# Selectively Strippable Silyl-Containing Aerospace Topcoats Using Environmentally Friendly Fluoride Salts

## SERDP WP20-1106

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**Washington, DC**

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The Technical Objectives of this project are as follows:

- Prove that silyl containing polyurethane (Silyl PU) topcoats can provide similar thermal, mechanical, and performance properties (e.g. solvent resistance, weatherability ) as a MIL PRF 85285 polyurethane aircraft topcoat
- Demonstrate that Silyl PU topcoats can be selectively degraded and removed from a strongly adhered non metallic substrate (e.g. anti corrosive epoxy primer) using a mild and environmentally friendly fluoride salt solution
- Confirm that non metallic substrates remain intact, with the chemical structure and mechanical properties unaltered, upon removal of the Silyl PU topcoat

**15. SUBJECT TERMS**

Selectively Strippable Silyl-Containing Aerospace Topcoats, Environmentally Friendly Fluoride Salts

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**Standard Form 298** (Rev. 8/98)
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# Project Team

Principal Investigator:

- Erick Iezzi, Ph.D., Naval Research Laboratory

Co-Performers:

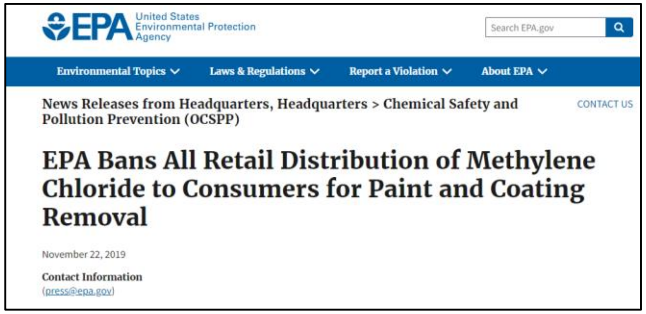
- Keith Sutyak, Ph.D., Naval Research Laboratory
- Grant Daniels, Ph.D., Naval Research Laboratory
- Eugene Camerino, Ph.D., Naval Research Laboratory
- Josh Walles, Naval Air Warfare Center – Aircraft Division

# Background

- This Limited Scope project addressed SERDP WPSON-20-C1 for “Development of Advanced Coatings”
  - Scalable, less complex application, curing and/or stripping technique(s) or method(s)
  - The ability to selectively strip or apply coatings

# Background

- Polyurethane (PU) topcoats and methods of removal



News Releases from Headquarters, Headquarters > Chemical Safety and Pollution Prevention (OCSPP)

**EPA Bans All Retail Distribution of Methylene Chloride to Consumers for Paint and Coating Removal**

November 22, 2019

**Contact Information**
(press@epa.gov)

**Chemical Strippers**
- Methylene chloride – 1 application (banned for consumer use)
- Benzyl alcohol and blends – up to 4 applications

**Abrasive Blasting**
- Plastic media

**Mechanical Removal**
- Orbital sanders
- Hand-sanding

**<u>Issues</u>:**
- Removal methods are non-selective for topcoat
- Topcoats are designed to be durable and not easily degraded or removed

**Polyurethanes are difficult to degrade due to their network of covalent bonds and tangled polymeric chains**

# Background

- Current removal methods cannot selectively remove the PU topcoat on aircraft without damaging the underlying non-metallic substrate (e.g. primer, composite)
  - Anti-corrosive epoxy primer is often in excellent condition, yet it is removed when the topcoat is stripped
    - Workers are exposed to toxic materials, such as hexavalent chromium ($Cr^{+6}$)
    - Costs associated with hazardous waste disposal and reapplication of primer
  - Topcoats over polymeric composites are only partially removed
    - Entire exterior of MV-22s are hand-sanded to prevent damage to the underlying composite
    - Labor intensive

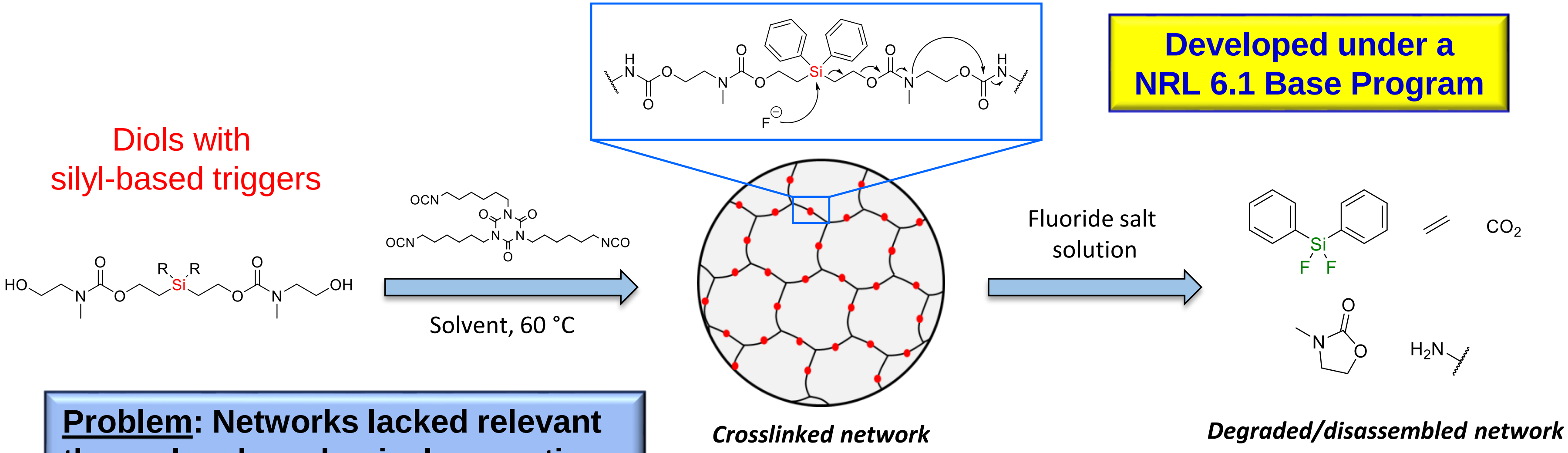
Sanded MV-22 at FRC-East

**Coating removal from non-metallic substrates will remain an issue due to increased composite use on Navy/USMC assets to reduce weight**

# Background

- Degradable networks in the literature have focused on single bond cleavages using harsh conditions (e.g. strong acid, heat)
- A commercial coating technology that is degradable on-demand using a mild and environmentally friendly chemical treatment does not exist
- NRL-developed degradable networks disassemble via cascading bond cleavages upon activation with fluoride ion (from fluoride salt) at RT

**Developed under a NRL 6.1 Base Program**



**<u>Problem</u>: Networks lacked relevant thermal and mechanical properties for an aircraft topcoat; length of silyl diols shorter than diols used in DoD polyurethane topcoats**

Iezzi, E. B.; Camerino, E.; Daniels, G. C.; Wynne, J. H. U.S. Patent 10,730,993, August 4, 2020.
Iezzi, E. B.; Camerino, E.; Daniels, G. C.; Wynne, J. H. *Coatings Tech.* **2020**, *17*, 26.
Daniels, G. C.; Camerino, E.; Wynne, J. H.; Iezzi, E. B. *Mater. Horiz.* **2018**, *5*, 831.

