HYBRID SOL–GEL CORROSION INHIBITORS

A Novel Approach to Corrosion Inhibitors for Coatings
Acknowledgments

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- Theresa Kretz, Intern Student
Established in 1972
Recognized Leader in Corrosion Inhibitor Technology
Reputation for Superior Technical Support
Brodest Corrosion Inhibitor Product Line in the Paints & Coatings Industry
www.halox.com
What are sol–gels?
Sol–Gel Metal Pretreatments
Sol–Gel Paint Additives
What are Sol–Gels?

- Sol–gel or “silica–gel”
- Inorganic–organic hybrid
- Liquid corrosion inhibitor/Adhesion Promoter

Illustration courtesy of Evonik Degussa GmbH
1. Silicone ester hydrolyzes to forms silanol

\[
\begin{align*}
\text{RO-Si-OH} + \text{H}_2\text{O} & \rightarrow \text{RO-Si-OH} + \text{ROH} \\
\text{RO-Si-OR} + \text{OR} & \rightarrow \text{RO-Si-OR} + \text{OR}
\end{align*}
\]

2. Siloxane bond forms

\[
\begin{align*}
\text{RO-Si-OH} + \text{OH-OR} + \text{OH-OR} + \text{OH-OH} & \rightarrow \text{RO-Si-O-Si-OR} + \text{ROH} \\
\text{RO-Si-OR} + \text{OR} + \text{OR} + \text{OR} & \rightarrow \text{RO-Si-O-Si-OR} + \text{ROH}
\end{align*}
\]

3. Gelation (Cross-linking)

\[
\begin{align*}
\text{RO-Si-O-Si-OR} + \text{OR} + \text{OR} + \text{OR} + \text{OR} & \rightarrow \text{RO-Si-O-Si-OR} + \text{ORH} \\
\text{RO-Si-O-Si-OR} + \text{OR} + \text{OR} + \text{OR} + \text{OR} & \rightarrow \text{RO-Si-O-Si-OR} + \text{ORH}
\end{align*}
\]
Inhibitive pigments or nano materials can be trapped underneath the network formed, thus providing excellent corrosion resistance of the pretreatment.
PART 1:
Pretreatments
Eco-friendly alternative
To find an aqueous Cr(VI)-free pretreatment for hot dipped galvanized and cold rolled steel substrates which will achieve superior corrosion resistance
Bare cold rolled steel panels were coated with a 10% sol-gel solutions

Polarization resistance was measured and compared

Pretreatments compared
- Bare metal
- Bonderite™ 952 and
- Bonderite™ 1000 P99X

Sol-gel pretreatment showed polarization resistance values similar to zinc and iron phosphated steels
Polarization

- Bare Cold Roll Steel
- Bonderite 952
- Bonderite 1000 P99X
- 10% Sol-Gel
Polarization resistance of cold rolled steel panels in aqueous 5.0% NaCl solution. (A) Bare cold roll steel (B) Bonderite® 952 (C) 10% Sol–Gel treated cold rolled steel (D) Bonderite® 1000 P99X
Sol Gel over Galvanized Steel

- Control @ 96 hrs SST
- Proprietary Sol Gel @ 96 hrs SST
- Proprietary Sol Gel @ 144 hrs SST

1-3 µm P/T
Galvanized Steel
PUD Pretreatment

**Cr-VI pretreatment**

- CCC
- HDG

**Cr-free pretreatment**

- PUD + Sol-Gel
- HDG

**TYPICAL PROPERTIES**

- Component: Polyester type polyurethane
- Appearance: Translucent dispersion
- Non Volatile (%): 34.0 - 36.0
- pH: 7.5 - 9.0
- Viscosity (mPa·s): 10 - 1,000
- Ionic type: Anionic
- Solvent (%): Water / N-Methyl-2-pyrrolidinone / Triethylamine (69/29/2)

**Source:** HYDRAN® 171 PUD is from DIC Corporation Sakai Plant, Japan
PUD Pretreatment

Blank  3% Organic Inhibitor A  3% Organic Inhibitor B  1.4% Sol Gel
Use of sol–gel in coatings
Why Sol-Gels?

