Improving Corrosion Resistance, Alkaline Resistance, and Weatherability of Waterborne Coatings with Organofunctional Bipodal Silanes

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Coatings Trends & Technologies Conference 2019
Agenda

1. Project Background
2. Silane Chemistry Introduction
3. Experimental Methods
4. Corrosion Resistance Performance
5. Electrochemical Impedance Spectroscopy Data
6. Alkaline Resistance Performance
7. Outdoor Weatherability Test Results
8. Q&A
Environmentally-friendly Corrosion Protection of Metals is an Important Topic for Evonik
Organofunctional Silanes are Bifunctional Molecules

Y—(CH₂)ₙSi(OR)₃

n = 0, 3
R = CH₃, C₂H₅, (CH₂)₂OCH₃
Y = Organofunctional group

Organofunctional group can react with polymers, resins…

Silicon functional group can react with inorganic fillers, metals, glass…

non-hydrolyzable

hydrolyzable
Hydrolysis of Silanes

In the presence of excess water...

OR = "Silicon-functional" group  |  Y = "Organofunctional" group
Silanes, Hydrolysis and Condensation

Polymer + Silane + Surface

Adhesion promotion

OR = "Silicon-functional" group | Y = "Organofunctional" group
Reactivity of Metal Substrates and Organofunctional Silanes

The reactivity of a silane towards a substrate depends on the hydroxyl concentration, functionality, and polarity of the surface.

<table>
<thead>
<tr>
<th>Metals</th>
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<tbody>
<tr>
<td>• Copper</td>
</tr>
<tr>
<td>• Aluminum</td>
</tr>
<tr>
<td>• Silver</td>
</tr>
<tr>
<td>• Cold Rolled Steel</td>
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<tr>
<td>• Zinc</td>
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<tr>
<td>• Gold</td>
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</tbody>
</table>

Metals

good

bad
Water-borne Sol-gel Silane Systems for Metal Corrosion Protection

Water-borne Sol-gel Silane Systems – a heavy metal & VOC free alternative corrosion protection

Using a silane enables:
- Surface passivation
- Barrier effect – water and chloride
- Improved adhesion of subsequent coating

“Sol-gel Silane System”
Water-borne, Sol-gel Silane System Containing Functionalized SiO₂ Nanoparticles
Bipodal Silanes for Improving the Corrosion Resistance of Water-borne Systems

Advantages

• Hydrophobic
• High crosslinking density
• Good surface passivation
• Compatible with water-borne systems

Bis(triethoxysilyl)ethane – “Bipodal Silane #1”

More hydrophobicity and surface passivation enhances corrosion resistance!

Additional crosslinking can reduce the need for high temperature curing!
Experimental Methods

**Silane Formulations**

- Mix Bipodal Silane #1 in water-borne systems for 24+ hours for full hydrolysis

**Application & Curing Procedures**

- Wipe metal substrate with isopropyl alcohol
- Alkaline wash metal substrate for 3 minutes at 140°F
- Dip coat substrate for ~60 secs
- Cure in oven at desired temperature: 23°C – 180°C

**Testing Procedures**

- Neutral Salt Spray test (ASTM B117)
- Electrochemical Impedance Spectroscopy (performed by Matergenics Inc.)
- Alkaline Resistance test (GMW 14665 – General Motors specification)
- Outdoor weatherability testing (Piscataway, NJ location)
Mixing 2 wt.% Bipodal Silane #1 in H$_2$O

1h after mixing

24h after mixing
Bipodal Silane #1 Hydrophobizes Metal Surfaces

Contact Angle: 
~44°

H₂O on Untreated Aluminum

Contact Angle: 
~72°

H₂O on 2% Bipodal Silane #1-treated Aluminum
Bipodal Silane #1 Crosslinks Sol-gel Silane System at Lower Temperatures

2% Sol-gel Silane System + 2% Bipodal Silane #1

4% Sol-gel Silane System

23°C cure (48 hours)  80°C cure (30 min)  180°C cure (30 min)

After 250h in neutral SST
Aluminum T6061
Bipodal Silane #1 Crosslinks Sol-gel Silane System at Lower Temperatures

2% Sol-gel Silane System
+ 2% Bipodal Silane #1

After 1000h in neutral SST
Aluminum T6061

4% Sol-gel Silane System

23°C cure (48 hours)  80°C cure (30 min)  180°C cure (30 min)
Electrochemical Impedance Spectroscopy (EIS) of Water-borne Sol-gel Systems

