Isocyanate Curing Times—Is It Dry Yet?

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Outline

1. Overview of isocyanates
2. Study design, materials and methods
3. Results
4. Discussion
5. Conclusions
I. Isocyanates and Their Structures
Isocyanates

• A group of light weight highly reactive chemicals
• Contain NCO functional group
• Aromatic
  ▪ TDI: toluene diisocyanate
  ▪ MDI: methylene diphenyl diisocyanate
• Aliphatic
  ▪ HDI: hexamethylene diisocyanate
  ▪ IPDI: isophorone diisocyanate
  ▪ HMDI: Dicyclohexylmethane 4, 4 – diisocyanate
Aliphatic Isocyanates

- 4,4'-Methylenedicyclohexyl diisocyanate (HMDI)
- Isophorone diisocyanate (IPDI)
- HDI Biuret
- HDI Isocyanurate
- HDI monomer

OCN

HDI monomer

OCN

HDI Isocyanurate

OCN

HDI Biuret

OCN

OCN

4,4'-Methylenedicyclohexyl diisocyanate (HMDI)
Diisocyanate Functional Group

• Each unit contains two free NCO groups which are available for cross-reactions:

$$\text{N} = \text{C} = \text{O}$$

• Functional groups are able to form bonds with polyols and water:

$$\text{HO-}R_1\text{-OH + OCN-}R_2\text{-NCO} \rightarrow \text{OCN-}R_2\left[\begin{array}{c}
\text{NH-C-O-R}_1\text{-O-C-NE-R}_2 \\
\text{NCO}
\end{array}\right]$$

Polyol  Diisocyanate  Polyurethane
Isocyanates and Asthma

- Isocyanates can cause sensitization leading to asthma
- Most commonly identified cause of occupational asthma
- 25% of all asthma cases in developed countries
- 5 - 20% of those exposed develop asthma
- >1/2 persistent after removal from exposure
- Asthma cases reported with auto body shop painters
Skin Exposure and Sensitization

• Animal studies
  ▪ Dermal contact with TDI causes airway hyperreactivity
  ▪ Intradermal injection used as effective way to induce sensitization of Guinea pigs
  ▪ Subsequent exposure induces pulmonary reaction
  ▪ HDI mouse model developed at Yale

• Human studies
  ▪ Data limited
  ▪ Mechanism in humans is unknown
  ▪ MDI skin stain found with higher asthmatic-like symptoms in a wood processing plant
Isocyanates and Regulation

- OSHA standards for airborne exposure
  - MDI monomer: 0.05 mg/m³ (0.02 ppm)
  - TDI monomer: 0.14 mg/m³ (0.02 ppm)
  - HDI monomer: none
  - MDI pre-polymers: none
  - TDI pre-polymers: none
  - HDI pre-polymers: none

- No other forms of isocyanate are currently regulated, nor are other routes of exposure in the USA (eg., dermal)
Auto Body Shop Refinishing

• Frame straightening and dent repair
• Replacement of damaged parts
• Spray painting (primer, sealer, basecoat and clearcoat)
• Drying (baking) of painted car or car parts
• Detailing (buffing, compounding and wash)
Isocyanates in Coatings

Contained in hardeners (activators) in specific ratios

[eg., primer : hardener : reducer (3 : 1 : 1)]

• **Primer**: contains isocyanates
• **Sealer**: contains isocyanates
• **Base coat**: no isocyanates
• **Clear coat**: contains isocyanates
Skin Contact Before Baking

Paint Mixing

Priming

Wet Sanding

Clear Coating
Heat Curing Mechanisms

- **Short-Wave Heat Lamp**
  - (Infrared waves utilized to dry from inside outward)

- **Down-Draft Booth**
  - (120°F for 25 Minutes)
Skin Contact After Baking

Un-Taping

Buffing/Compounding

Polishing

Detailing
III. Study Hypothesis, Objectives, Design and Methods
Hypothesis

• Isocyanates on the coated automobile surfaces do not fully cure following a curing period
• Free NCO groups will continue to be available for a prolonged period of time
• Uncured NCO groups provide contact exposure opportunities
Objectives

1. Determine the curing time
2. Evaluate any differences by curing method
3. Examine the relationship between qualitative vs. quantitative assessments
Curing Time

- Defined in this study as the time required, following the completion of painting or baking, to achieve a negative test (no color change on qualitative pads)
Study Design and Methods: Determining Curing Time

