Non-Isocyanate Polymer Design and Coating Development

Project Number WP-2315

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Brief to the Scientific Advisory Board
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Performers

- **PPG Industries Inc.**
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  - Mr. David Walters - Research Associate, Corp Science and Technology
- **Army Research Lab**
  - Mr. John Escarsega - Team Leader Coatings Group, DoD CARC Mgr.
  - Mr. Fred Lafferman - Senior Scientist, Organic Coatings Team
- **NAVAIR**
  - Ms. Julia Russell – Chemist
- **Marine Depot Maintenance Center (MDMC) Albany**
  - Mr. Steve Allen - Manager of Coating Operations

Problem Statement

- 1.2 million gallons of Chemical Agent Resistant Coating (CARC) purchased in 2011
  - ♦ Up to 30% Hexamethylene diisocyanate (HDI) by weight (0.7% monomeric HDI)
  - ♦ NIOSH recommends a ceiling value of 0.02 ppm for any 10 minute sampling period and time weighted average of 0.005 ppm
  - ♦ Despite isocyanate sensitization issues no alternatives are available which meet military specifications
- Alternatives are needed to reduce exposures while maintaining very low gloss, ambient temperature cure, and chemical agent resistance

Technical Objective

Apply PPG's polymer synthesis, coating design, and analytical capabilities to develop high performance coatings meeting one or more military specifications without the use of isocyanate crosslinkers

Technical Background – Current Coatings

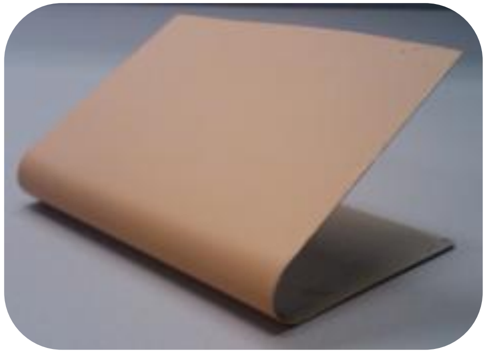
- Existing CARC and Aerospace topcoats are formulated as aqueous or solvent based compositions
- **Application** - hand-held spray guns
- **Conditions** - ambient temperature, wide range of environmental conditions
- **Personal Protective Equipment** - gloves, paint suits and supplied air respirators
- **Cure** – dry to touch in hours, returned to service within a few days

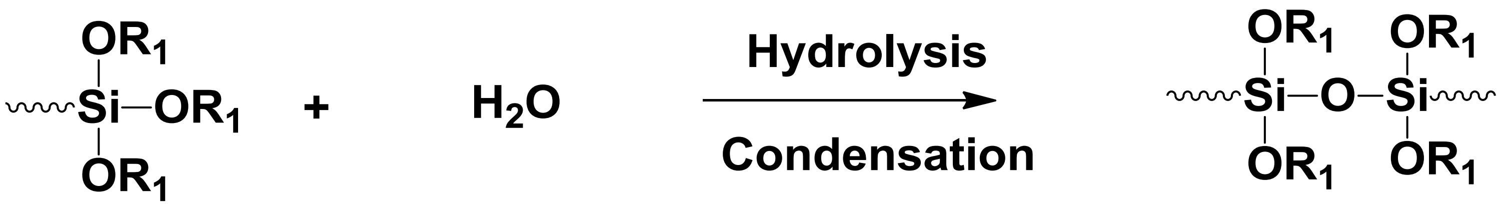
Technical Background

- Over 30 years R&D and 100+ patents for alternatives to isocyanate coatings
- Existing materials fail to meet military specification requirements
- PPG proposes three candidate technologies
  - ♦ Polysiloxane
  - ♦ Polyuretidione
  - ♦ Cyclic Carbonate-Amine

Technical Background - Polysiloxane

- **Technical Rationale**
  - Widely used in commercial applications such as bridges and ships (PSX®700 type)
  - Low viscosity/VOC
  - Excellent weatherability/hydrophobicity
  - Prototypes with desired cure rate demonstrated
- **Research Challenges**
  - Increase initial hardness, decrease brittleness
  - Reduce effect of humidity on cure rate



