</u> | | | | | | |
| | Run time [Min] | <u>152</u> | <u>88</u> | <u>240 total</u> | | | | | |
| | Sample Volume [L] | | | <u>47.95</u> | | | | | |
| Cross out if not used | | | | | | | | | |

Sample collected by (print): Karthik Sivaraman

Modified for Hygieia
1/23/04

Respiratory Protection used? Y / N TYPE / FILTER: _____

Sample device placement: D / R _____

| Chemicals for Analysis | Countermeasure |
|------------------------|----------------------------------|
| | Ventilation (type / performance) |
| | Eye / Face Protection |
| | Skin |
| | Foot |
| | Protective Apparel |

| | | | |
|-----------------|--|-----------------------|---------------------------------|
| Comments | <u>Smoking Break x 9:30 am / lunch 11 am - Putt stop pump/ remove Shut pump off, cap, remove apparatus → time: 910A, started @ 925 stopped 1053A</u> | | |
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| | | | |
| | PRODUCTION RECORD: | | |
| | Representative Conditions? Y / N | Blank sample #: _____ | Entered into IH database? Y / N |
| | Record Code: S-7790-740-006-000 | | |

Air Sampling Data Collection Form

Location: XXXXXXXXXX Department: Paint
 SEG Name: BPA-Paint Mix SEG Number: XXXXXXXXXX
 General Activities: Isocyanate Sampling Sample Date: 6/24/15
 Associate / #: XXXXXXXXXX
 Pump #: 03010 Calibration Standard: 132008 / Defendex S10

| Pump | Measurement description | Result | Method Standard | Note: Consult the air sampling pump manual for calibration instructions. | | | | | |
|---|------------------------------|---------------|-----------------|--|--|--|--|--|--|
| Pump on, verify flow using calibration standard, adjust | Pre-use calibration [L/min] | 0.2012 | Asset | | | | | | |
| Pump on, verify flow using calibration standard | Post-use calibration [L/min] | 0.2017 | | | | | | | |
| Battery Indicator | Battery Check | OK | | | | | | | |
| | Average Flow Rate [L/min] | 0.2015 | +/- 5% OK | (Pre + Post Calibration) / 2 | | | | | |
| | Sample Number | MAP-15-A-0031 | | | | | | | |
| Pump on | Start time | 6:44 AM | | | | | | | |
| Pump off | Stop time | 10:30 | | | | | | | |
| | Run time [Min] | 226 | | | | | | | |
| | Sample Volume [L] | 45.58 | | | | | | | |
| Cross out if not used | | | | | | | | | |

Sample collected by (print): Karthik Sivaraman

Modified for Hygieia
1/23/04

Respiratory Protection used? Y N TYPE / FILTER: _____

Sample device placement: D/R _____

| Chemicals for Analysis | Countermeasure |
|------------------------|----------------------------------|
| | Ventilation (type / performance) |
| | Eye / Face Protection |
| | Skin |
| | Foot |
| | Protective Apparel |

| | | | | |
|----------------------------------|--|---------------------------------|---------------------------------|--|
| Comments | <u>Non-Smoker / lunch 10:30 AM</u> <u>break - 8:30</u> <u>8:12a → moved media and tubing R → L side</u> <u>took pump off and set it on table.</u> | | | |
| | | | | |
| PRODUCTION RECORD: | | | | |
| Representative Conditions? Y / N | Blank sample #: _____ | Entered into IH database? Y / N | Record Code: S-7790-740-006-000 | |

Air Sampling Data Collection Form

Location: XXXXXXXXXX Department: Paint
 SEG Name: LI-Paint Mix SEG Number: XXXXXXXXXX
 General Activities: ISOCyanate Sampling Sample Date: 6/24/15
 Pump #: 17192 Associate / #: XXXXXXXXXX
 Calibration Standard: Terry 132008 DeGardur 500

| Pump | Measurement description | Result | Method Standard | Note: Consult the air sampling pump manual for calibration instructions. | | |
|---|------------------------------|--------------------------|---|--|--|--|
| Pump on, verify flow using calibration standard, adjust | Pre-use calibration [L/min] | <u>0.203</u> | Asset | | | |
| Pump on, verify flow using calibration standard | Post-use calibration [L/min] | <u>0.1994</u> | | | | |
| Battery Indicator | Battery Check | <u>OK.</u> | OK | | | |
| | Average Flow Rate [L/min] | 6.2003 | +/- 5% OK | (Pre + Post Calibration) / 2 | | |
| | Sample Number | MAP-15-A-0032 | | | | |
| Pump on | Start time | <u>653A</u> | | | | |
| Pump off | Stop time | <u>1004A.</u> | | | | |
| | Run time [Min] | 187 | | | | |
| | Sample Volume [L] | <u>37.46</u> | | | | |
| <i>Cross out if not used</i> | | | | | | |