- 23 autobody parts assessed
- Coating type: priming or clear coating
- Curing mechanisms: heat lamp, booth baking and air
- A qualitative CLI Surface SWYPE™ pad used
- Samples taken at regular intervals until a negative test is achieved
Sampling Set-Up
CLI Surface SWYPE™

- Each grid wiped 3 times
- Start from outside, moving inside concentrically
- Pad changed color when in contact with free NCO
- Color intensity proportional to free NCO
Color Rating Scale

- No Color                      0
  (Actual pad color)
- Light orange                  1+
- Orange                        2+
- Deep orange                   3+
- Red-orange                    4+
- Deep red                      5+
Quantitative Sampling

- 2 autobody parts assessed
- Qualitative and quantitative done side by side
- Wiping conducted for each time point
- Same wiping method
Quantitative Wipe

- 4 x 4 cm² polypropylene glycol (PPG) moistened pad used
- Wore clean nitrile gloves for wiping
- Pad immediately placed in a vial containing 1-9-anthracenylmethyl piperazine (MAP) in methylene chloride for derivatization
- Analyzed using HPLC
IV. Results
Overview of NCO Availability vs. Time Across 5 Sampled Paint Formulations

For Qualitative Results
## Summary Results

<table>
<thead>
<tr>
<th>Group</th>
<th>GM</th>
<th>GSD</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Series (n=23)</td>
<td><strong>49.3 hrs</strong></td>
<td>3.73</td>
<td>0.8–768 hrs</td>
</tr>
<tr>
<td>Clearcoat (n=16)</td>
<td>66 hrs</td>
<td>2.66</td>
<td>0.8–768 hrs</td>
</tr>
<tr>
<td>Air Cured (n=3)</td>
<td><strong>157.9 hrs</strong></td>
<td>1.33</td>
<td>98–334.5 hrs</td>
</tr>
<tr>
<td>Heat Cured (n=13)</td>
<td>53.9 hrs</td>
<td>2.91</td>
<td>0.8–768 hrs</td>
</tr>
</tbody>
</table>
Qualitative Comparison of Air vs. Heat Dry Methods on NCO Availability for Auto Parts Coated with Brand 4 Clearcoat
Comparison of Paired Qualitative Surface SWYPE Positivity and Total NCO (uG) vs. Time for Sample 22

Brand 4, Clearcoat, Baked

Time (hours) vs. Qualitative Result (positivity) vs. Total NCO (ug)

- Pink line: Qualitative Result
- Green line: Quantitative Result

Sample data points:
- Time: 0.5, Total NCO: 2.9, Qualitative Result: 3.5
- Time: 2.9, Total NCO: 2.98, Qualitative Result: 3.1
- Time: 3.98, Total NCO: 50.48, Qualitative Result: 2.7
- Time: 50.48, Total NCO: 272.68, Qualitative Result: 2
V. Discussion, Recommendations and Conclusions
Limitations

• Sample size small in each type
• Unable to determine effects of other factors: temperature and humidity, paint manufacturers (brand), amount of paint used
• Quantitative measurement conducted with only 2 car parts
Conclusions

• Isocyanate functional groups (NCO) remain on surfaces for prolonged periods of time
• Curing time shorter following heat curing mechanisms
• Qualitative pad good tool for evaluating surface NCO contamination (relationship indicated with quantitative assessment)
• Uncured NCO presents an opportunity for dermal exposure
Recommendations

• Autobody shop workers and customers avoid direct contact with uncured surfaces

• Gloves be worn when performing tasks following baking (un-taping, buffing, wet sanding and detailing)

• Recently painted autobody parts be kept in a well ventilated area following baking or coating
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Autobody Shops

Participating Shop Workers
THANK YOU!
Isocyanate Quantification

- 10 µL acetic anhydride added to remove excess MAP
- Processed through a 0.45 µm filter and solid phase extraction cartridge
- Eluted from solid phase extraction cartridge with acetonitrile/methanol
- Evaporated under vacuum and nitrogen to almost dryness
- Volume brought up to 1 mL with acetonitrile
- Analyzed on HPLC
Isocyanates and Asthma

- Isocyanates are a primary cause of occupational asthma
- Mechanism in humans is unknown
- Animal models indicate that dermal exposure leads to respiratory sensitization
- No contact exposure data available