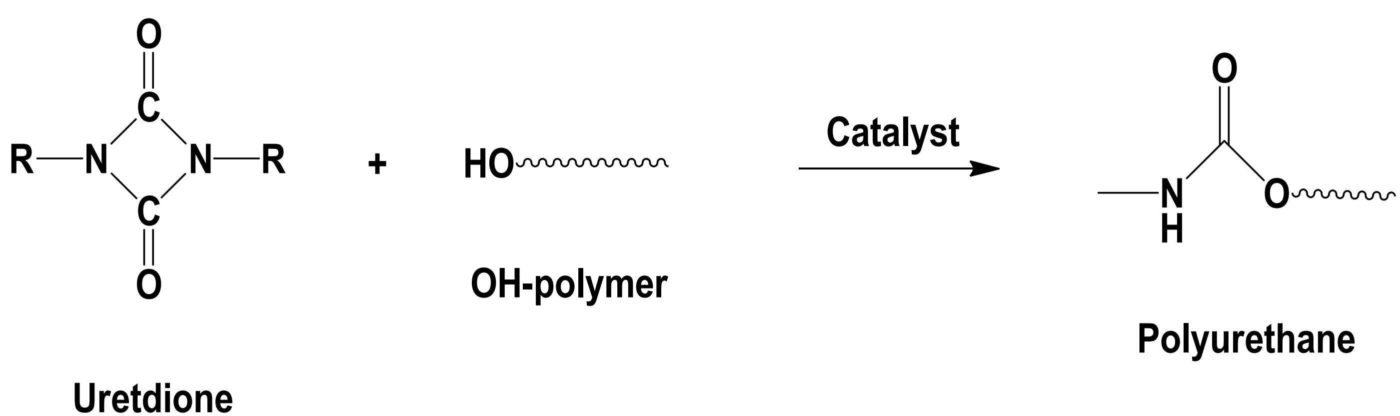


Alkoxysilane

COATING

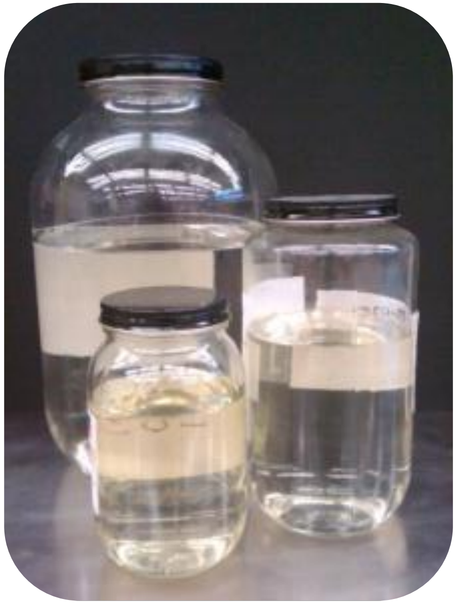
Technical Background - Polyuretidione

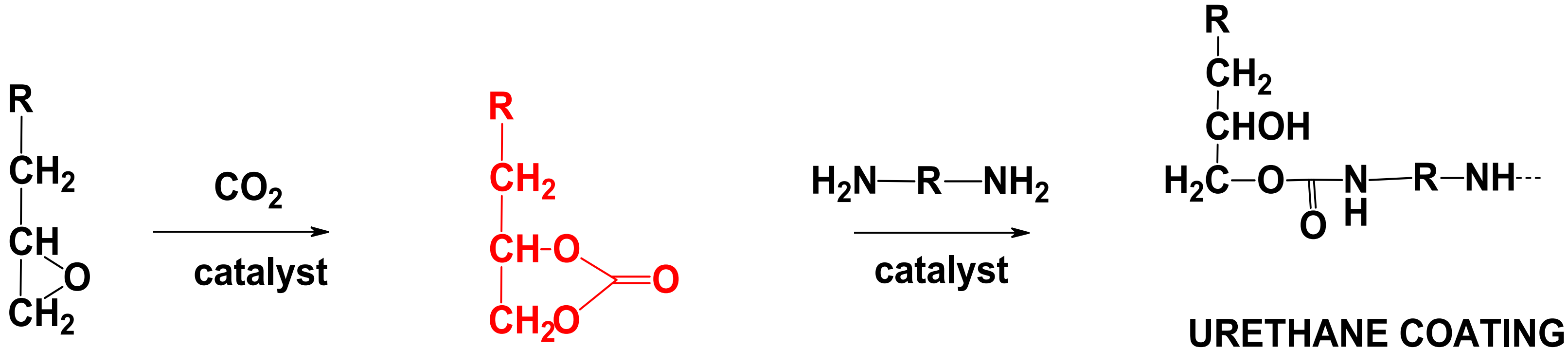
- **Technical Rationale**
  - Uretdiones used in commercial powder coatings
  - Crosslinking reaction results in durable ***urethane*** linkages
  - Demonstrated cure at < 60 °C
- **Research Challenges**
  - Reduce VOC
  - Reduce cure temperature
  - Identify catalyst type and level



Technical Background – Cyclic Carbonate

- **Technical Rationale**
  - Provides ***urethane*** coating using non-isocyanate materials
  - Good accelerated weathering performance
  - Established laboratory process for resin preparation
  - Good film properties at 90 °C
- **Research Challenges**
  - Develop robust low temperature cure
  - Improve film properties; hardness, solvent resistance
  - Understand role of humidity in cure response





Technical Approach

Phase 1

- Task 1 Benchmarking
- Task 2 Initial Formulation Development
- Task 3 Initial CARC Testing

Down Select Chemistry →

Phase 2

- Task 4 Targeted Development
- Task 5 Formulation CARC Testing

Down Select Formulation →

Phase 3

- Task 6 Optimization
- Task 7 Mil-Spec Testing
- Task 8 Transition Planning

Technical Approach

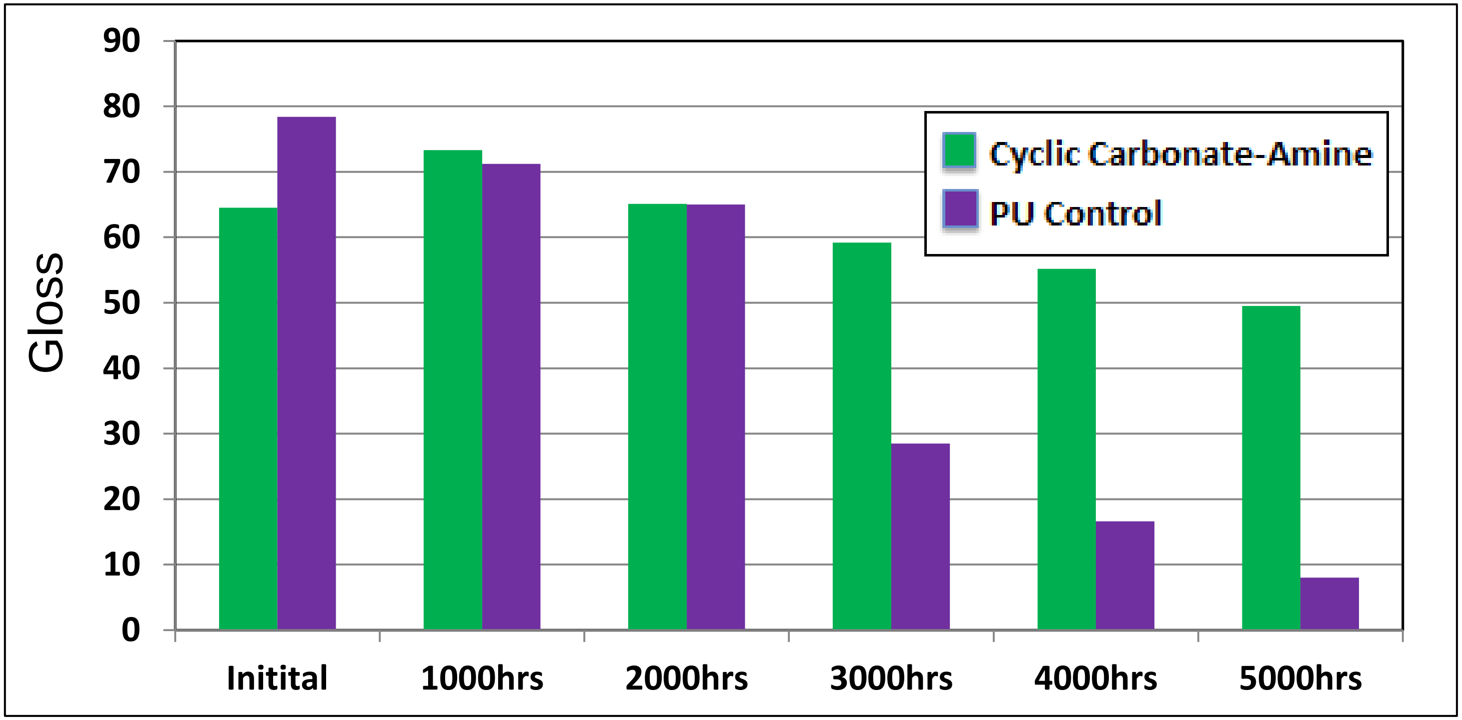
- **Project Management Principles**
  - ♦ Frequent sample exchanges to ensure reproducibility and maintain program focus
  - ♦ Monthly team meetings to ensure development is addressing military needs
  - ♦ High-throughput techniques to streamline development
  - ♦ A three-tier test protocol to achieve continuous improvement