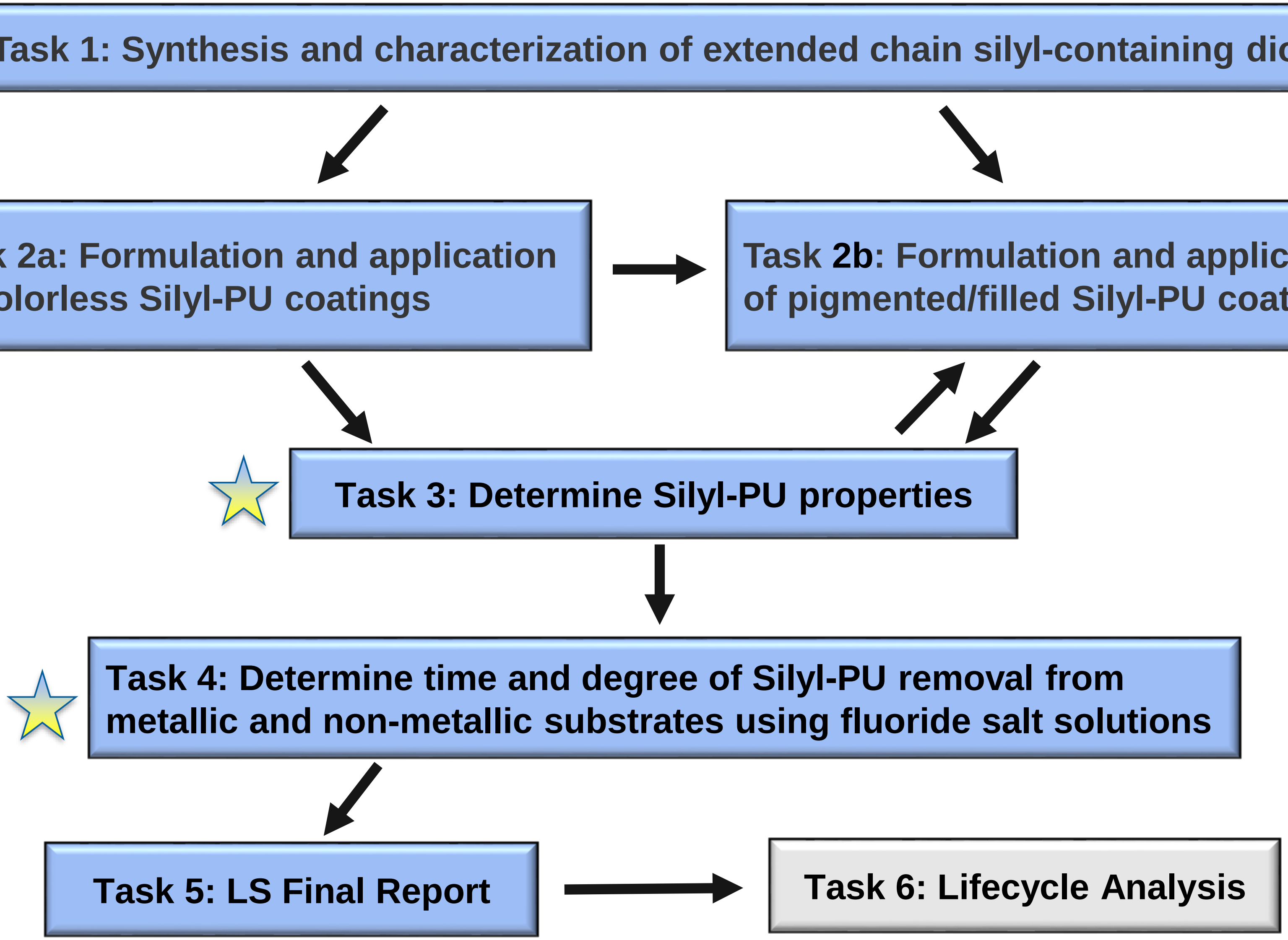
# Technical Objectives

- Prove that silyl-containing polyurethane (Silyl-PU) topcoats can provide similar thermal, mechanical, and performance properties (e.g. solvent resistance, weatherability) as a MIL-PRF-85285 polyurethane aircraft topcoat

- Demonstrate that Silyl-PU topcoats can be selectively degraded and removed from a strongly adhered non-metallic substrate (e.g. anti-corrosive epoxy primer) using a mild and environmentally friendly fluoride salt solution

- Confirm that non-metallic substrates remain intact, with the chemical structure and mechanical properties unaltered, upon removal of the Silyl-PU topcoat

# Technical Approach



Task 1: Synthesis and characterization of extended chain silyl-containing diols

Task 2a: Formulation and application of colorless Silyl-PU coatings

Task 2b: Formulation and application of pigmented/filled Silyl-PU coatings

Task 3: Determine Silyl-PU properties

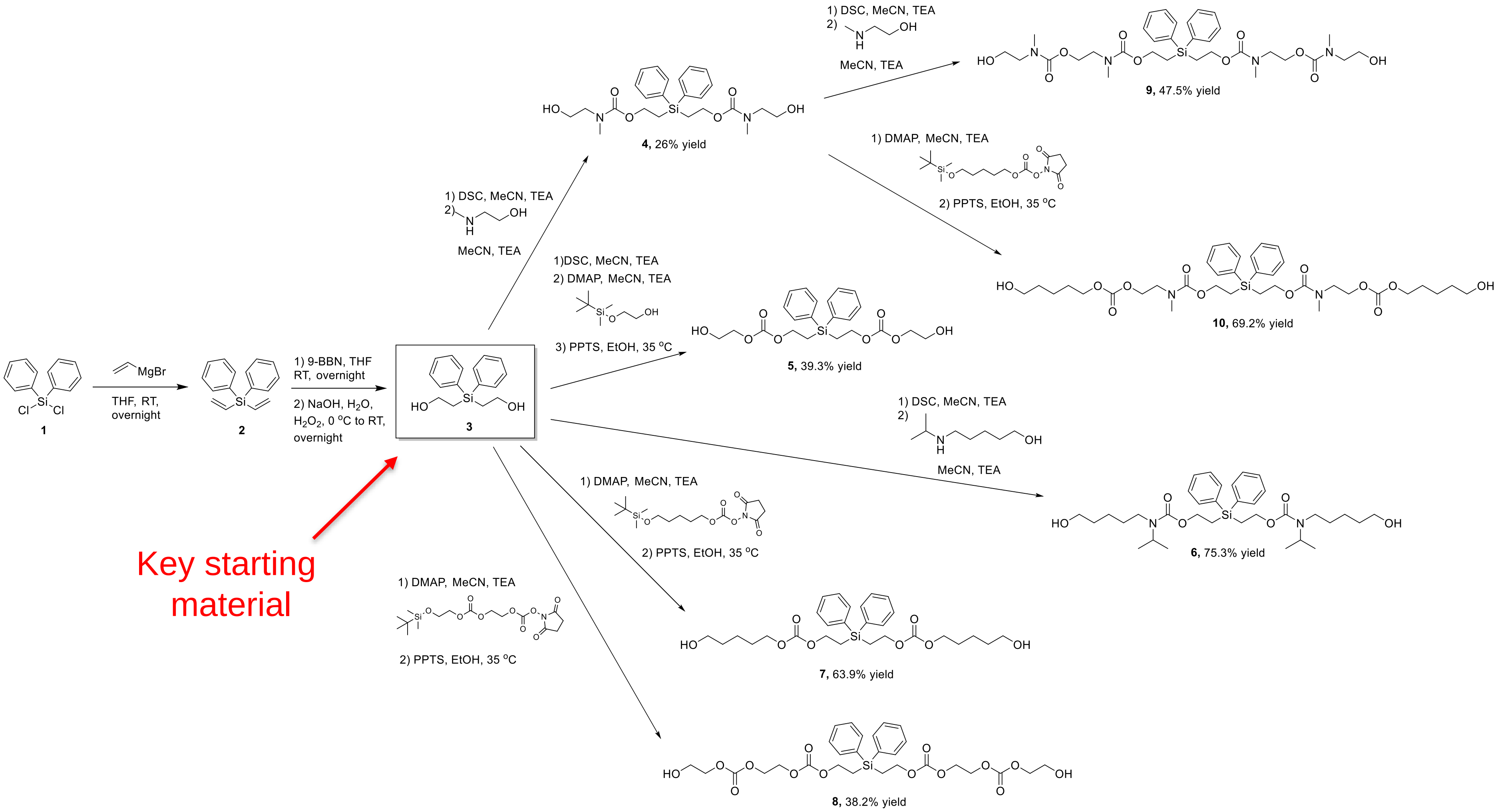
Task 4: Determine time and degree of Silyl-PU removal from metallic and non-metallic substrates using fluoride salt solutions