Sample collected by (print): Karthik Swaraman

Modified for Hygieia
1/23/04

Respiratory Protection used? Y / N TYPE / FILTER: _____
 Sample device placement: L / R _____

| Chemicals for Analysis | Countermeasure |
|------------------------|----------------------------------|
| | Ventilation (type / performance) |
| | Eye / Face Protection |
| | Skin |
| | Foot |
| | Protective Apparel |

| | | | | | | |
|----------------------------------|---|-----------------------|---------------------------------|---------------------------------|--|--|
| Comments | <i>Break 800 → met 2750A Lunch 1600</i> | | | | | |
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| | | | | | | |
| | | | | | | |
| PRODUCTION RECORD: | | | | | | |
| Representative Conditions? Y / N | | Blank sample #: _____ | Entered into IH database? Y / N | Record Code: S-7790-740-006-000 | | |



AIHA Laboratory Accreditation Programs, LLC

acknowledges that

Bureau Veritas North America, Inc.

22345 Roethel Drive, Novi, MI 48375

Laboratory ID: 100967

along with all premises from which key activities are performed, as listed above, has fulfilled the requirements of the AIHA Laboratory Accreditation Programs (AIHA-LAP), LLC accreditation to the ISO/IEC 17025:2005 international standard, *General Requirements for the Competence of Testing and Calibration Laboratories* in the following:

LABORATORY ACCREDITATION PROGRAMS

| | |
|--|-----------------------------------|
| <input checked="" type="checkbox"/> INDUSTRIAL HYGIENE | Accreditation Expires: 08/01/2015 |
| <input checked="" type="checkbox"/> ENVIRONMENTAL LEAD | Accreditation Expires: 08/01/2015 |
| <input checked="" type="checkbox"/> ENVIRONMENTAL MICROBIOLOGY | Accreditation Expires: 08/01/2015 |
| <input type="checkbox"/> FOOD | Accreditation Expires: |
| <input type="checkbox"/> UNIQUE SCOPES | Accreditation Expires: |

Specific Field(s) of Testing (FoT)/Method(s) within each Accreditation Program for which the above named laboratory maintains accreditation is outlined on the attached **Scope of Accreditation**. Continued accreditation is contingent upon successful on-going compliance with ISO/IEC 17025:2005 and AIHA-LAP, LLC requirements. This certificate is not valid without the attached **Scope of Accreditation**. Please review the AIHA-LAP, LLC website (www.aihaaccreditedlabs.org) for the most current Scope.

A handwritten signature in black ink, appearing to read 'Larry S. Pierce'.

Larry S. Pierce
Chairperson, Analytical Accreditation Board

Revision 13: 03/12/2013

A handwritten signature in black ink, appearing to read 'Cheryl O. Morton'.

Cheryl O. Morton
Managing Director, AIHA Laboratory Accreditation Programs, LLC

Date Issued: 07/31/2013

AIHA Laboratory Accreditation Programs, LLC

SCOPE OF ACCREDITATION

Bureau Veritas North America, Inc.
22345 Roethel Drive, Novi, MI 48375

Laboratory ID: 100967
Issue Date: 02/26/2015

The laboratory is approved for those specific field(s) of testing/methods listed in the table below. Clients are urged to verify the laboratory's current accreditation status for the particular field(s) of testing/Methods, since these can change due to proficiency status, suspension and/or withdrawal of accreditation.