Task 1 Benchmarking

- **Candidate technologies compared to commercial controls**
  - ♦ Determine relative strengths and weaknesses
  - ♦ Tier 1 Testing to include:
    - Gloss, Appearance, Hiding
    - Accelerated weathering
    - Flexibility, Adhesion

Initial Performance Determined

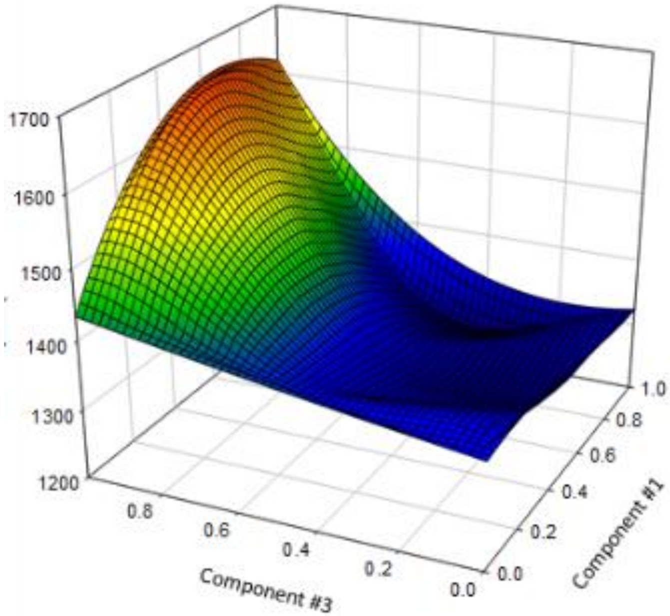
Task 1 Benchmarking



Accelerated weathering of cyclic carbonate-amine coating vs. conventional polyurethane

Task 2 Initial Formulation Development

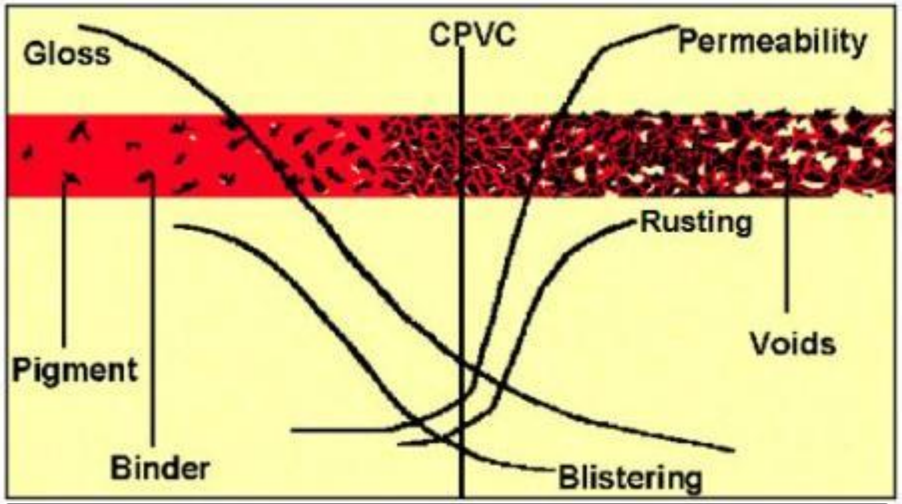
- **Experimental Design Techniques used to develop prototype formulations**
  - ♦ Develop understanding of how combinations of variables affect performance properties
- **Develop Strategies for obtaining very low gloss**
  - ♦ Pigmentation type and levels
  - ♦ Introduction of incompatible resins



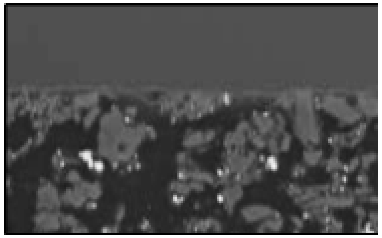
Example Response Curve for Multi-Component Mixture

Task 2 Initial Formulation Development

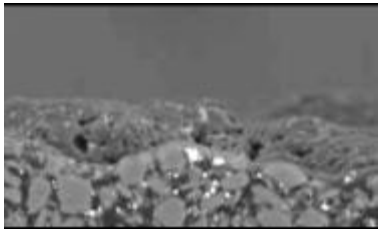
- Critical Volume Concentration defines pigmentation limits