- Thin film applications (<10 μm)
- Replacement of heavy metal anti-corrosives
Synergy of Sol Gels with Anti-Corrosive Pigments

Inhibitive pigments can be trapped underneath the network formed, thus providing excellent corrosion resistance
HALOX SOL–GEL FEATURES

- An additive for protective primers (S/B & W/B)
  - Etch primer
  - General primers
  - High gloss DTM finishes

- Liquid adhesion promoter & corrosion inhibitor

- Synergistic complement to Zinc Phosphate

- Stand alone metal pretreatment alternative to Cr\(^{6+}\) compounds
Replace ZnCrO$_4$ in wash primers
Replace Cr$^{6+}$ salts in epoxy alkyd or PU primers
Minimize white rust on GI and Al substrates
Minimize black rust on Galvalume® (Al–Zn alloy)
<table>
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<tr>
<th>Coating</th>
<th>Type</th>
<th>How</th>
<th>Outcome</th>
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| Waterborne      | Water reducible alkyd direct-to-metal (DTM) enamel | Added in grind       | Boosted salt spray
|                 |                                         |                      | Boosted blister resistance                  |
| Waterborne      | Acrylic lacquer sealant                 | Added in base        | Reduced black corrosion                      |
| Solventborne    | Vinyl butyral wash primer              | Added in the grind   | Replacement for Cr-based corrosion inhibitor |
| Solventborne    | Medium oil alkyd primer                 | Added in grind       | Increased adhesion on galvanized steel       |
Water Reducible Alkyd Enamel DTM

336 hrs Salt Spray – Cold Roll Steel
(DFT: 60 µm)

- Blank
- 2% Ammonium Benzoate
- 2% Competitive Organic Inhibitor
- 2% Sol Gel
Water Reducible Alkyd Enamel DTM

Salt Spray – 96 hrs – Cold Rolled Steel– 18 µm

Control 3% HALOX 310            3% HALOX 310/0.5% Sol Gel

3% HALOX 310
1200 hrs Salt Spray – Galvalume
(DFT: 23 μm)
240 hrs Salt Spray – Hot Dip Galvanized  
(DFT: 58 µm)
Thin Films
- GI substrate
- WB Acrylic lacquer
- 336 hrs Salt Spray

5 µm W/B clear coat

Galvanized Iron (GI)

SrCrO_4
3% Sol Gel
3% ACP
Etch Primer (Replace toxic Cr$_6^+$ in this layer)

5-6 µm etch primer
Substrate

ZnCrO$_4$ free
Key Concerns

Reduce intercoat adhesion failures with ALKYD, PU, EPOXY primers.
ETCH PRIMER COMPLETE SYSTEM

Substrate

Alkyd Primer
1000 hrs
SALT SPRAY
GI substrate

25 µm
5-6 µm

Substrate

Topcoat Only

7% Zinc Chromate

1.5% Sol Gel
5% ACP
ETCH PRIMER COMPLETE SYSTEM

2K PU Primer
576 hrs
SALT SPRAY
Cold Roll Steel

25 µm
5-6 µm

Substrate

Topcoat Only

7% Zinc Chromate

1.5% Sol Gel
5% ACP
ETCH PRIMER COMPLETE SYSTEM

2K Epoxy Primer
1000 hrs SALT SPRAY Aluminum

25 µm
5-6 µm

Substrate

Topcoat Only

7% Zinc Chromate

1.5% Sol Gel 5% ACP
Acrylic DTM Post-Adds

Acrylic DTM
48 hrs SALT SPRAY
Cold Rolled Steel
1.5 mils

Blank 1.4% HALOX 515 1.4% Sol Gel
Summary of Hybrid Sol–Gel Corrosion Inhibitors

Eco-friendly

✓ Cr(VI) free metal pretreatment
✓ Replace use of Cr(VI) pigments
✓ Waterborne
✓ Embed anticorrosive pigments
✓ Room temperature curable
✓ Suitable as additive for coatings
THANK YOU!

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