Task 5: LS Final Report

Task 6: Lifecycle Analysis

# Results

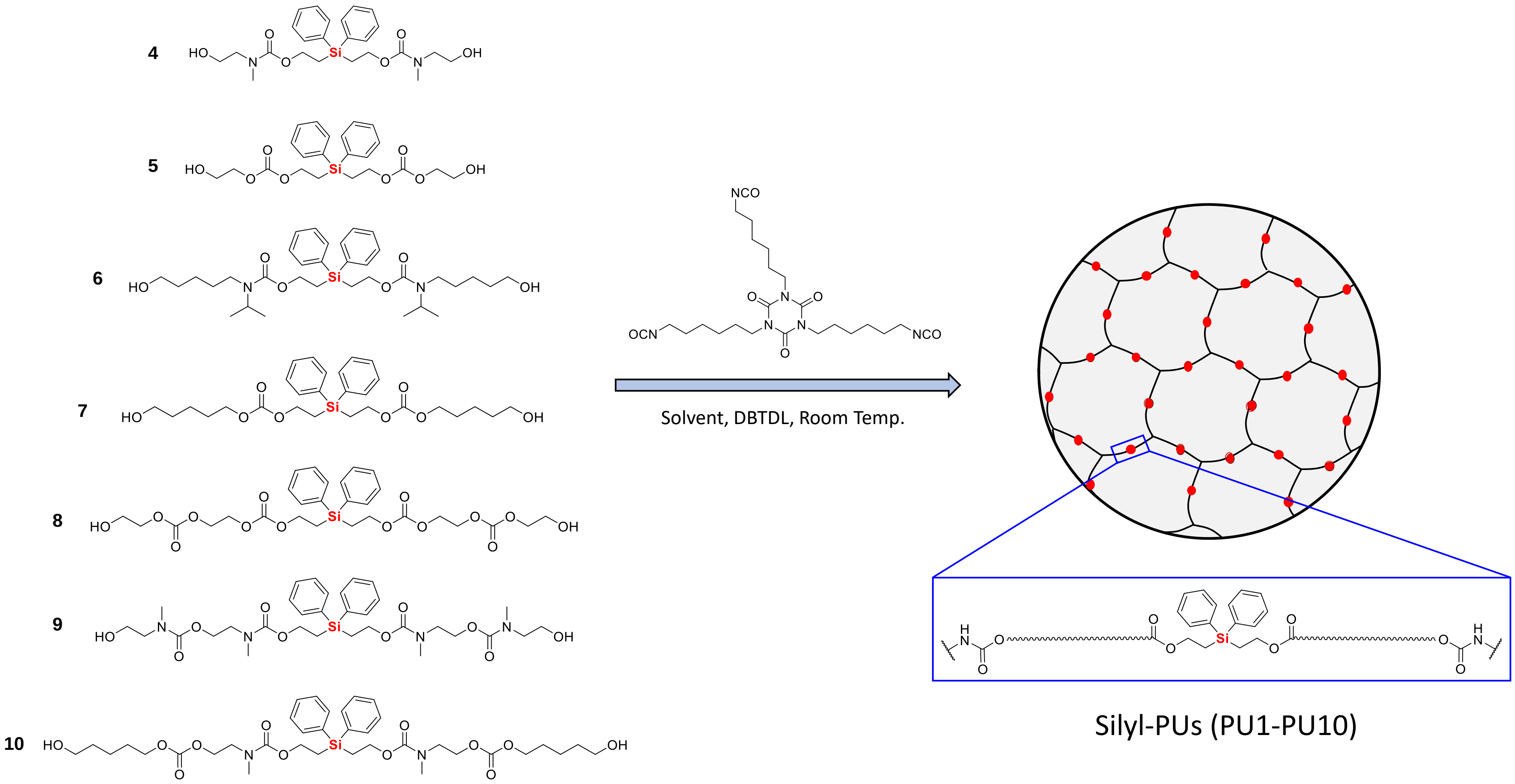
- Synthesis of extended and double extended chain diphenylsilyl diols



Key starting material

# Results

- Formation of Silyl-PU coatings from synthesized diphenylsilyl diols and aliphatic isocyanate(s)



Silyl-PUs (PU1-PU10)

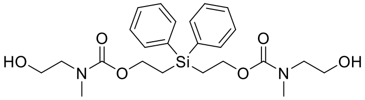
# Results

- Formulation and application of Silyl-PU coatings based on synthesized diphenylsilyl diols and aliphatic isocyanate(s)
  - colorless vs. pigmented/filled
  - film forming bar vs. spray application

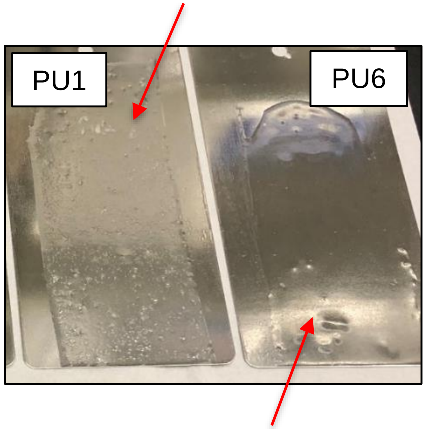
| Silyl Diol | Aliphatic Isocyanate | Coating | Pigment and Filler | Appearance | Gloss @ 60° Angle |
|---|---|---|---|---|---|
| **4** | HDI oligomer | **PU1** | No | Colorless | N/A |
| **5** | HDI oligomer | **PU2** | No | Colorless | N/A |
| **6** | HDI oligomer | **PU3** | No | Colorless | N/A |
| **7** | HDI oligomer | **PU4** | No | Colorless | N/A |
| **8** | HDI oligomer | **PU5** | No | Colorless | N/A |
| **9** | HDI oligomer | **PU6** | No | Colorless | N/A |
| **9** | 50/50 blend of HDI oligomers | **PU7** | No | Colorless | N/A |
| **10** | HDI oligomer | **PU8** | No | Colorless | N/A |
| **9** | 50/50 blend of HDI oligomers | **PU9** | Yes | Low-gloss gray | 1.40 GU |
| **9** | 50/50 blend of HDI oligomers | **PU10** | Yes | Gloss white | 93.5 GU |

**PU11** (control) = MIL-PRF-85285, Type IV camouflage gray polyurethane topcoat

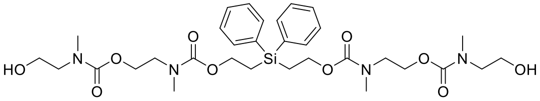
**PU1-PU8** fabricated with a 3 mil film forming bar
**PU9-PU11** fabricated via high-volume, low-pressure (HVLP) spray



Silyl diol **4** crystallized during cure and had limited miscibility with HDI oligomer, thereby generating a hazy coating