Exceed CPVC = Loss of Film Integrity



Below CPVC, Gloss = 3.1

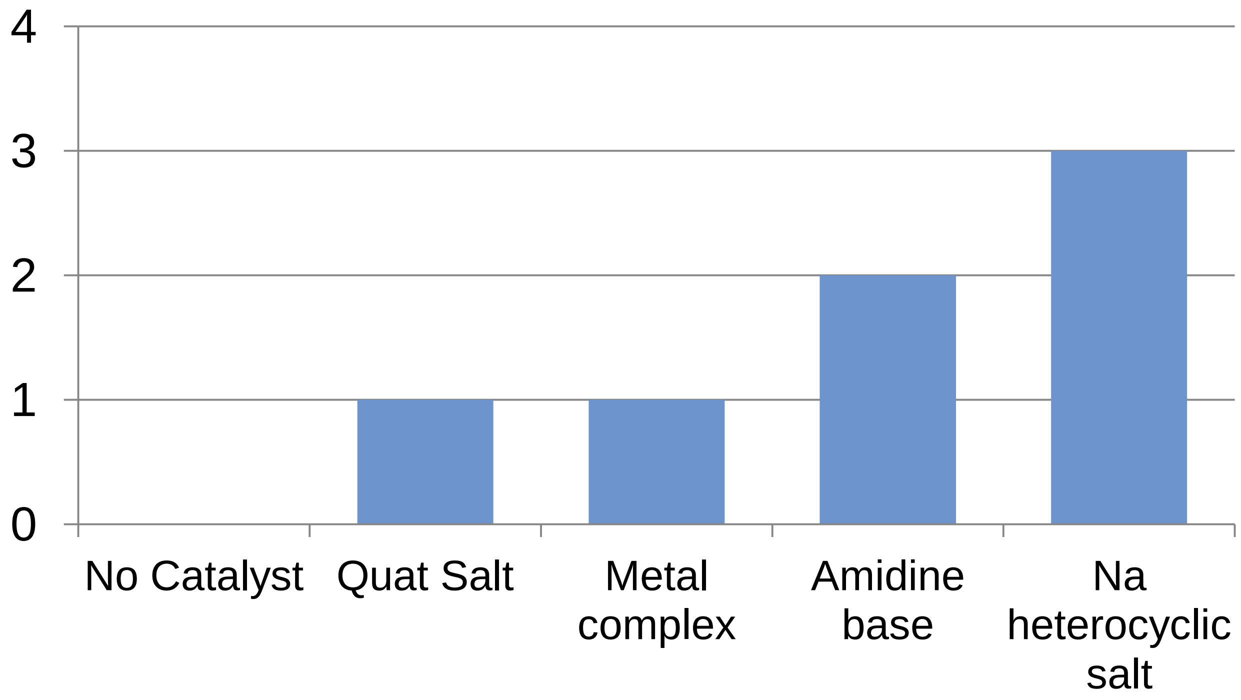


Above CPVC, Gloss = 0.6

- All of the candidate chemistries will require pigment dispersion and resin design factors to achieve low gloss

Task 2 Initial Formulation Development

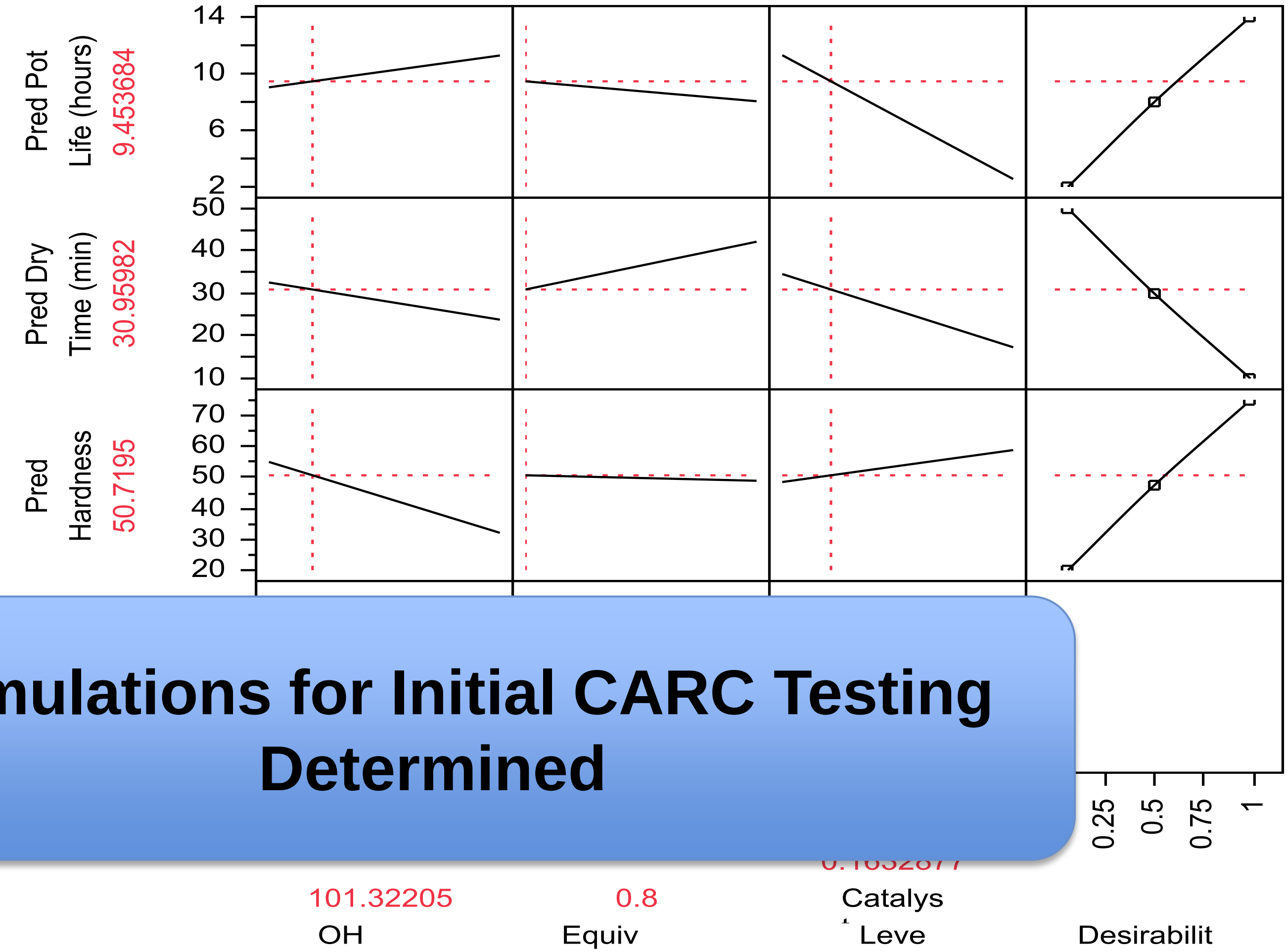
- **Catalyst Screening for Polyuretidione Formulations**



Gel Time
0 = no gel
1 = 168 hours
2 = 24 hours
3 = 1 hour

Task 2 Initial Formulation Development

Example "Prediction Profiler" resulting from statistical analysis of experimental design r



Formulations for Initial CARC Testing Determined

Task 3 Initial CARC Testing

- **Candidate coating compositions will be submitted for Chemical Agent Resistance Testing**
  - ♦ ARL to coordinate sample submissions
- **Tier 2 testing to also include:**
  - ♦ Recoat adhesion, Storage stability
  - ♦ Water/fluid/acid (when applicable)/super tropical bleach resistance

