CPWR TECHNICAL REPORT

Risk of Isocyanate Exposure in the Construction Industry

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CPWR THE CENTER FOR CONSTRUCTION RESEARCH AND TRAINING

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Abstract

Background
Isocyanates are reactive chemicals used extensively in the production of polyurethane foams, coatings, and adhesives, and are a leading cause of occupational asthma. A number of construction sites in Connecticut are using polyurethane (PU) products. This study focuses on identifying and collecting data on PU products that are commonly used and most likely to present skin exposure risk to applicators or others in the work area. A major concern when working with PU products is the extent to which free isocyanate groups may persist on the surface of the material following application. Such information is necessary for understanding the potential for isocyanate skin exposure that could lead to asthma or other respiratory outcomes in product applicators or bystanders.

Methods
A database of information was compiled on PU products commonly used in construction. Five PU foam products were tested, some more than once, to determine amount of free surface NCO over time, using both qualitative and quantitative SWYPE^{TM} pads. Decay curves were generated. Core samples of the dry foam were also analyzed for free NCO. To determine the utility of the qualitative SWYPE^{TM} pads, they were correlated to quantitative samples.

Results
Polyurethane foams have variable curing times and can have free NCO after they appear dry. There is a need for skin protection when handling foam. The core of the polyurethane foam may not be fully cured for as long as 24 hours after application and can release free NCO if punctured or otherwise disturbed. Qualitative aromatic SWYPE^{TM} pads are not as reliable as aliphatic pads, but a negative test appears to indicate a lower level of NCO. Further study is needed with other products and particularly more industrial ones.

Key Findings

1) Polyurethane foams have variable curing times and can have free NCO after they appear dry. There is a need for skin protection when handling foam.

2) The core of the polyurethane foam may not be fully cured for as long as 24 hours after application and can release free NCO if punctured or otherwise disturbed.

3) Qualitative aromatic SWYPE^{TM} pads are not as reliable as aliphatic pads, but a negative test appears to indicate a lower level of NCO.

4) Further study is needed with other products and particularly more industrial ones.

Final Report

Isocyanates are reactive chemicals used extensively in the production of polyurethane foams, coatings, and adhesives, and are a leading cause of occupational asthma. A number of construction sites in Connecticut are using polyurethane (PU) products. This study focuses on identifying and collecting data on PU products that are commonly used and most likely to present skin exposure risk to applicators or others in the work area. A major concern when working with PU products is the extent to which free isocyanate groups may persist on the surface of the material following application. Such information is necessary for understanding the potential for isocyanate skin exposure that could lead to asthma or other respiratory outcomes in product applicators or bystanders.

Objectives and Results

Aim 1) Identify the more commonly used PU products in the construction industry and determine the extent to which free NCO may persist on the surfaces of these products after end-user application.

Aim 1A) Identify the more commonly used PU products in the construction industry, such as PU spray foam.

Information on PU products is often scattered, difficult to find, and variable in accuracy. For this task, internet searches, emails and phone calls to manufacturers and distributors, visits to home improvement stores, and discussion with industry workers generated a list of major construction products. Product material safety data sheets, technical sheets, and labels were consulted to verify the presence of isocyanate in the chemical composition of these products. At this time, over 100 products, including foam insulation, adhesives, caulking, and sealants have been compiled in a database (see attached Table 1). This database includes information on chemical composition, type of isocyanate, presence of other potentially hazardous ingredients, and product characteristics, as well as links to manufacturer websites for more information.

Notably, in all the collected relevant information, many product manufacturers and distributors did not provide the time at which the applied product was fully cured and safe to the touch, having no detectable free isocyanate groups. This lack of data is an issue in protecting workers from health risk due to skin contact with PU products during the application process.

We are continuing to add to this product database as we proceed with our CPWR construction grant (OH009375). Ultimately, this database of available information could be a resource to the construction industry, and could be disseminated to individuals who work with PU products to increase knowledge of the materials that are used.

Aim 1B) Evaluate the extent to which free NCO may be present on the surface of these PU products after end-user application, and persist over time (curing time).

To determine the amount of unbound isocyanate after application, five different representative, mostly home-use, PU foam products were tested by wipe sampling. Product selection focused mainly on PU spray foams listing MDI as a primary component. In order to provide a representation of materials used in the construction industry, both open and closed cell foam products from a number of different major manufacturers were tested. Open cell products are more flexible and less dense, and are typically marketed towards the do-it-yourself consumer. Closed cell formulations produce a more rigid, dense foam and are used mainly by insulation professionals. Two of these products were tested twice, in different ambient temperature and humidity conditions. Three additional products have been tested and are awaiting lab analysis.