Industrial Hygiene Laboratory Accreditation Program (IHLAP)

Initial Accreditation Date: 06/01/1974

| IHLAP Scope Category | Field of Testing (FoT) | Technology sub-type/ Detector | Published Reference Method/Title of In-house Method | Method Description or Analyte (for internal methods only) |
|----------------------|------------------------|-------------------------------|---|---|
| Chromatography Core | Gas Chromatography | GC/FID | EPA 18 | |
| | | | EXXFID 1, 10, 11, 2, 3, 4, 5, 6, 7, 8, 9 | Proprietary |
| | | | GCIH11 | Siloxanes |
| | | | GCIH14 | Propyl Bromide |
| | | | GCIH21 | Decafluoropentane |
| | | | GCIH25 | Methyl Bromide |
| | | | GCIH27 | Dimethyl Sulfoxide (DMSO) |
| | | | GCIH29 | Acrylates |
| | | | GCIH43 | HFE-7100 & HFE-7200 |
| | | | GCIH54 | Bis (2-dimethylaminoethyl) ether |
| | | | GCIH61 | Aminofunctional Siloxanes |
| | | | GCIH71 | C7-C9 Alcohols |
| | | | GCIH80 | 2,2,2-Trifluoroethanol |
| | | | GCIH84 | Chloroformates and Phosgene |
| | | | GCIH90 | Polyfunctional Aziridine |
| | | | GCIH94 | Proprietary Compounds |
| | | | GCIH99 | Methyl Pyridine Isomers |
| | | | MON004 | Proprietary Compounds |
| | | | NIOSH 1000 | |
| | | | NIOSH 1001 | |

Effective: 03/12/2013

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| IHLAP Scope Category | Field of Testing (FoT) | Technology sub-type/ Detector | Published Reference Method/Title of In-house Method | Method Description or Analyte (for internal methods only) |
|----------------------|------------------------|-------------------------------|---|---|
| Chromatography Core | Gas Chromatography | GC/FID | NIOSH 1003 | |
| | | | NIOSH 1005 | |
| | | | NIOSH 1006 | |
| | | | NIOSH 1007 | |
| | | | NIOSH 1010 | |
| | | | NIOSH 1011 | |
| | | | NIOSH 1014 | |
| | | | NIOSH 1015 | |
| | | | NIOSH 1017 | |
| | | | NIOSH 1018 | |
| | | | NIOSH 1019 | |
| | | | NIOSH 1024 | |
| | | | NIOSH 1300 | |
| | | | NIOSH 1301 | |
| | | | NIOSH 1400 | |
| | | | NIOSH 1401 | |
| | | | NIOSH 1402 | |
| | | | NIOSH 1403 | |
| | | | NIOSH 1405 | |
| | | | NIOSH 1450 | t-Butyl Acetate (N1450) |
| | | | NIOSH 1450 | Esters I (OSH7) |
| | | | NIOSH 1453 | |
| | | | NIOSH 1500 | |
| | | | NIOSH 1500 (Modified) | |
| | | | NIOSH 1501 | |
| | | | NIOSH 1550 | |
| | | | NIOSH 1551 | |
| | | | NIOSH 1552 | |
| | | | NIOSH 1603 | |
| | | | NIOSH 1604 | |
| | | | NIOSH 1606 | |
| | | | NIOSH 1608 | |
| | | | NIOSH 1609 | |
| | | | NIOSH 1612 | |
| | | | NIOSH 1613 | |
| | | | NIOSH 1615 | |
| | | | NIOSH 1619 | |
| | | | NIOSH 2000 | |
| | | | NIOSH 2002 | |
| | | | NIOSH 2004 | |

| IHLAP Scope Category | Field of Testing (FoT) | Technology sub-type/ Detector | Published Reference Method/Title of In-house Method | Method Description or Analyte (for internal methods only) |
|----------------------|------------------------|-------------------------------|---|---|
| Chromatography Core | Gas Chromatography | GC/FID | NIOSH 2005 | |
| | | | NIOSH 2013 | |
| | | | NIOSH 2017 | |
| | | | NIOSH 2500 | |
| | | | NIOSH 2505 | |
| | | | NIOSH 2507 | |
| | | | NIOSH 2508 (Modified) | |
| | | | NIOSH 2510 | |
| | | | NIOSH 2519 | |
| | | | NIOSH 2521 | |
| | | | NIOSH 2526 | |
| | | | NIOSH 2527 | |
| | | | NIOSH 2529 | |
| | | | NIOSH 2530 | |
| | | | NIOSH 2537 | |
| | | | NIOSH 2545 | |
| | | | NIOSH 2546 | |
| | | | NIOSH 2553 | |
| | | | NIOSH 2554 (Modified) | |
| | | | NIOSH 2555 | |
| | | | NIOSH 2560 | |
| | | | NIOSH 5021 | |
| | | | NIOSH 5523 | |
| | | | NIOSH S-264 | |
| | | | OSHA 07 | |
| | | | OSHA 100 | |
| | | | OSHA 1002 | |
| | | | OSHA 1004 | |
| | | | OSHA 1005 | |
| | | | OSHA 1013 | |
| | | | OSHA 1014 | |
| | | | OSHA 103 | |
| | | | OSHA 104 | |
| | | | OSHA 106 | |
| | | | OSHA 111 | |
| | | | OSHA 29 | |
| | | | OSHA 35 | |
| | | | OSHA 56 | |
| | | | OSHA 59 | |
| | | | OSHA 72 | |