Data Required for Chemistry Down-Selection Obtained

Task 4 Targeted Development

Polysiloxane Focus Areas

- Decrease long term brittleness
- Reduce effect of humidity on cure rate

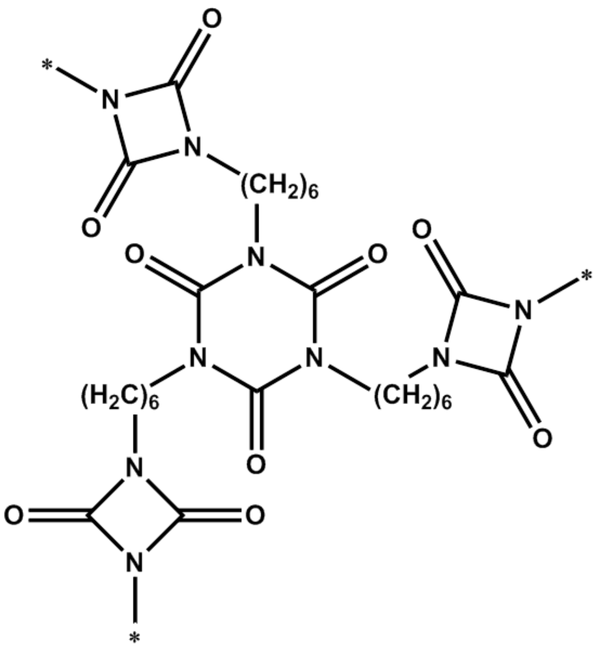
Strategies

- Organic polymer design to reduce crosslink density
- Mono-functional reactants to prevent excess crosslinking
- Reducing solvent blend and catalyst levels optimized for humidity ranges

Task 4 Targeted Development

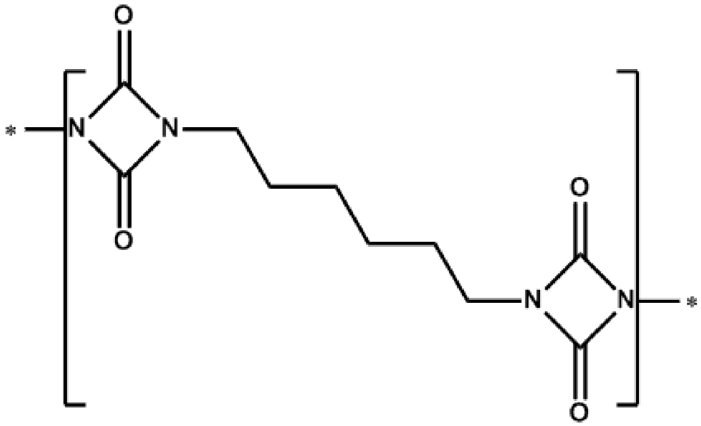
Polyuretidione Focus Areas

- Reduce VOC
- Reduce cure temperature



Strategies

- Alternative polyuretidione synthesis schemes based on type of starting material
- Additional catalyst studies and optimization



Task 4 Targeted Development

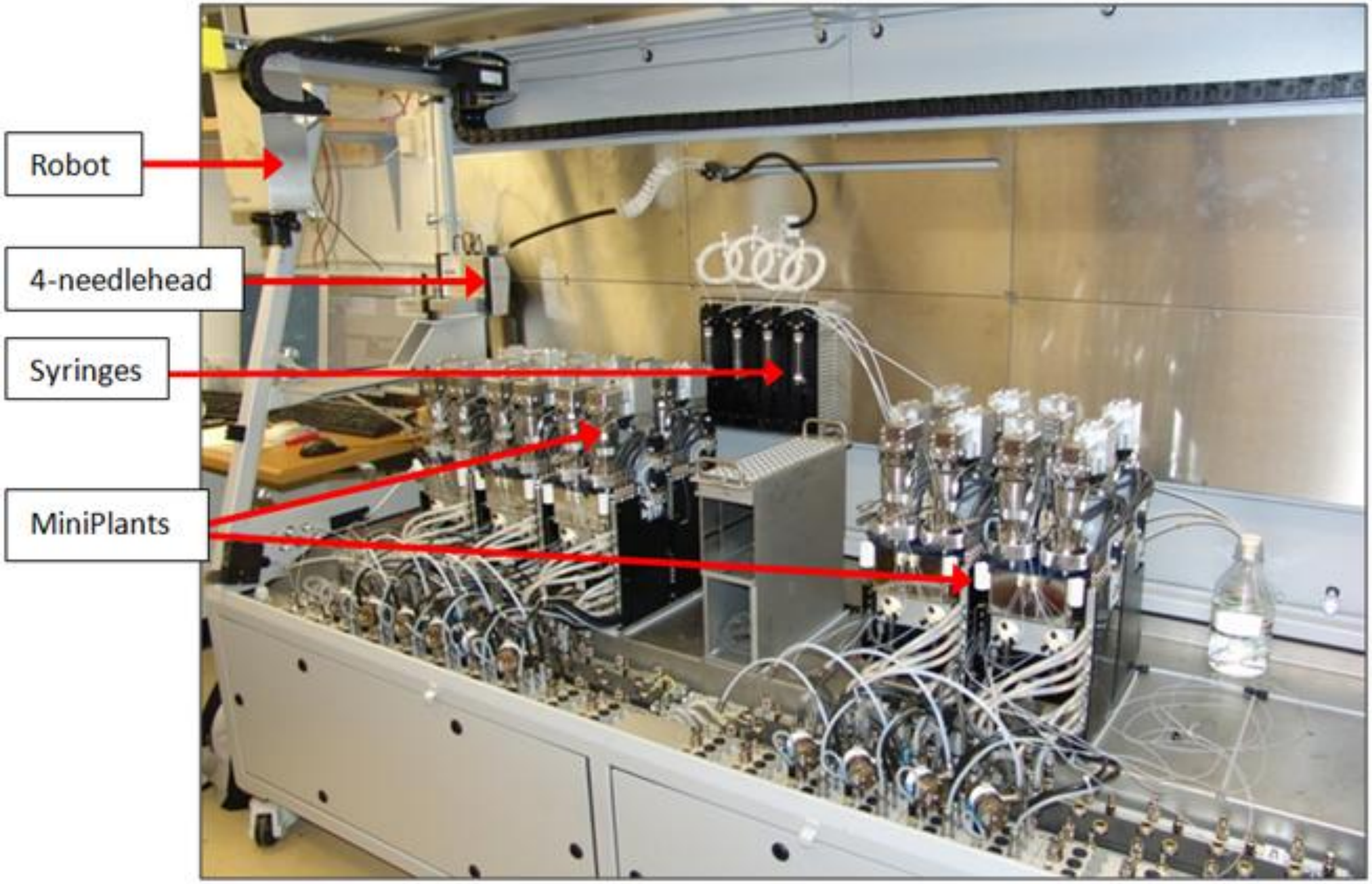
Cyclic Carbonate Focus Areas

- Develop robust low temperature cure
- Improve film properties; hardness, solvent resistance

Strategies

- Extensive catalyst studies including controlled environment application
- High-throughput synthesis of cyclic carbonate functional polymers
- Optimize the resin composition, Ew, Mw, Tg

