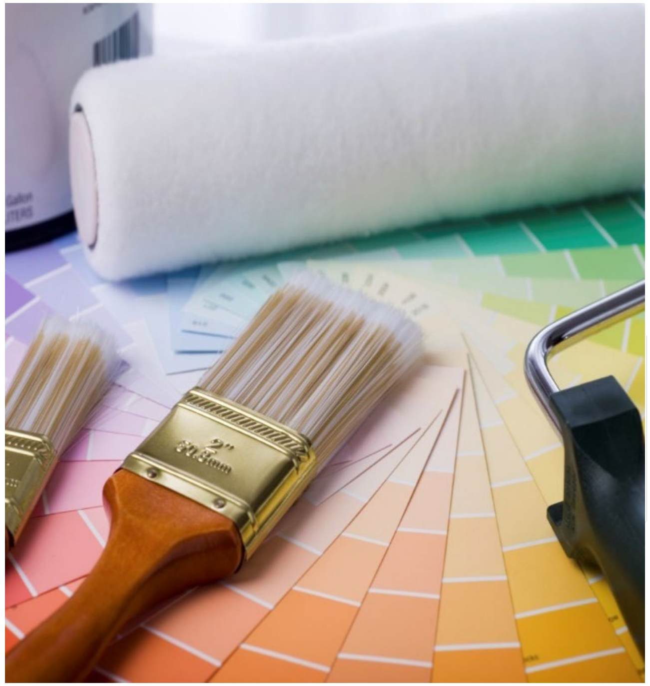
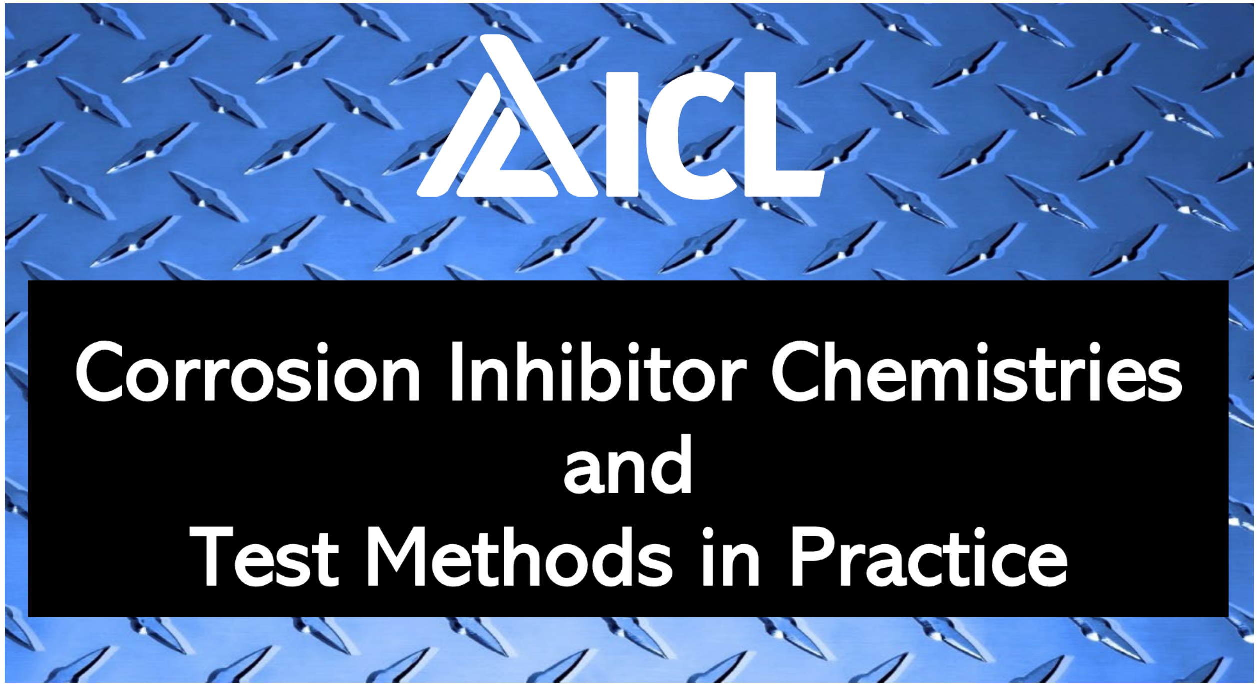