| IHLAP Scope Category | Field of Testing (FoT) | Technology sub-type/ Detector | Published Reference Method/Title of In-house Method | Method Description or Analyte (for internal methods only) |
|----------------------|------------------------|-------------------------------|---|---|
| Chromatography Core | Gas Chromatography | GC/FID | OSHA 80 | |
| | | | OSHA 82 | |
| | | | OSHA 89 | |
| | | | OSHA 91 | |
| | | | OSHA 94 | |
| | | | OSHA PV2003 | |
| | | | OSHA PV2009 | |
| | | | OSHA PV2010 | |
| | | | OSHA PV2011 | |
| | | | OSHA PV2016 | |
| | | | OSHA PV2019 | |
| | | | OSHA PV2020 | |
| | | | OSHA PV2021 | |
| | | | OSHA PV2022 | |
| | | | OSHA PV2025 | |
| | | | OSHA PV2026 | |
| | | | OSHA PV2033 | |
| | | | OSHA PV2039 | |
| | | | OSHA PV2040 | |
| | | | OSHA PV2041 | |
| | | | OSHA PV2047 | |
| | | | OSHA PV2048 | |
| | | | OSHA PV2053 | |
| | | | OSHA PV2060 | |
| | | | OSHA PV2077 | |
| | | | OSHA PV2078 | |
| | | | OSHA PV2079 | |
| | | | OSHA PV2080 | |
| | | | OSHA PV2101 | |
| | | | OSHA PV2108 | |
| | | | OSHA PV2118 | |
| | | | OSHA PV2123 | |
| | | | OSHA PV2130 | |
| | | | OSHA PV2141 | |
| | | GC/ECD | EPA 8081 | |
| | | | EPA 8082 | |
| | | | EPA TO-10 | |
| | | | EXXECD1 | Proprietary |
| | | | GCIH22 | Proprietary |
| | | | GCIH59 | Proprietary |

| IHLAP Scope Category | Field of Testing (FoT) | Technology sub-type/ Detector | Published Reference Method/Title of In-house Method | Method Description or Analyte (for internal methods only) |
|----------------------|------------------------|-------------------------------|---|---|
| Chromatography Core | Gas Chromatography | GC/ECD | GCIH60 | Proprietary Herbicides |
| | | | MON 003, 005, 006 | Proprietary Compounds |
| | | | NIOSH 2543 | |
| | | | NIOSH 5503 | |
| | | | NIOSH 5510 | |
| | | | NIOSH 5517 | |
| | | | NIOSH 5602 | |
| | | | NIOSH S-274 | |
| | | | OSHA 1010 | |
| | | | OSHA 1012 | |
| | | | OSHA 112 | |
| | | | OSHA 49 | |
| | | | OSHA 50 | |
| | | | OSHA 57 | |
| | | | OSHA 65 | |
| | | | OSHA 71 | |
| | | | OSHA 97 | |
| | | | OSHA PV2023 | |
| | | | OSHA PV2055 | |
| | | | OSHA PV2063 | |
| | | | OSHA PV2071 | |
| | | | OSHA PV2103 | |
| | | GC/NPD | GCIH10 | Formamide |
| | | | GCIH45 | Nitroanilines |
| | | | GCIH63 | Proprietary |
| | | | GCIH64 | Proprietary |
| | | | GCIH97 | Proprietary |
| | | | MON 001, 007, 008 | Proprietary |
| | | | NIOSH 1302 | |
| | | | NIOSH 2004 | |
| | | | NIOSH 2007 | |
| | | | NIOSH 2010 | |
| | | | NIOSH 2522 (Modified) | |
| | | | NIOSH 2544 | |
| | | | NIOSH 5293 | |
| | | | OSHA 21 | |
| | | | OSHA 37 | |
| | | | OSHA 52 | |
| | | | OSHA 61 | |
| | | | OSHA 66 | |