Chemspeed Autoplant A100TM



Task 5 Formulation CARC Testing

- **Additional Chemical Agent Resistance Testing**
  - ARL to coordinate sample submissions
- **Formulation details are evaluated within a given coating chemistry**
  - More granularity in analysis of results

Data Required for Coating Formulation Down-Selection Obtained

Task 6 Optimization

- **Coating formulations selected by agency partners based on previous results**
- **Optimize application characteristics such as flow, leveling and sag resistance under controlled temperature/humidity**

Task 7 Mil Spec Testing

- **MIL-DTL-53039D (Army CARC)**
- **MIL-PRF-85285D (Aerospace Topcoats)**

Performance in Simulated Environments Optimized

Task 8 Transition Planning

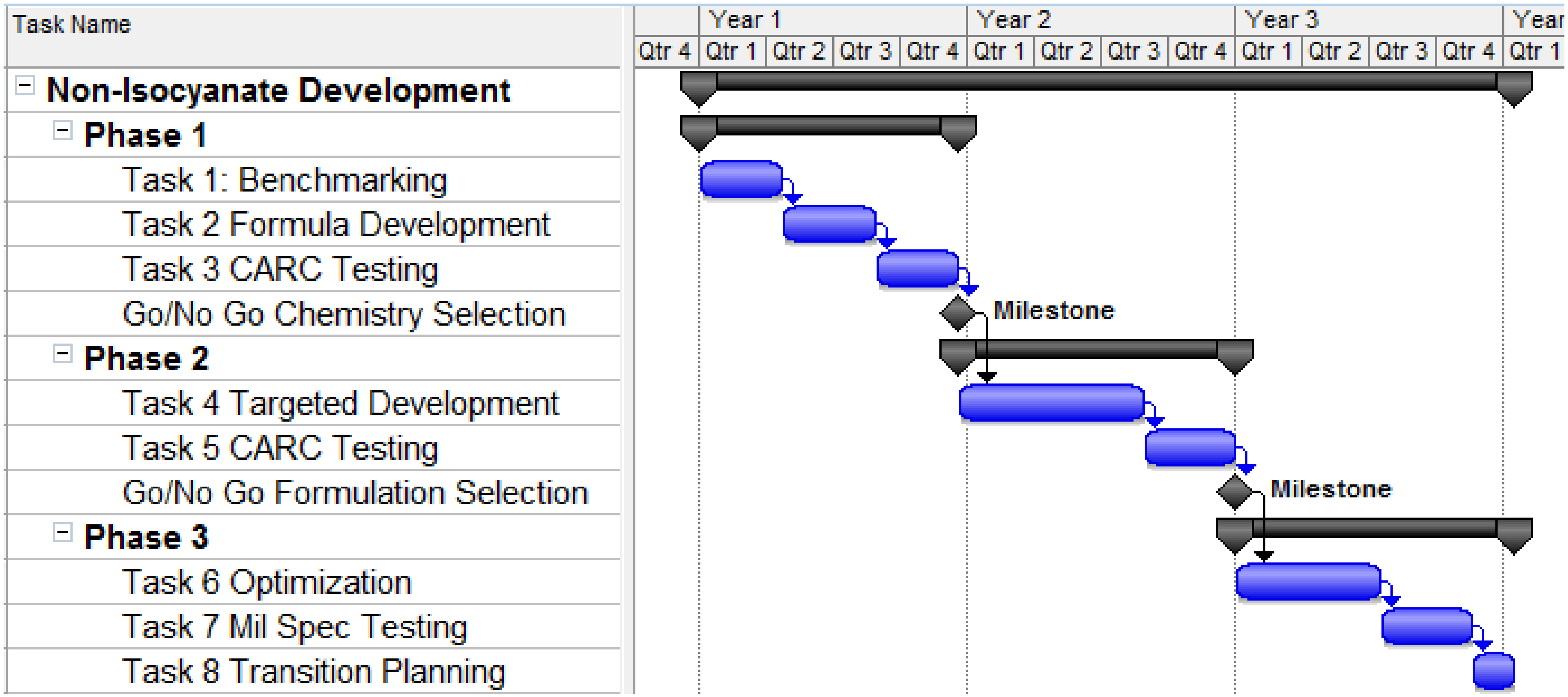
- Production, Distribution and Tech Service pathways identified
- Strategy for demonstration in an operational environment
- Strategy for new specification or modification of existing spec

Path to Implementation Defined

Year 1 Project Plan

Task	Amount ($K)
Task 1 Benchmarking	$249
Task 2 Initial Formulation Development	$248
Task 3 CARC Testing	$99
Total	$596

Overall Project Plan



GO/NO GO Decision for chemistries targets development on a **coating type**

GO/NO GO Decision for formulation targets development on a **coating details**

Project Funding

$K	SERDP
Year 1	596
Year 2	641
Year 3	616
Total	1,853

Deliverables

- Gap analysis of initial experimental formulations against current CARC/Aerospace topcoat formulations
- Results of Chemical Agent Resistance testing for three unique coating types
- Summary Report for the Go/No Go decision on specific ***chemistries***
- Prototype coating coupons and wet samples to partner organizations
- Summary Report for the Go/No Go decision on specific ***formulations***
- Results of performance testing to MIL-DTL-53039D and MIL-PRF-85285D
- Final Report

Thank You

Backup Slides

Reviewer Comments

Comment: Research should concentrate on the polysiloxane coatings and the polyuretdione coatings, with the high-risk work on the cyclic carbonate/amine coatings removed