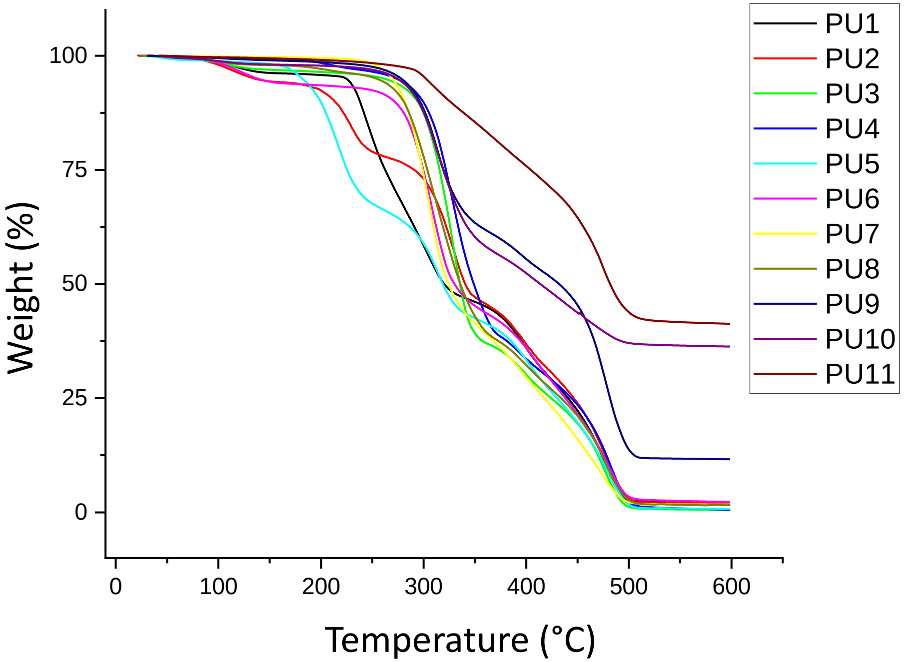


Silyl diol **9** did not crystallize during cure and was miscible with HDI oligomer, thereby generating a clear coating



# Results

- Thermal degradation profile of Silyl-PUs and control via TGA

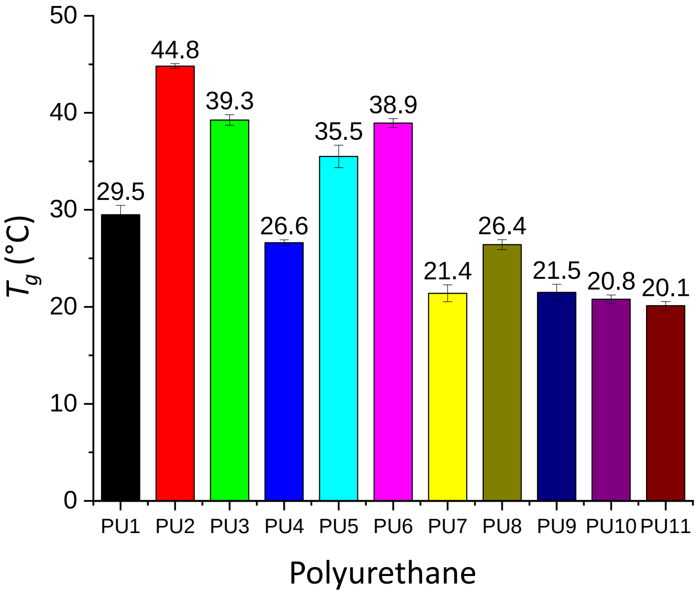


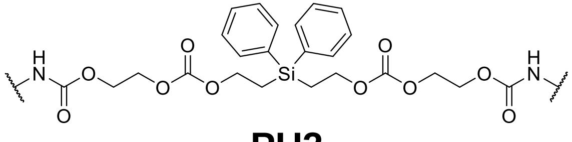
| Coating | Onset Degradation Temperature (°C) |
|---|---|
| **PU1** | 229.5 |
| **PU2** | 210.2 |
| **PU3** | 301.7 |
| **PU4** | 300.9 |
| **PU5** | 189.1 |
| **PU6** | 282.4 |
| **PU7** | 279.3 |
| **PU8** | 276.4 |
| **PU9** | 288.7 |
| **PU10** | 287.4 |
| **PU11 (control)** | 285.5 |

- In general, Silyl-PU coatings with carbamate linkages demonstrated greater onset degradation temperatures than those with carbonate linkages
- Pigmented/filled Silyl-PUs (**PU9** & **PU10**) demonstrated similar onset degradation temperatures as PU control (**PU11**), although weight loss was greater due to lower loading of solid particles compared to control

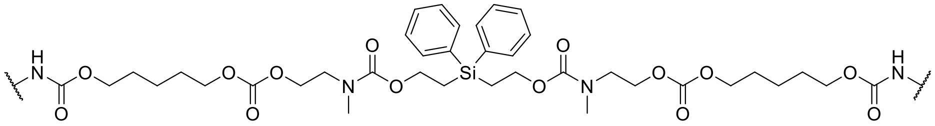
# Results

- Glass transition temperature ($T_g$) of Silyl-PUs and control via DSC





**PU2**

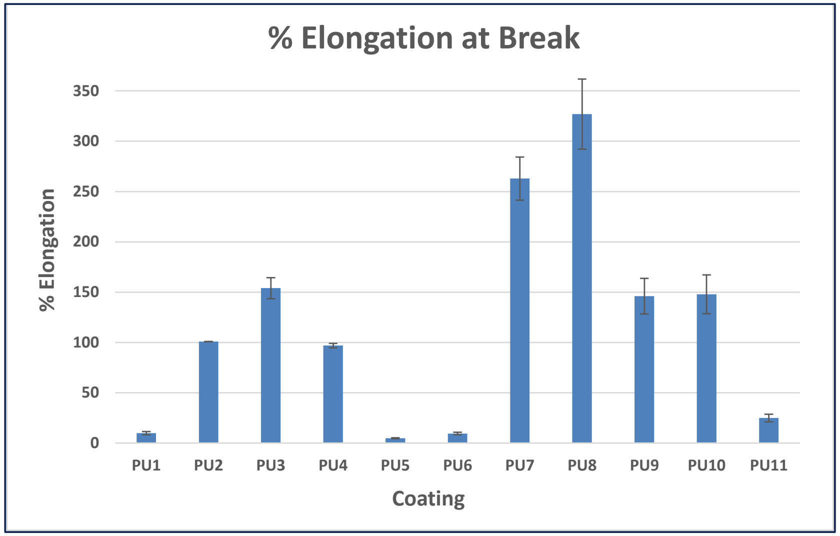


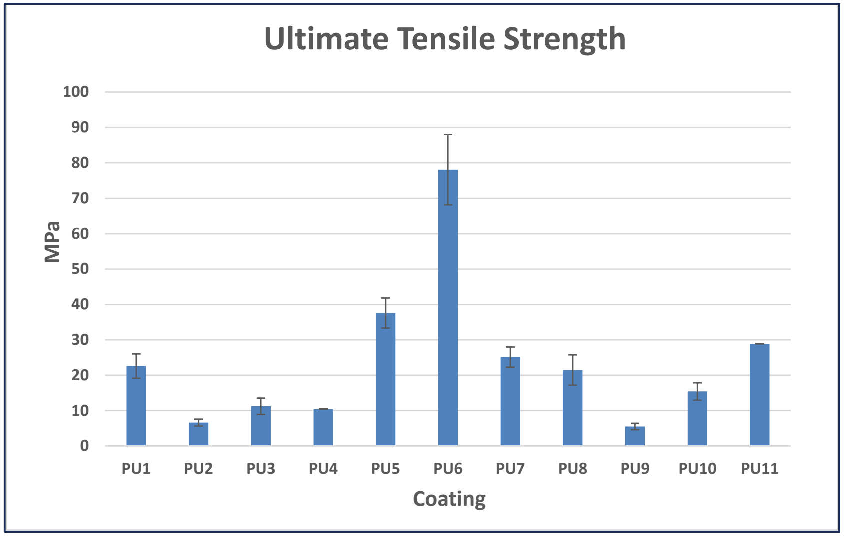
**PU8**

- $T_g$ of colorless Silyl-PUs ranged from 21.4-44.8 °C
  - Max. value for **PU2** due to greatest crosslink density
  - Networks with pentylene linkages (**PU3**, **PU4** & **PU8**) showed reduced values due to increased bond rotations and reduced crosslink density
- $T_g$ of pigmented/filled Silyl-PUs (**PU9** = 21.5 °C and **PU10** = 20.8 °C) were similar to PU control (**PU11** = 20.1 °C)