Background & Benefits of EIS

- Measures resistance & capacitance of coated metals in salt-based solution
- Higher impedance of coating, $|Z|$, indicates a more efficient barrier to surrounding water & salts

Analysis of Results

- At 0.1 Hz, Bipodal Silane #1 improved the impedance of the thermally cured system by 34%
- Thermal curing procedure more effective at improving impedance than Bipodal Silane #1

![Graph showing impedance vs. frequency for different systems and conditions.](image)
Improving Resistance to Alkaline Media with Bipodal Silanes

Importance of Alkaline Resistance

- Alkaline detergents commonly used for car wash applications
- Crucial performance requirement for automotive coatings industry

Testing Procedure

- Prepare 10% NaOH, 90% DI H₂O solution
- Coat Aluminum T6061 and cure at 180°C for 30m
- Immerse coated samples in alkaline solution
- Place alkaline-immersed samples in salt spray test for further evaluation
- GMW 14665 – General Motors Specification

After 6 minutes immersion in 10% NaOH solution

4% Sol-gel Silane System

2% Sol-gel Silane System + 2% Bipodal Silane #1
Improving Resistance to Alkaline Media with Bipodal Silanes

<table>
<thead>
<tr>
<th>CTT 2019</th>
<th>Improving Corrosion Resistance, Alkaline Resistance, and Weatherability of Waterborne Coatings with Organofunctional Bipodal Silanes</th>
<th>2% Sol-gel Silane System + 2% Bipodal Silane #1</th>
</tr>
</thead>
<tbody>
<tr>
<td>After 100h in neutral SST</td>
<td>Aluminum T6061</td>
<td></td>
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</table>

2% Sol-gel Silane System + 2% Bipodal Silane #1

4% Sol-gel Silane System

No alkaline immersion

10 min alkaline immersion
Weight Loss Comparisons of Post-Alkaline Test Aluminum 2024 Substrates

<table>
<thead>
<tr>
<th>Condition</th>
<th>Substrate Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before alkaline immersion</td>
<td>35</td>
</tr>
<tr>
<td>No coating</td>
<td>33</td>
</tr>
<tr>
<td>4% Sol-gel Silane System RT cure (48 hours)</td>
<td>-7.62%</td>
</tr>
<tr>
<td>4% Sol-gel Silane System 180°C cure (30 min)</td>
<td>-10.26%</td>
</tr>
<tr>
<td>2% Sol-gel Silane System / 2% Bipodal Silane #1 RT cure (48 hours)</td>
<td>-13.20%</td>
</tr>
<tr>
<td>2% Sol-gel Silane System / 2% Bipodal Silane #1 180°C cure (30 min)</td>
<td>-0.44%</td>
</tr>
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</table>
Improving Weatherability of Coated Cold Rolled Steel with Bipodal Silanes

10% Sol-gel Silane System

After 7 days left outside in NJ

Cold-rolled Steel

5% Sol-gel Silane System
5% Bipodal Silane #1

RT cure (48 hours) 180°C cure (30 min)

No coating
Improving Weatherability of Coated Cold Rolled Steel with Bipodal Silanes

| CTT 2019 | Improving Corrosion Resistance, Alkaline Resistance, and Weatherability of Waterborne Coatings with Organofunctional Bipodal Silanes

After 14 days left outside in NJ

Cold-rolled Steel

No coating

10% Sol-gel Silane System

5% Sol-gel Silane System

5% Bipodal Silane #1

RT cure (48 hours) 180°C cure (30 min)
Improving Weatherability of Coated Cold Rolled Steel with Bipodal Silanes

10% Sol-gel Silane System

5% Sol-gel Silane System

5% Bipodal Silane #1

RT cure (48 hours) 180°C cure (30 min)

After 30 days left outside in NJ

No coating
Conclusion & Future Work

**Conclusion**

- Bipodal Silanes can offer:
  - Improved hydrophobicity and corrosion resistance in water-borne coatings
  - Increased crosslinking in water-borne sol-gel silane systems at lower than required temperatures
  - Enhanced resistance to alkaline media

**Future Work**

- Evaluate other Organofunctional Silanes for room-temperature curing of water-borne corrosion protection technology
- Optimize corrosion protection on other metals (CRS, HDG Steel, other Aluminum alloys, etc……)
- Outdoor weatherability testing in various regional environments
For Further Assistance

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Please keep in mind ...

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