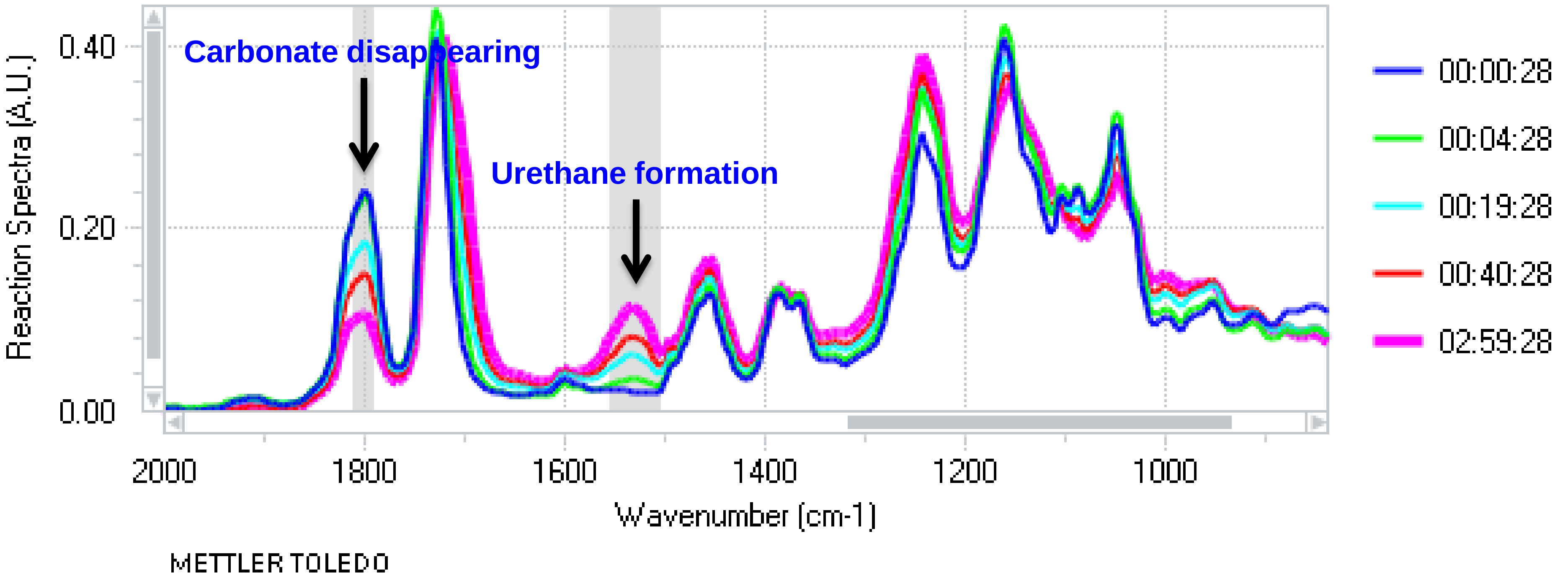
Response: We agree the cyclic carbonate work is a higher risk approach but have recent results suggesting excellent UV resistance and reduced temperature cure. Nonetheless we have inserted a go/no go decision point for the chemistry selection once the first round of chemical agent testing has been completed.

Comment: Address intellectual property issues

Response: PPG has an extensive portfolio of pre-existing intellectual property which is in the public domain and can be freely shared during the execution of this project. New IP would be governed by applicable contract clauses granting government use rights. PPG does not typically protect intellectual property through trade secret designations.

Cyclic Carbonate Reaction

- **Example IR Spectroscopy Scans for cyclic carbonate reactivity**



Reviewer Comments

Comment: Criticism of the of the cyclic carbonate-amine based systems since they will have hydroxyl groups in the final structure

Response: If the primary or secondary hydroxyl group affects performance properties it will be determined in the first year and the chemistry down-selection may eliminate this approach

Comment: Cost considerations should be part of down-selection process and be considered early in the program

Response: The proposed technologies are expected to be very cost competitive with existing materials. For example, current CARC coatings sell for about $30-50/gallon and the PSX type coatings (which are the basis for the siloxane approach) are sold for about $45/gallon.

Reviewer Comments

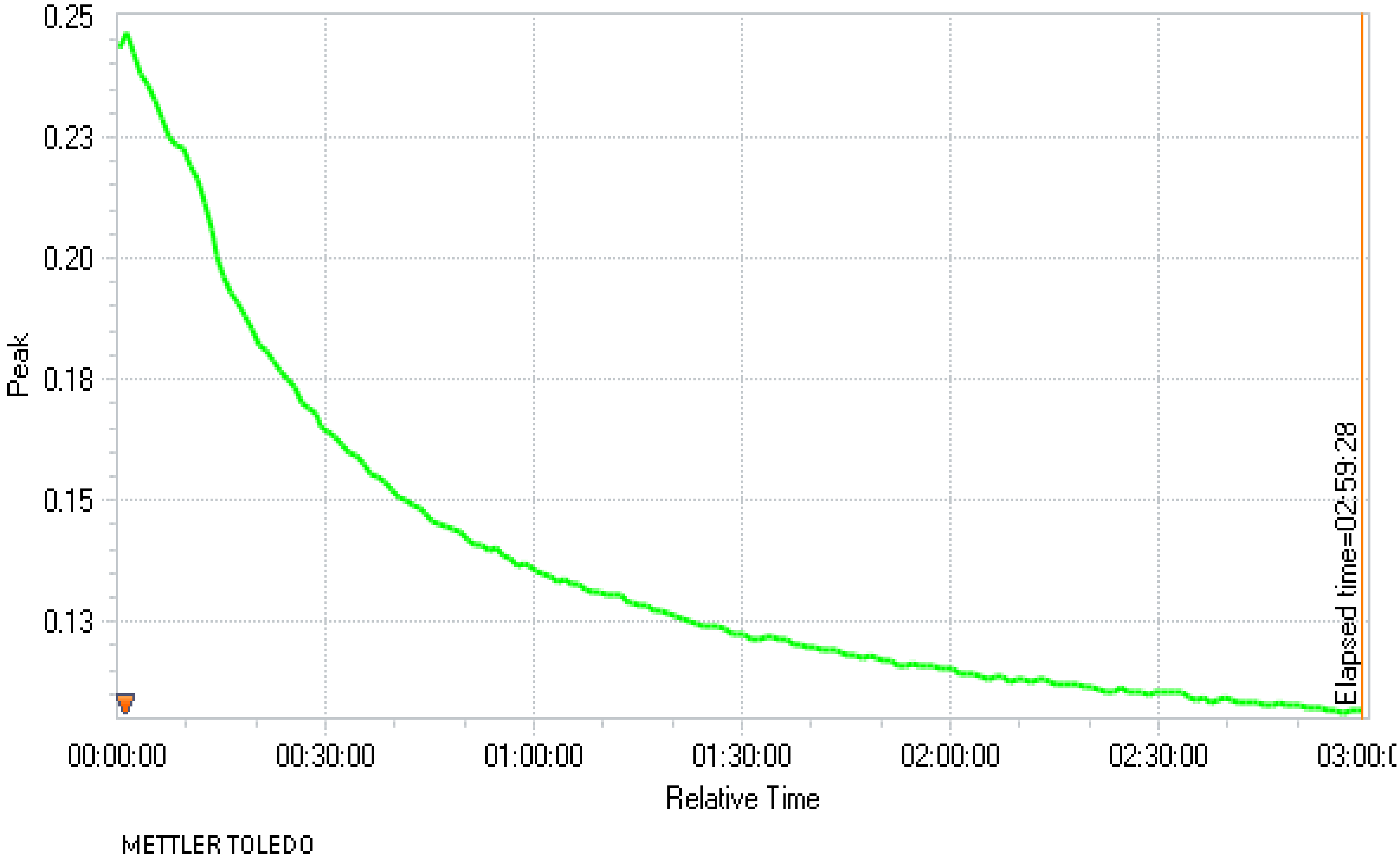
Comment: Incomplete cost proposal information

Response: There were missing pieces of information in the budget forms but the total amounts and amounts by year were correct. Full and complete budget forms will be provided to SERDP program office with no changes in total amounts.