# Results

- Mechanical properties of Silyl-PUs and control PU via tensile tester



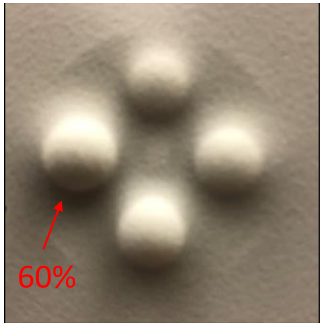


- Elongation values of Silyl-PU coatings ranged from 4.80-327.0%
  - Greatest values were for **PU7** (262.8%) and **PU8** (327.0%) due to structure of diols and crosslink density
  - Pigmented/filled Silyl-PUs (**PU9** & **PU10**) had elongation values of 146.1% and 147.9%, respectively, which were nearly 6 times that of PU11 (control) at 24.9%
- Tensile strength of PU control (**PU11**) was 28.9 MPa compared to pigmented/filled Silyl-PUs (**PU9** = 5.4 MPa, **PU10** = 15.4 MPa) due to slightly greater crosslink density

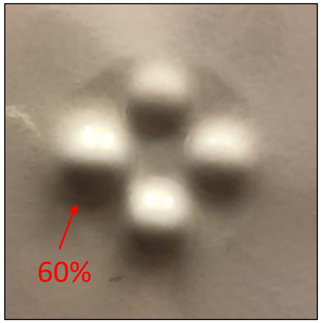
# Results

- Performance properties of polyurethane coatings

| Coating | König Pendulum Hardness (oscillations) | 0.25-Inch Cylindrical Mandrel Bend | MEK Solvent Resistance (double rubs) | Room Temperature Flexibility via GE Impact |
|---|---|---|---|---|
| **PU1** | 8 | No cracking | 100 – no marring | 20-40% elongation |
| **PU2** | 73 | No cracking | 100 – no marring | 60% elongation |
| **PU3** | 27 | No cracking | 100 – no marring | 60% elongation |
| **PU4** | 62 | No cracking | 100 – no marring | 60% elongation |
| **PU5** | 127 | No cracking | 100 – no marring | 60% elongation |
| **PU6** | 13 | No cracking | 100 – no marring | 40% elongation |
| **PU7** | 38 | No cracking | 100 – no marring | 60% elongation |
| **PU8** | 14 | No cracking | 100 – slight marring | 60% elongation |
| **PU9** | 26 | No cracking | 100 – no marring | 60% elongation |
| **PU10** | 13 | No cracking | 100 – no marring | 60% elongation |
| **PU11 (control)** | 25 | No cracking | 100 – no marring | 40% elongation |

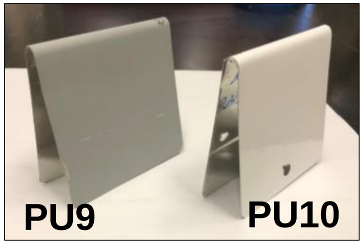


**PU9**



**PU10**

- Pigmented/filled Silyl-PUs (**PU9** & **PU10**) demonstrated similar surface hardness, mandrel flexibility, and solvent resistance, yet better GE Impact flexibility, than Type IV PU control (**PU11**)



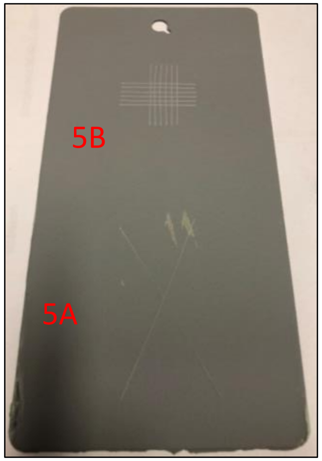
# Results

- Performance properties of polyurethane coatings

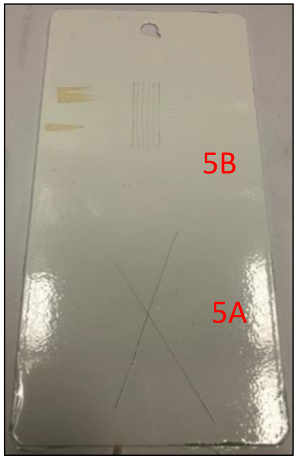
MIL-PRF-23377, Type I, Class N (non-chromate) epoxy primer

Application of Silyl-PUs via HVLP spray equipment, then 14 day cure

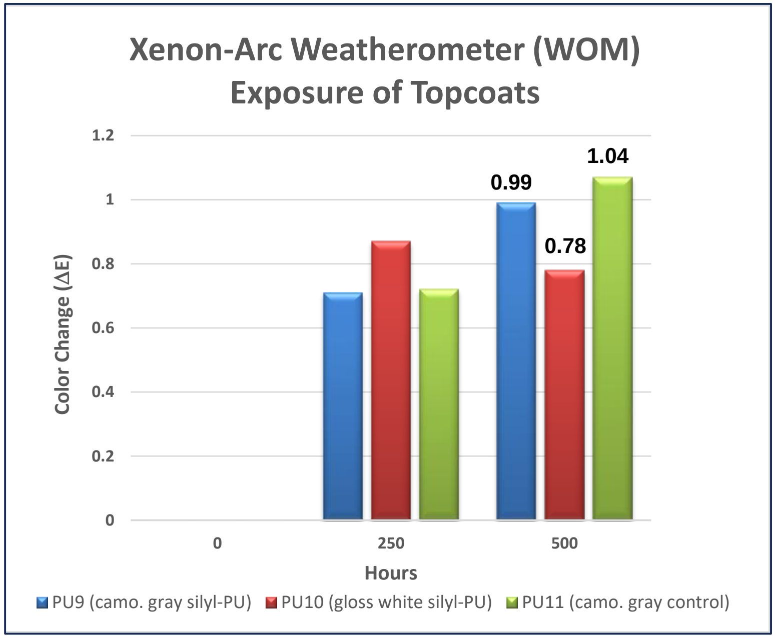
**PU9**



**PU10**



- Silyl-PUs demonstrated excellent X-Cut and Cross-Cut adhesion to epoxy primer



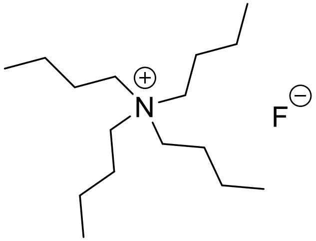
- Unclear why PU control (**PU11**) demonstrated insufficient weatherability for a Type IV topcoat

- Silyl-PUs **PU9** and **PU10** met MIL-PRF-85285, Type I weatherability <u>without</u> stabilizers/additives

# Results

- Exposure of coatings to static solutions of fluoride salt stimuli

Tetrabutylammonium fluoride (TBAF)



**TBAF·$H_2O$** (solid) – Per SDS: no acute inhalation or dermal toxicity; no carcinogenicity

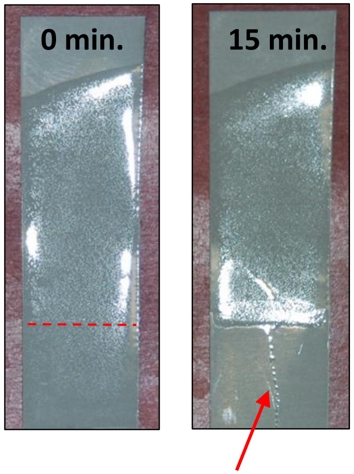
**Methylene chloride** (liquid) – Per SDS: chronic inhalation health hazard and known carcinogen; recently banned by the EPA for consumer use