After application, the foam product was allowed to harden until it was considered "tack-free" or no longer rising, from 30 seconds up to twenty minutes after application depending on product. This "tack-free" time was noted as time zero. Paired wipe samples, including both a qualitative and quantitative wipe, were collected at intervals of 5 minutes for the first half hour, then at one hour, 2 hours, end of the work shift, 24 hours, and 48 hours. The number of sampling points within the first half hour was increased from our initial proposal, after observing that the presence of unbound isocyanate may decrease more quickly immediately after application. Paired samples were taken from areas 5x5 cm^2 using a qualitative SWYPE™ pad and a quantitative pad (Colormetric Laboratories, Inc., Des Plaines, IL). In the presence of unbound isocyanate, the SWYPE™ pad changes from a pale yellow to a range of oranges. Changes in color intensity were noted at each time interval.

Paired quantitative wipe samples were taken and immediately placed into vials containing derivatizing solution (MAP (1-(9-anthracenylmethyl) piperazine). Samples were shipped to Dr. Dhimiter Bello's lab for quantitative analysis using HPLC methodology to determine the amount of free isocyanate (NCO) that was transferred from the surface of the material to the wipe pad. Duplicates and triplicates of the samples were taken to assess accuracy and validity of the testing method, as well as bulk samples of the PU foam product. In total, 116 samples have been analyzed; another 53 samples are pending analysis.

Figure 1. The amount of MDI (ug NCO) detected on the surface of several PU foam products over time, starting when the product appeared dry and tack free (time 0).

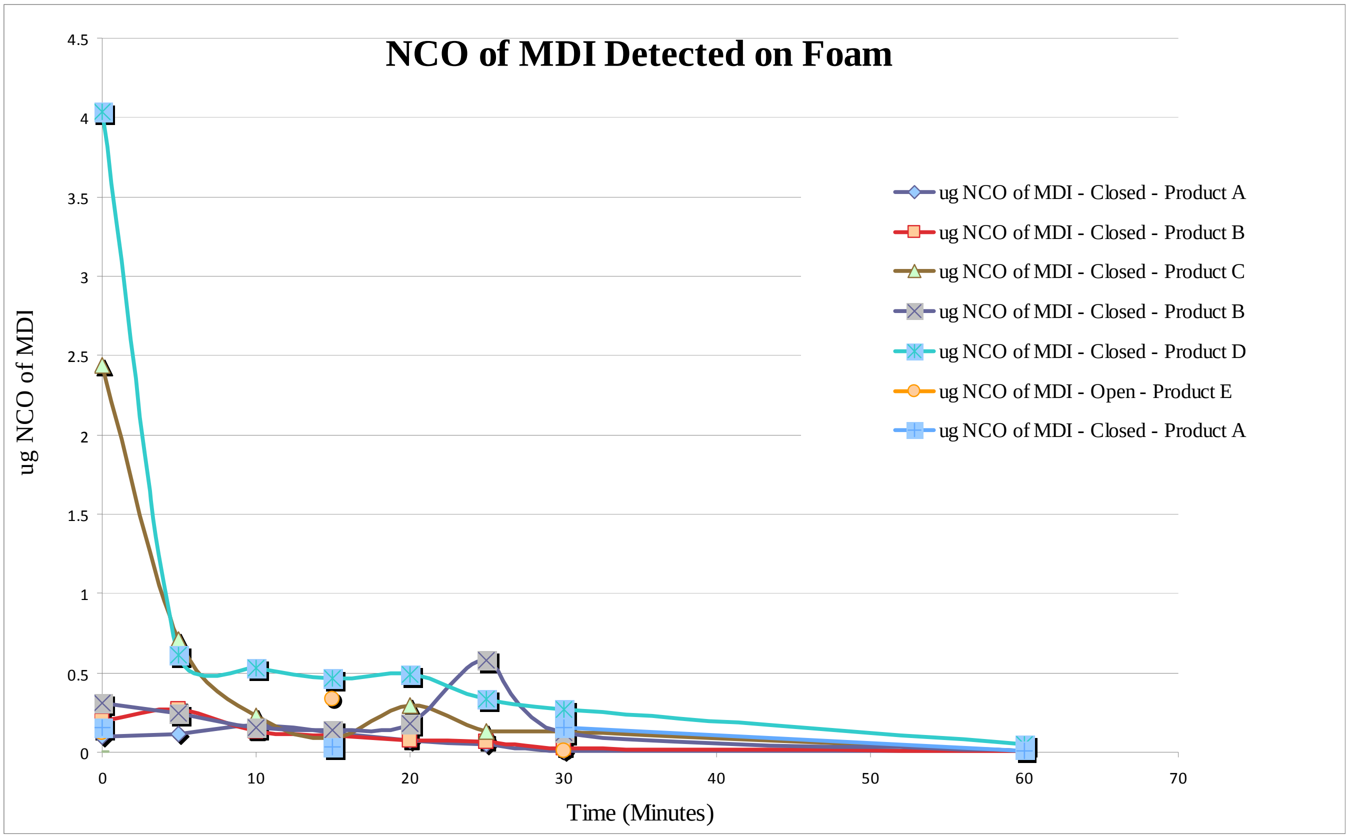
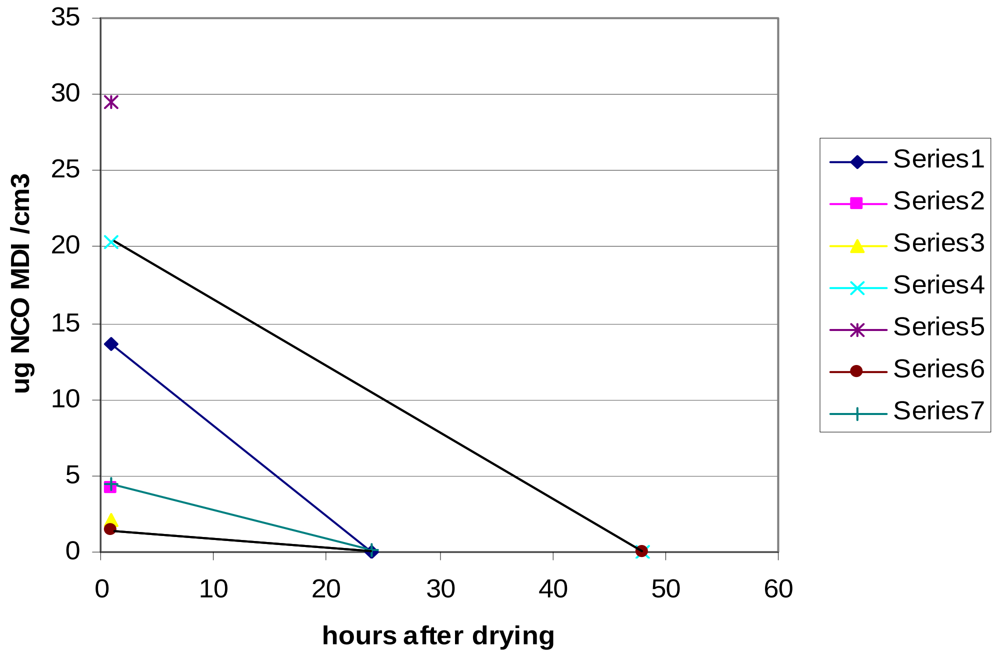