| IHLAP Scope Category | Field of Testing (FoT) | Technology sub-type/ Detector | Published Reference Method/Title of In-house Method | Method Description or Analyte (for internal methods only) |
|----------------------|---|-------------------------------|---|---|
| Chromatography Core | Gas Chromatography | GC/NPD | OSHA CSI | Cyanogen Chloride |
| | | | OSHA PV2096 | |
| | | GC/FPD | APCA | Proprietary |
| | | | GCIH12 | Diethyl Sulfate |
| | | | GCIH38 | Proprietary Compound |
| | | | GCIH5 | 2-Mercaptoethanol |
| | | | GCIH56 | Phosphorous |
| | | | GCIH6 | Dimethyl Disulfide and Dimethyl Sulfide |
| | | | GCIH70 | Organotins |
| | | | GCIH73 | Organotins |
| | | | NIOSH 1600 | |
| | | | NIOSH 2524 | |
| | | | NIOSH 2525 | |
| | | | NIOSH 2542 | |
| | | GC/MS | NIOSH 5034 | |
| | | | NIOSH 5037 | |
| | | | NIOSH 5038 | |
| | | | NIOSH 5526 | |
| | | | NIOSH 5600 | |
| | | | NIOSH 7905 | |
| | | | OSHA 62 | |
| | | | OSHA PV2075 | |
| | | | EPA TO-15 | |
| | | | EPA TO-17 | |
| Chromatography Core | Gas Chromatography (Diffusive Samplers) | | EXX MS PNA | |
| | | | NIOSH 2549 | |
| | | | 3M Guidance | |
| | | | AT Labs Guidance | |
| | | | OSHA 1001 | |
| | | | OSHA 1002 | |
| | | | OSHA 1004 | |
| | | | OSHA 1005 | |
| | | | OSHA 1009 | |
| | | | OSHA 111 | |
| | Ion Chromatography (IC) | | OSHA 7 | |
| | | | SKC Guidance | |
| | | | NIOSH 2011 | |
| | | | NIOSH 6004 | |

| IHLAP Scope Category | Field of Testing (FoT) | Technology sub-type/ Detector | Published Reference Method/Title of In-house Method | Method Description or Analyte (for internal methods only) |
|----------------------|-------------------------|-------------------------------|---|---|
| Chromatography Core | Ion Chromatography (IC) | | NIOSH 6016 | |
| | | | NIOSH 7903 | |
| | | | OSHA ID-1008 | |
| | | | OSHA ID-101 | |
| | | | OSHA ID-1011 | |
| | | | OSHA ID-108 | |
| | | | OSHA ID-111 | |
| | | | OSHA ID-113 | |
| | | | OSHA ID-182 | |
| | | | OSHA ID-186 | |
| | | | OSHA ID-190 | |
| | | | OSHA ID-200 | |
| | | | OSHA ID-211 | |
| | | | OSHA ID-214 | |
| | | | OSHA ID-215 | |
| | | | OSHA PV2115 | |
| | | | OSHA PV2119 | |
| | | | OSHA W4001 | |
| | | | WCIC1 | Oxalic Acid |
| Chromatography Core | Liquid Chromatography | HPLC/FL | NIOSH 5041 | |
| | | | NIOSH 5521 | |
| | | | NIOSH 5525 | |
| | | | OSHA 54 | |
| | | HPLC/UV | EPA IP-6 | |
| | | | EPA TO-11 | |
| | | | EXXLC1 | Tetraethyl Lead on XAD-2 Sorbent Tubes by HPLC/UV |
| | | | LC109 | Proprietary Herbicide |
| | | | LC167 | Proprietary Method for Proprietary Herbicide |
| | | | LC168 | Proprietary Compounds |
| | | | LC187 | Dicumyl Peroxide |
| | | | LC197 | Bis (4-chlorophenyl) sulphone |
| | | | LC200 | Peroxyacetic Acid on Treated Sorbent Tubes by HPLC/UV |
| | | | LC3 | Acylamide and Acrylic Acid |
| | | | MDA_HUN | Methylenedianiline |
| | | | MON002 | Proprietary |