**Tetrahydrofuran (THF), acetone, and benzyl alcohol (BzOH) used as solvents for TBAF**

| Coating | Time of Removal from Pretreated AA with 1.0 M TBAF (THF) (minutes)* |
|---|---|
| **PU1** | 120 |
| **PU2** | 30 |
| **PU3** | 75 |
| **PU4** | 30 |
| **PU5** | 30 |
| **PU6** | 60 |
| **PU7** | 60 |
| **PU8** | 15 |
| **PU9** | 30 |
| **PU10** | 30 |

*Chromic acid anodized AA 2024-0 panels

**PU8**



Complete removal

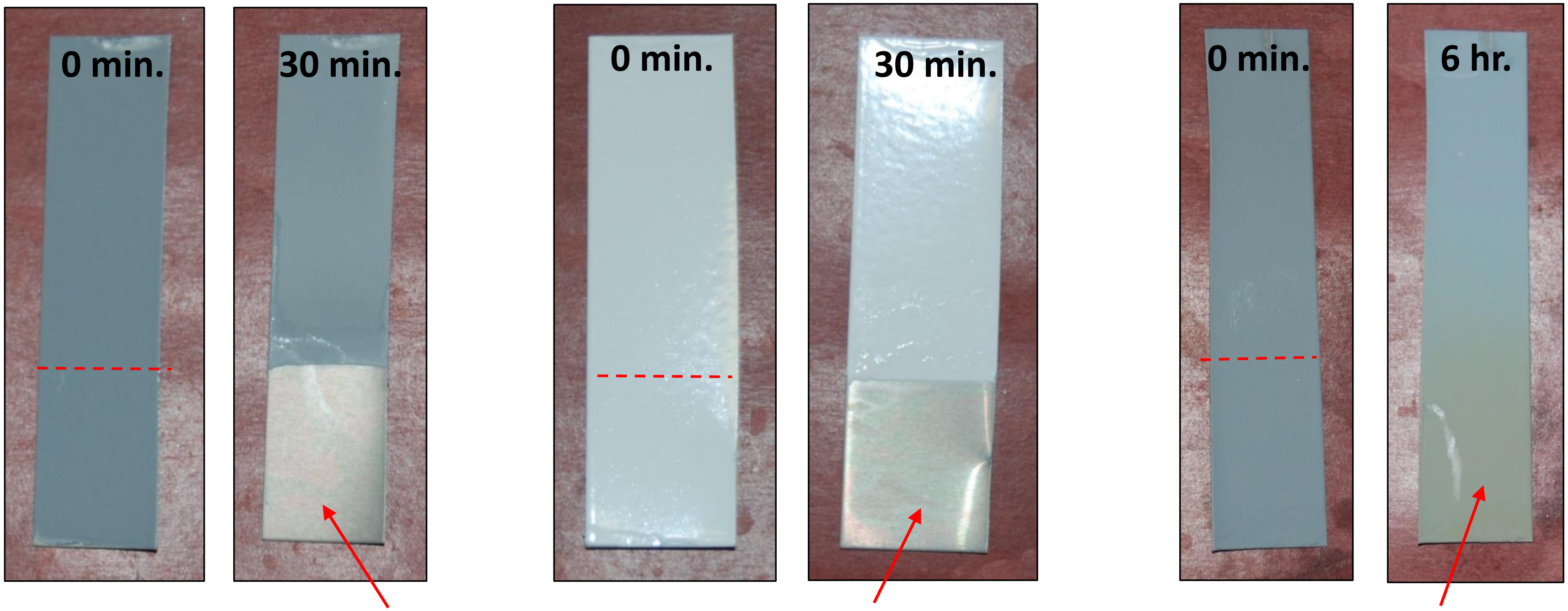
# Results

- Exposure of coatings to static solutions of fluoride salt and other stimuli
  - 1.0 M TBAF (THF) at room temperature

Silyl-PU: **PU9**

Silyl-PU: **PU10**

85285 control: **PU11**



Complete removal from pretreated AA

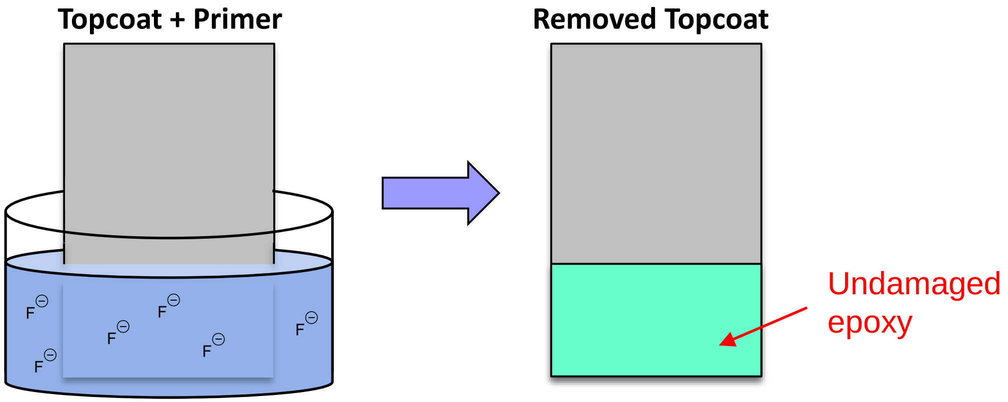
Not removed or damaged

**PU9** and **PU10** were not removed or damaged after 3 hours in 1.0 M HCl (aq.), 1.0 M NaOH (aq.), 1.0 M NaCl (aq.), or 1.0 M TBACl (THF)

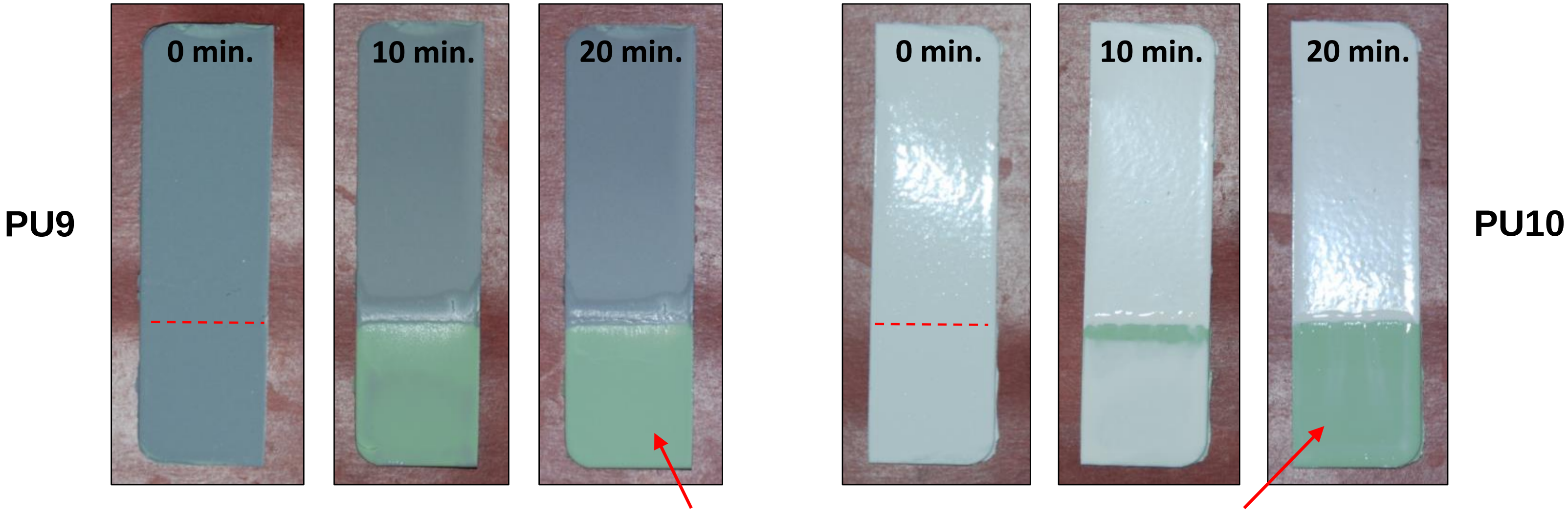
**PU11** (control) showed minor staining, but no blistering, softening, peeling or other deformities after 6 hours immersion