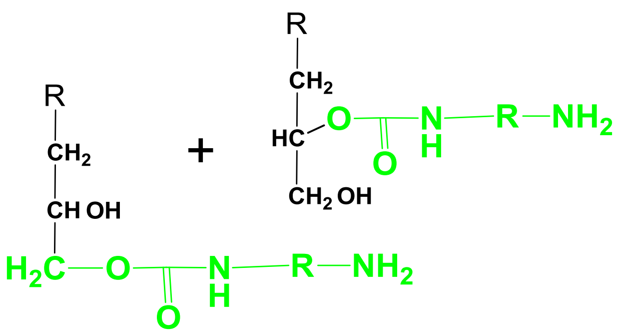
Comment: The siloxane amine uses amines, which are known sensitizers to some individuals but lack the acute toxicity of the isocyanates. There is little consideration of the health effects at the proposal stage.

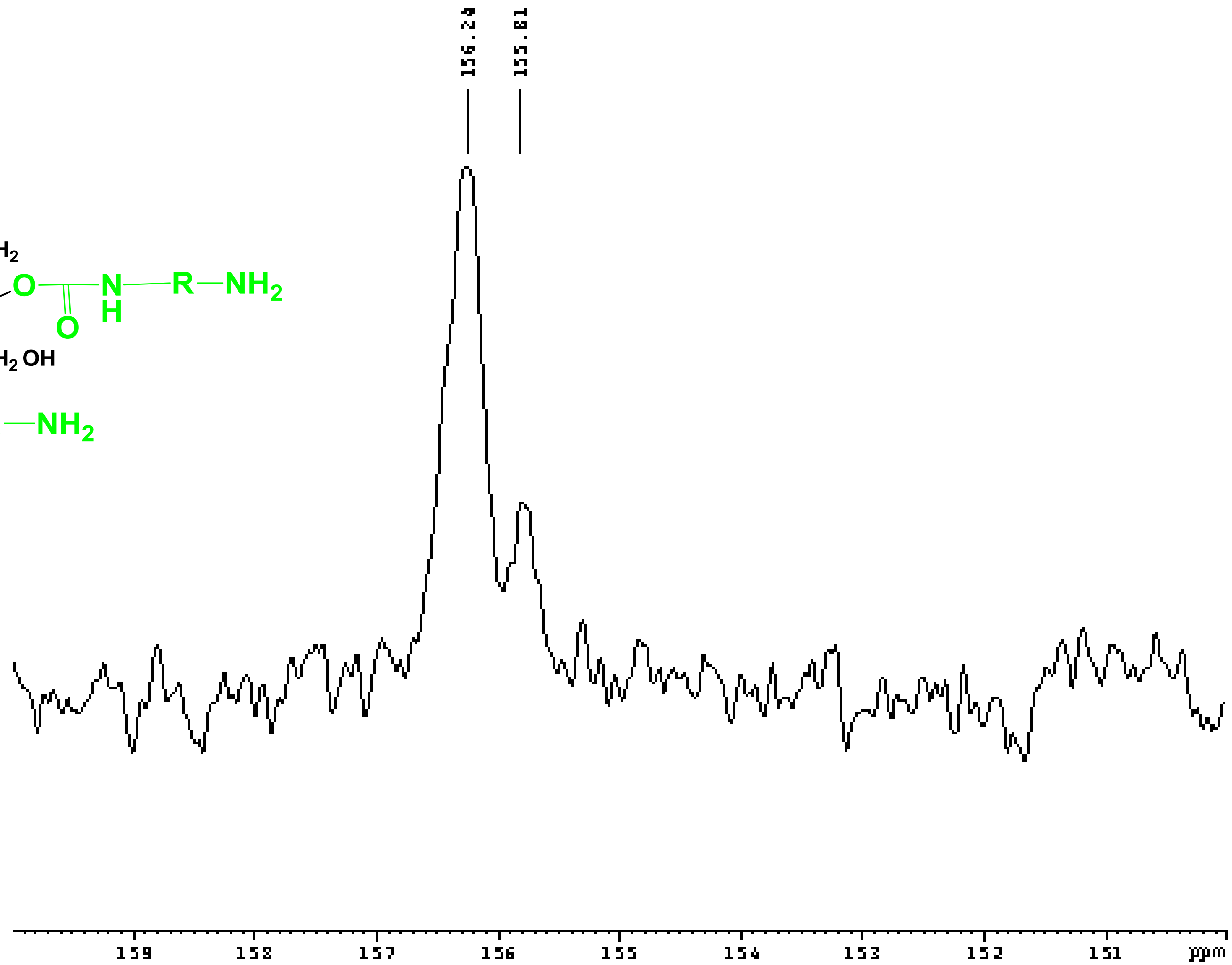
Response: Amine functional materials envisioned for this project are commercially available, used in similar coatings and well characterized for toxicity. New materials entering the PPG Coatings Innovation Center must be evaluated by EH&S prior to being brought on site. A detailed health assessment for the prototype coatings is planned during project execution but cannot be completed until the formulations are better defined.

Rate of Carbonate IR Peak Reduction



NMR Determination of Reaction Products





Tasks Cyclic carbonate Amine Proposal

- Optimize the resin composition, Ew, Mw, Tg
- Improve hardness of coating
- Improve the extent of reaction between cyclic carbonate and amine- through catalyst use
- Understand the solvent effect on cure, and coating properties, especially solvent resistance
- Understand the robustness of cure response at range of temperature and humidity
- Decrease VOCs of coatings-Mw or using diluents
- Improve appearance of the coating; particularly, compatibility of resin, haze
- Evaluate adhesion to various coating

Transition Plan

- Transitioning to demonstration and validation may be accomplished through a proposed ESTCP project, through private investment or a combination of public and private funding.
- The proposal team was selected, in part, based on their ability to support such demonstration efforts. Potential demonstration sites include the Marine Depot Maintenance Center (MDMC) Albany and a representative from that organization is included in the projet team.
- Final field use will require introducing a new specification or modification of existing specs. ARL stakeholders are well positioned to facilitate these changes