| IHLAP Scope Category | Field of Testing (FoT) | Technology sub-type/ Detector | Published Reference Method/Title of In-house Method | Method Description or Analyte (for internal methods only) |
|----------------------|------------------------|-------------------------------|---|---|
| Chromatography Core | Liquid Chromatography | HPLC/UV | NIOSH 2014 | |
| | | | NIOSH 2016 | |
| | | | NIOSH 2514 | |
| | | | NIOSH 2532 | |
| | | | NIOSH 2540 | |
| | | | NIOSH 333 | |
| | | | NIOSH 5001 | |
| | | | NIOSH 5003 | |
| | | | NIOSH 5004 | |
| | | | NIOSH 5008 | |
| | | | NIOSH 5009 | |
| | | | NIOSH 5029 | |
| | | | NIOSH 5031 | |
| | | | NIOSH 5506 | |
| | | | NIOSH 5521 | |
| | | | NIOSH 5525 | |
| | | | NIOSH 5601 | |
| | | | NIOSH 5700 | |
| | | | Omega ISO-CHEK | Isocyanates |
| | | | OSHA 1007 | |
| | | | OSHA 104 | |
| | | | OSHA 108 | |
| | | | OSHA 25 | |
| | | | OSHA 28 | |
| | | | OSHA 32 | |
| | | | OSHA 39 | |
| | | | OSHA 40 | |
| | | | OSHA 41 | |
| | | | OSHA 42 | |
| | | | OSHA 45 | |
| | | | OSHA 47 | |
| | | | OSHA 54 | |
| | | | OSHA 55 | |
| | | | OSHA 58 (Modified) | |
| | | | OSHA 60 | |
| | | | OSHA 63 | |
| | | | OSHA 64 | |
| | | | OSHA 70 | |
| | | | OSHA 86 | |
| | | | OSHA 87 | |

| IHLAP Scope Category | Field of Testing (FoT) | Technology sub-type/ Detector | Published Reference Method/Title of In-house Method | Method Description or Analyte (for internal methods only) |
|----------------------|----------------------------|-------------------------------|---|---|
| Chromatography Core | Liquid Chromatography | HPLC/UV | OSHA 90 | |
| | | | OSHA 95 | |
| | | | OSHA 98 | |
| | | | OSHA PV2004 | |
| | | | OSHA PV2005 | |
| | | | OSHA PV2012 | |
| | | | OSHA PV2016 | |
| | | | OSHA PV2032 | |
| | | | OSHA PV2034 | |
| | | | OSHA PV2046 | |
| | | | OSHA PV2055 | |
| | | | OSHA PV2059 | |
| | | | OSHA PV2067 | |
| | | | OSHA PV2092 | |
| | | LC/MS | OSHA PV2094 | |
| | | | OSHA PV2125 | |
| | | | OSHA PV2126 | |
| | | | OSHA PV2135 | |
| | | | ISO 17734 | |
| | | | LCMS004 | Proprietary |
| | | | LCMS006 | Proprietary |
| | | | LCMS008W | Perfluorooctanoic Acid (Wipe) |
| Spectrometry Core | Atomic Absorption | CVAA | LCMS008W | Perfluorooctanoic Acid |
| | | | LCMS013 | Proprietary |
| | | | LCMS016W | Proprietary |
| | Inductively-Coupled Plasma | ICP/MS | NIOSH 6009 | |
| | | | OSHA ID-140 | |
| | | | OSHA ID-145 | |
| | | | MEIH3 | Metals/Elements by ICP/MS |
| | | | MEIH4 | Metals/Elements by ICP/MS |
| | | | NIOSH 6001 (Modified) | |
| | | | NIOSH 6007 (Modified) | |
| | | ICP/AES | NIOSH 7300 (Modified) | |
| | | | NIOSH 7303 (Modified) | |
| | | | OSHA ID-125 (Modified) | |
| | | | PZR70-AA | Cisplatin |
| | | | 40 CFR 50, Appendix G | Lead on Hi-Vol Filters |
| | | | NIOSH 7300 (Modified) | |