# Results

- Selective removal of Silyl-PU topcoats from epoxy primer



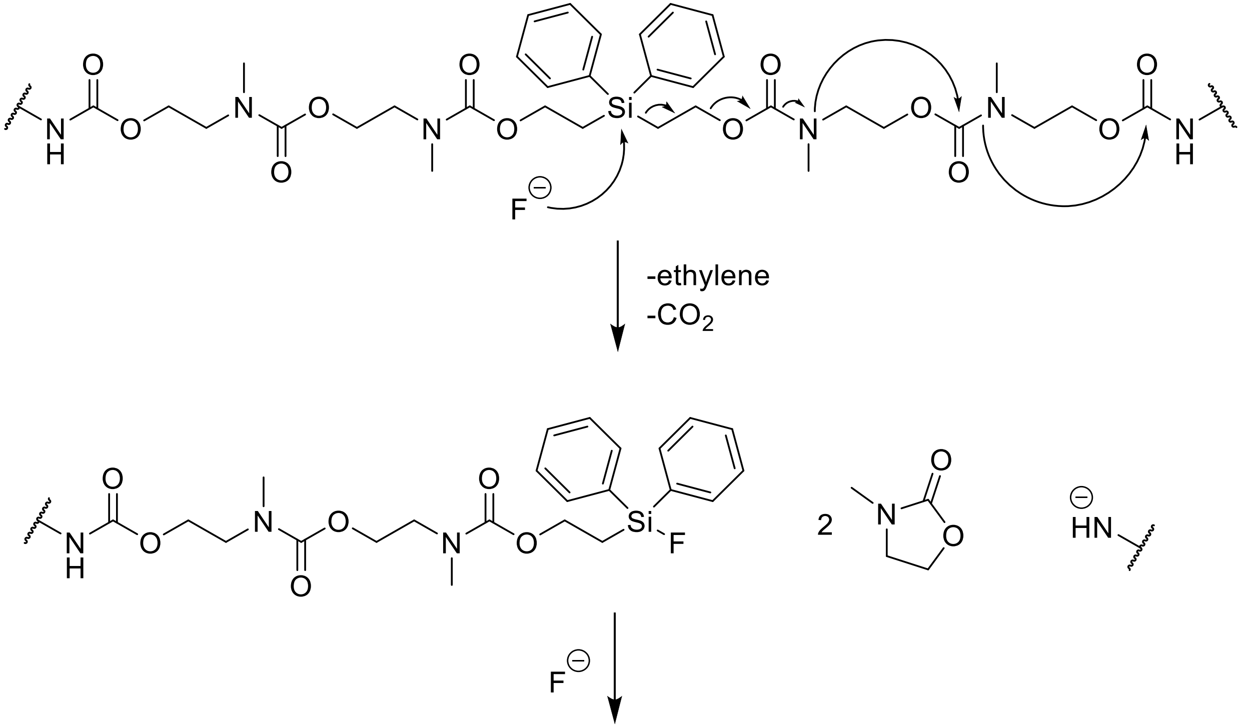
- 1.0 M TBAF (THF) at room temperature



Complete removal from epoxy primer

# Results

- Proposed mechanism of degradation for Silyl-PU topcoats **PU9** and **PU10**

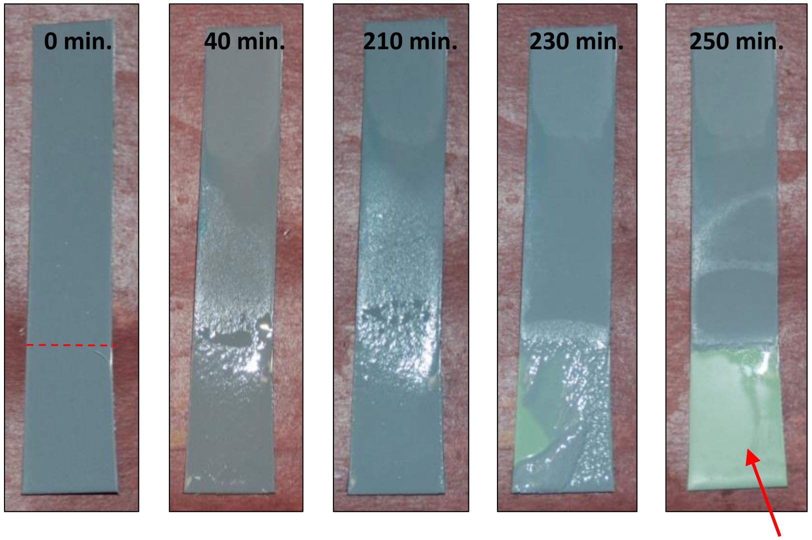


**Complete network disassembly via cascading bond cleavages**

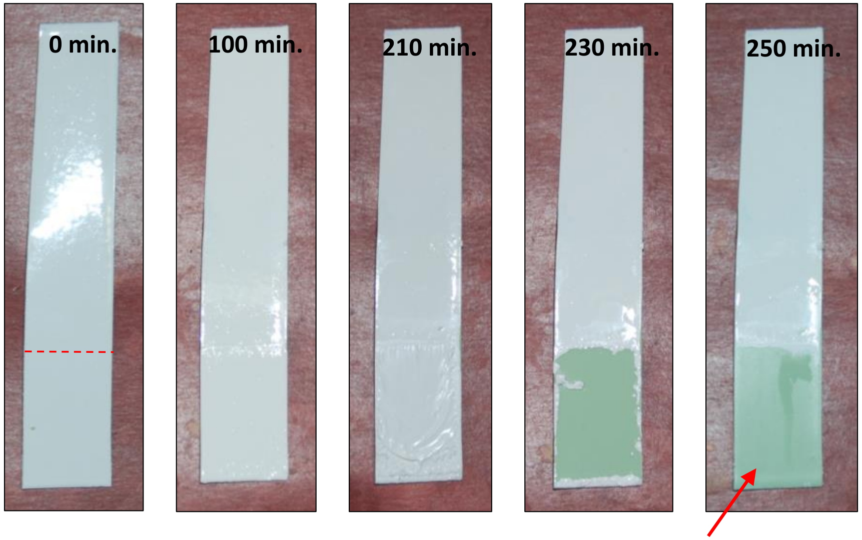
# Results

- Selective removal of Silyl-PU topcoats from epoxy primer
  - 1.0 M TBAF in acetone and benzyl alcohol (BzOH) at room temperature