Figure 1 shows decay curves of the 5 different PU products. Of note, of the products tested to date, those products marketed for home use by the consumer showed lower initial free isocyanate (NCO) levels than those products designed to be applied by a contractor (the two higher initial NCO levels in Figure 2).

Figure 2: Foam Cores



In addition to qualitative and quantitative surface wipe samples, we also used punch biopsy tools to extract cores from the foam product. These cores of the full thickness of foam were taken 60 minutes, 24 and 48 hours after application. To date 11 core samples have been analyzed by Dr. Bello to determine the amount of free isocyanate in the product.

Results of the core biopsies indicate that PU products are not fully cured when they appear tack free, and that free NCO in the product decreases over time following application but can persist 24 hrs after application (Figure 2). An additional 4 core samples await lab analysis.

Aim 2) Evaluate the extent to which particles and dust that construction workers are likely to have contact with contain free NCO.

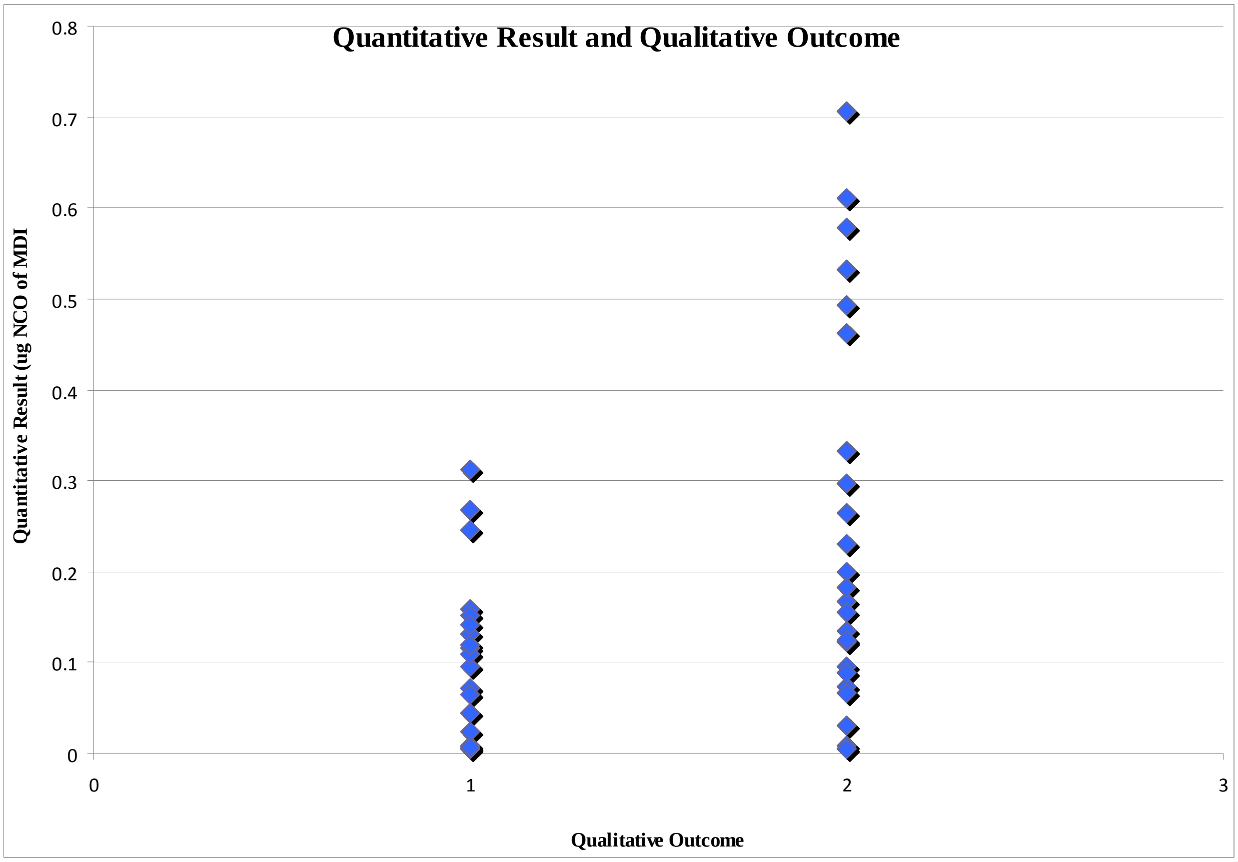
This is a critical question, but field sampling and analytical laboratory methods may need further laboratory development to enable the detection of free NCO on dust particles. Currently, we are developing approaches to evaluate the free isocyanate content of particles and dust that workers are likely to have contact with. One method we are pursuing is to re-create dust conditions by sanding or filing the surface of applied polyurethane foam. Initial results are pending lab analysis.

Aim 3) Evaluate the performance and utility of the inexpensive, rapid and practical qualitative aromatic SWYPE™ colorimetric indicators, using paired HPLC quantitative laboratory analysis.

In order to have a practical tool that can be used to assess surface and skin aromatic (MDI) isocyanate exposures in construction work settings, we have attempted to validate the easy to use and cost effective SWYPE™ colorimetric wipe sampling pad against our more sensitive and costly quantitative wipe sampling method. While utilizing SWYPE™ wipes for Aim 1B, we performed side-by-side sampling with quantitative wipe samples, which were shipped to UMass Lowell for analysis in Dr. Bello's laboratory. 83 paired samples have been obtained; 57 have been analyzed and 26 more are pending analysis.
Quantitative samples ranged from <0.005 (Limit of Detection) to 0.74 ug MDI NCO in these tests. In general, the qualitative SWYPE™ samples provide only a rough indication of the presence of isocyanate. Intensity of color change on the wipes did not dramatically change across products or intervals tested, and this color change was often faint and difficult to assess. As an unanticipated outcome, the surface of the foam product itself, in addition to or instead of the SWYPE™ pad, tended to exhibit a color change after sampling.

The aromatic (MDI) SWYPE™ wipes appear to be less specific and sensitive than their aliphatic counterpart but negative readings appear to indicate low levels of free MDI NCO (Figure 3). The first column is negative qualitative values of the SWYPE™ indicators; the second is the positive values. Modifications that may improve the performance of these SWYPE™ indicators may be explored given their potential usefulness for workers.

Figure 3. Comparison of the quantitative amount of MDI detected on contaminated surfaces and the corresponding qualitative SWYPE™ result. Outcome 1=Negative qualitative SWYPE™, Outcome 2 = positive qualitative SWYPE™



More sampling will be done to determine the performance of SWYPEs across the range of exposures encountered in the CPWR construction grant (OH009375).

Publications or Presentations

1) Turek SJ. Isocyanate Exposure Potential In Construction Industry Polyurethane Product Use. 2010. MPH Thesis. Yale library.

2) Turek SJ, Opare-Addo P, Stowe MH, Sparer J, Redlich, CA. Risk of Isocyanate Exposure in the Construction Industry. 2010. In preparation.