| IHLAP Scope Category | Field of Testing (FoT) | Technology sub-type/ Detector | Published Reference Method/Title of In-house Method | Method Description or Analyte (for internal methods only) |
|-------------------------------|-------------------------------|-------------------------------|---|--|
| Spectrometry Core | Inductively-Coupled Plasma | ICP/AES | NIOSH 7301 | |
| | | | NIOSH 7303 (Modified) | |
| | | | NIOSH 7901 (Modified) | |
| | | | NIOSH 9102 (Modified) | |
| | | | OSHA 1003 | |
| | | | OSHA ID-125 | |
| | | | TIO2_F | Titanium Dioxide |
| | X-ray Diffraction (XRD) | | NIOSH 7500 | |
| | | | NIOSH 7506 | |
| | UV/VIS (Colorimetric) | | ID 124 Modified | Hydrogen Peroxide on Treated Quartz Filters By Hect et, al 2004 |
| | | | NIOSH 3500 | |
| | | | NIOSH 6010 | |
| | | | NIOSH 6014 | |
| | | | NIOSH 7600 | |
| | | | OSHA ID-124 | |
| | | | OSHA ID-205 | |
| | | | WCIH3 | Proprietary |
| | | | NIOSH 5026 | |
| | Infrared | | | |
| Miscellaneous Core | Titrimetric | | NIOSH 7401 | |
| | Gravimetric | | MDHS 14/3 | |
| | | | NIOSH 0500 | |
| | | | NIOSH 0600 | |
| | | | NIOSH 5000 | |
| | | | NIOSH 5042 | |
| | | | NIOSH 5524 | |
| | | | OSHA 58 | |
| | | | OSHA ID-196 | |
| | Ion-selective electrode (ISE) | | NIOSH 7902 | |
| | | | NIOSH 7904 | |
| | | | NIOSH S-347 | |
| | | | OSHA ID-110 | |
| | | | OSHA ID-110 (Modified) | |
| | | | OSHA ID-120 | |
| | | | OSHA ID-212 | |
| | Thermo-optical Analysis (TOA) | | NIOSH 5040 | |
| Pharmaceutical Testing | Liquid Chromatography | HPLC/ FL | LCP Various | Proprietary |

| IHLAP Scope Category | Field of Testing (FoT) | Technology sub-type/ Detector | Published Reference Method/Title of In-house Method | Method Description or Analyte (for internal methods only) |
|-------------------------------|----------------------------|-------------------------------|---|---|
| Pharmaceutical Testing | Liquid Chromatography | HPLC/ UV | LC Various | Proprietary |
| | | | LCMSPZR Various | Proprietary |
| | | | LCP Various | Proprietary |
| | | | NIOSH 5044 | |
| | | | OSHA PV2001 | |
| | | LC/MS | LCMS002 | Proprietary |
| | | | LCMS002W | Proprietary |
| | | | LCMS003W | Proprietary |
| | | | LCMS005 | Proprietary |
| | | | LCMS007 | Proprietary |
| Beryllium Testing | Inductively-Coupled Plasma | ICP/MS | LCMS009 | Proprietary |
| | | | LCMS010W | Proprietary |
| | | | LCMS011 | Proprietary |
| | | ICP/AES | ID-125 (Modified) | |
| | | | NIOSH 7300 (Modified) | |
| | | | NIOSH 7303 (Modified) | |
| | | | EPA SW-846 3050B (Modified) | |
| | | | EPA SW-846 6010C | |
| | | | EPA SW-846 6020A | |
| | | | NIOSH 7300 (Modified) | |
| | | | NIOSH 7303 (Modified) | |
| | | | OSHA ID-125 | |

A complete listing of currently accredited Industrial Hygiene laboratories is available on the AIHA-LAP, LLC website at: <http://www.aihaaccreditedlabs.org>

AIHA Laboratory Accreditation Programs, LLC

SCOPE OF ACCREDITATION

Bureau Veritas North America, Inc.
22345 Roethel Drive, Novi, MI 48375

Laboratory ID: **100967**
Issue Date: 07/31/2013

The laboratory is approved for those specific field(s) of testing/methods listed in the table below. Clients are urged to verify the laboratory's current accreditation status for the particular field(s) of testing/Methods, since these can change due to proficiency status, suspension and/or withdrawal of accreditation.