**PU9**



**PU10**

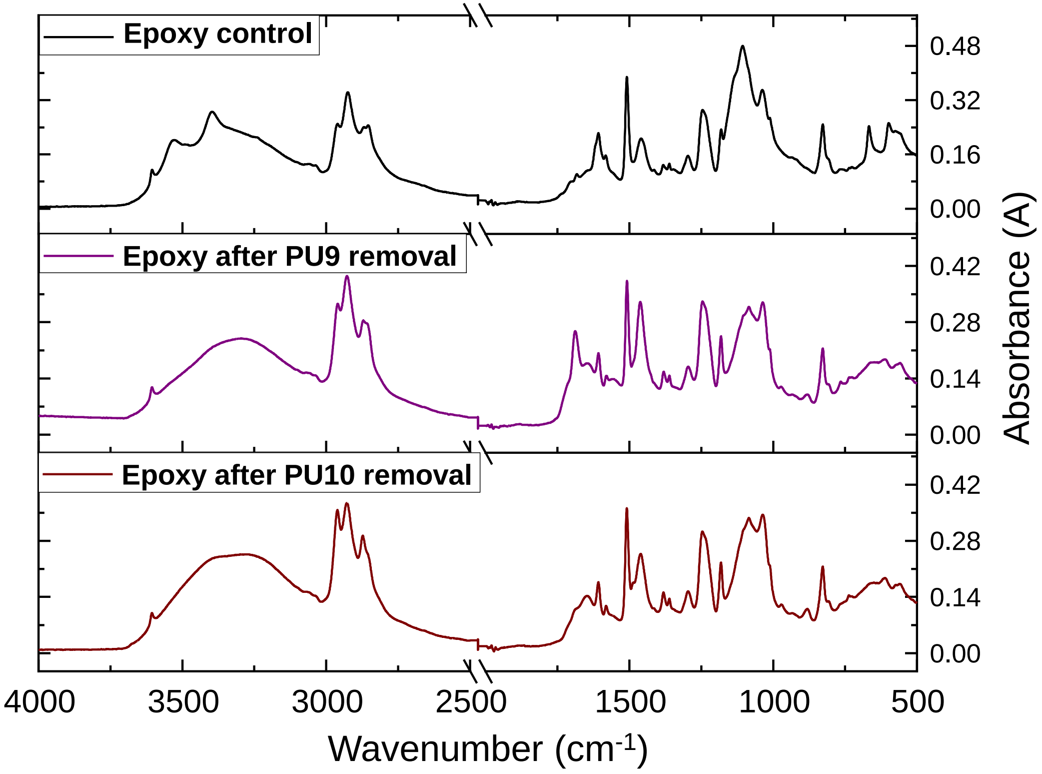


Complete removal from epoxy primer with 1.0 M TBAF (acetone)

- Acetone is a “green” solvent, but complete removal was ~12X slower than in THF due to reduced swelling and reduced nucleophilicity of fluoride ion
- Topcoat removal with 1.0 M TBAF (BzOH) even slower (i.e. >8 hours) due to greater stabilization of fluoride ion

# Results

- Selective removal of Silyl-PU topcoats from epoxy primer with 1.0 M TBAF (THF) exposure



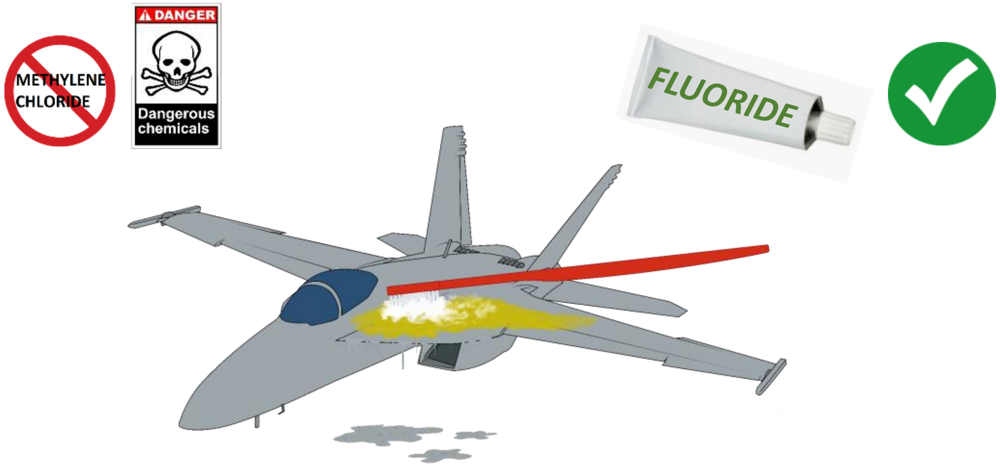
Chemical structure of epoxy primer unchanged after removal of Silyl-PU topcoats

# Technology Transfer

- Transition to a full SERDP project
- Technical presentations at American Coatings Conference, SERDP-ESTCP Symposium, ASETS Defense, CoatingsTech Conference, and American Chemical Society National Meeting
- Increase interactions with DoD stakeholders from NAVAIR and Air Force who oversee painting and de-painting operations

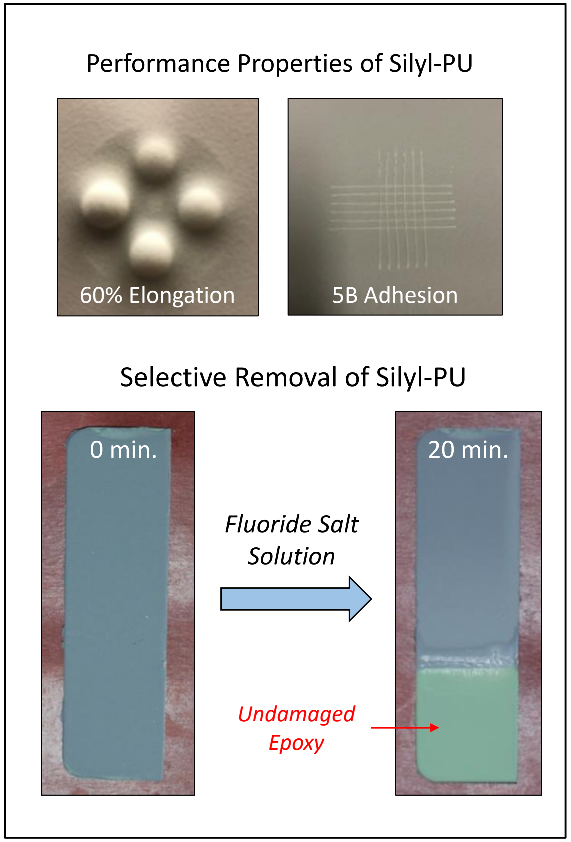
# Key Points

- Silyl-PU topcoats demonstrated similar performance as a MIL-PRF-85285, Type IV polyurethane topcoat, except for weathering – potential to meet Type IV weathering with additives/stabilizers
- Silyl-PU topcoats were selectively removed from an epoxy primer with fluoride salt solutions under mild conditions, thereby eliminating the use of methylene chloride and other hazardous paint strippers
- Underlying epoxy primer was not damaged upon removal of strongly adhered Silyl-PU topcoat – potential exist to apply another topcoat with minimal-to-no surface preparation



# WP20-1106: Selectively Strippable Silyl-Containing Aerospace Topcoats Using Environmentally Friendly Fluoride Salts

**Performers:** NRL and NAWC-AD



Performance Properties of Silyl-PU

Selective Removal of Silyl-PU

## Technology Focus

- *High-performance and selectively strippable silyl-containing polyurethane (Silyl-PU) topcoats for aircraft and GSE*

## Research Objectives

- *Demonstrate, as a proof-of-concept, that Silyl-PU topcoats provide similar performance properties as MIL-PRF-85285 polyurethanes, yet can also be selectively removed from a non-metallic substrate (e.g. anti-corrosive epoxy primer), without damaging the substrate, using an environmentally friendly fluoride salt solution*

## Project Progress and Results

- *Silyl-PUs met several MIL-PRF-85285, Type IV performance requirements (e.g. MEK solvent resistance, GE Impact)*
- *Silyl-PUs were removed from an epoxy primer within 20 min. using a static solution of fluoride salt at room temperature*

## Technology Transition

- *Transition to a full SERDP project*
- *Increase interactions with DoD stakeholders and industry*