The EPA recognizes the AIHA-LAP, LLC ELLAP program as meeting the requirements of the National Lead Laboratory Accreditation Program (NLLAP) established under Title X of the Residential Lead-Based Paint Hazard Reduction Act of 1992 and includes paint, soil and dust wipe analysis. Air analysis is not included as part of the NLLAP.

Environmental Lead Laboratory Accreditation Program (ELLAP)

Initial Accreditation Date: 07/15/1999

| Field of Testing (FoT) | Method | Method Description (for internal methods only) |
|-------------------------------|--------------------------------|---|
| Paint | EPA SW-846 3050B (Modified) | |
| | EPA SW-846 6010C | |
| | EPA SW-846 6020A | |
| Soil | EPA SW-846 3050B (Modified) | |
| | EPA SW-846 6010C | |
| | EPA SW-846 6020A | |
| Settled Dust by Wipe | EPA SW-846 3050B (Modified) | |
| | EPA SW-846 6010C | |
| | EPA SW-846 6020A | |
| | NIOSH 9102 (Modified) | |
| | OSHA ID-125 | |
| | OSHA ID-125 (Modified) | |
| Airborne Dust | 40 CFR 50, Appendix G | Lead on Hi-Vol Filters |
| | NIOSH 7300 (Modified) | Prep & Analysis of Filters by ICP-OES |
| | NIOSH 7300 (Modified) | Metals Scan Elements by ICP/MS |
| | NIOSH 7303 (Modified) | Metals Scan Elements by ICP/MS |
| | NIOSH 7303 (Modified) | Prep & Analysis of Filters by ICP-OES |
| | OSHA ID-125 | |
| | OSHA ID-125 (Modified) | |



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AIHA Laboratory Accreditation Programs, LLC

SCOPE OF ACCREDITATION

Bureau Veritas North America, Inc.
22345 Roethel Drive, Novi, MI 48375

Laboratory ID: **100967**
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Environmental Microbiology Laboratory Accreditation Program (EMLAP)

Initial Accreditation Date: 09/01/2003

| EMLAP Category | Field of Testing (FoT) | Method | Method Description (for internal methods only) |
|----------------|------------------------------|--|---|
| Fungal | Air - Culturable | Air CAMNEA Fungal Culturing, Analysis, and Calculations Air (processed Fungal Culturing, Analysis and Calculations | |
| | Bulk - Culturable | Bulk Fungal Culturing, Analysis, and Calculations | |
| | Surface - Culturable | Swab Fungal Culturing, Analysis, and Calculations | |
| | Air - Direct Examination | Total Fungal Structures in Air | |
| | Bulk - Direct Examination | Direct Microscopic Assessment for Fungi | |
| | Surface - Direct Examination | Direct Fungal Examination of Samples | |

A complete listing of currently accredited Environmental Microbiology laboratories is available on the AIHA-LAP, LLC website at: <http://www.aihaaccreditedlabs.org>



RESEARCH INTEGRITY AND COMPLIANCE
Institutional Review Boards, FWA No. 00001669
12901 Bruce B. Downs Blvd., MDC035 • Tampa, FL 33612-4799
(813) 974-5638 • FAX (813) 974-7091

1/25/2016

Karthik Sivaraman
Environmental and Occupational Health
300 Legacy Dr.
Plano, TX 75023

RE: Not Human Subjects Research Determination

IRB#: Pro00024887

Title: Hexamethylene Diisocyanate Homopolymer and Monomer Exposure Assessment and Characterization at an Automobile Manufacturer in the United States

Dear Mr. Sivaraman:

The Institutional Review Board (IRB) has reviewed your application and determined the activities do not meet the definition of human subjects research. Therefore, this project is not under the purview of the USF IRB and approval is not required. If the scope of your project changes in the future, please contact the IRB for further guidance.

All research activities, regardless of the level of IRB oversight, must be conducted in a manner that is consistent with the ethical principles of your profession. Please note that there may be requirements under the HIPAA Privacy Rule that apply to the information/data you will utilize. For further information, please contact a HIPAA Program administrator at 813-974-5638.

We appreciate your dedication to the ethical conduct of research at the University of South Florida. If you have any questions regarding this matter, please call 813-974-5638.

Sincerely,

A handwritten signature in blue ink, reading "Vjorgensen MD". The signature is fluid and cursive, with "Vjorgensen" being the first name and "MD" being the title.

E. Verena Jorgensen, M.D., Chairperson
USF Institutional Review Board