Corrosion Inhibitor Chemistries and Test Methods in Practice

Michelle Bauer
Senior Chemist

Agenda

MARKET TRENDS

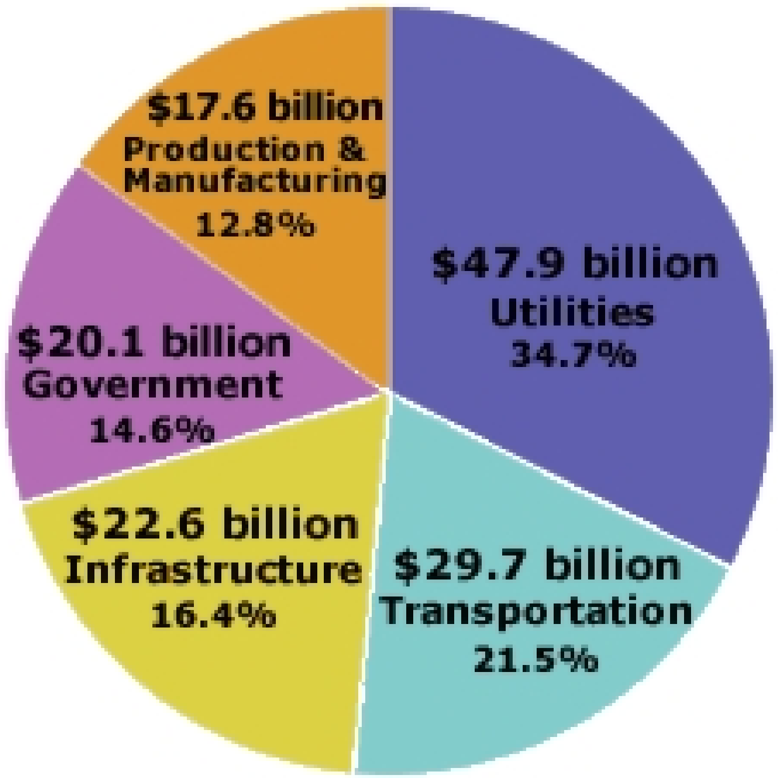
CORROSION INHIBITOR CHEMISTRIES

FORMULATING GUIDANCE

CORROSION TEST METHODS

Annual Cost of Corrosion

$276 Billion in US
$3.5 Trillion Globally



Infrastructure:	Highway Bridges Gas and Liquid Transmission Pipelines Waterways and Ports Hazardous Materials Storage Airports Railroads
Utilities:	Gas Distribution Drinking Water and Sewer Systems Electrical Utilities Telecommunications
Transportation:	Motor Vehicles Ships Aircraft Railroad Cars Hazardous Materials Transport
Production and Manufacturing:	Oil and Gas Exploration and Production Mining Petroleum Refining Chemical, Petrochemical, and Pharmaceutical Pulp and Paper Agricultural Food Processing Electronics Home Appliances
Government:	Defense Nuclear Waste Storage

www.corrosioncost.com

ICL Phosphate Specialty

Challenges in the Corrosion World

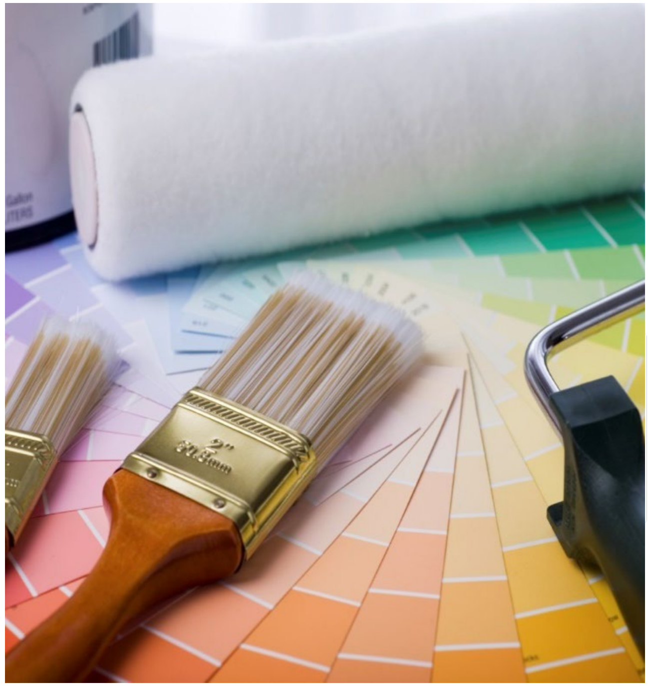
- Regulatory landscape is more complex.
- Heavy metals are facing increased regulatory restrictions.
  - Chromium
  - Lead
  - Zinc
  - Barium
- Additive and coating manufacturers are adapting to replace these chemistries with less harmful substances.

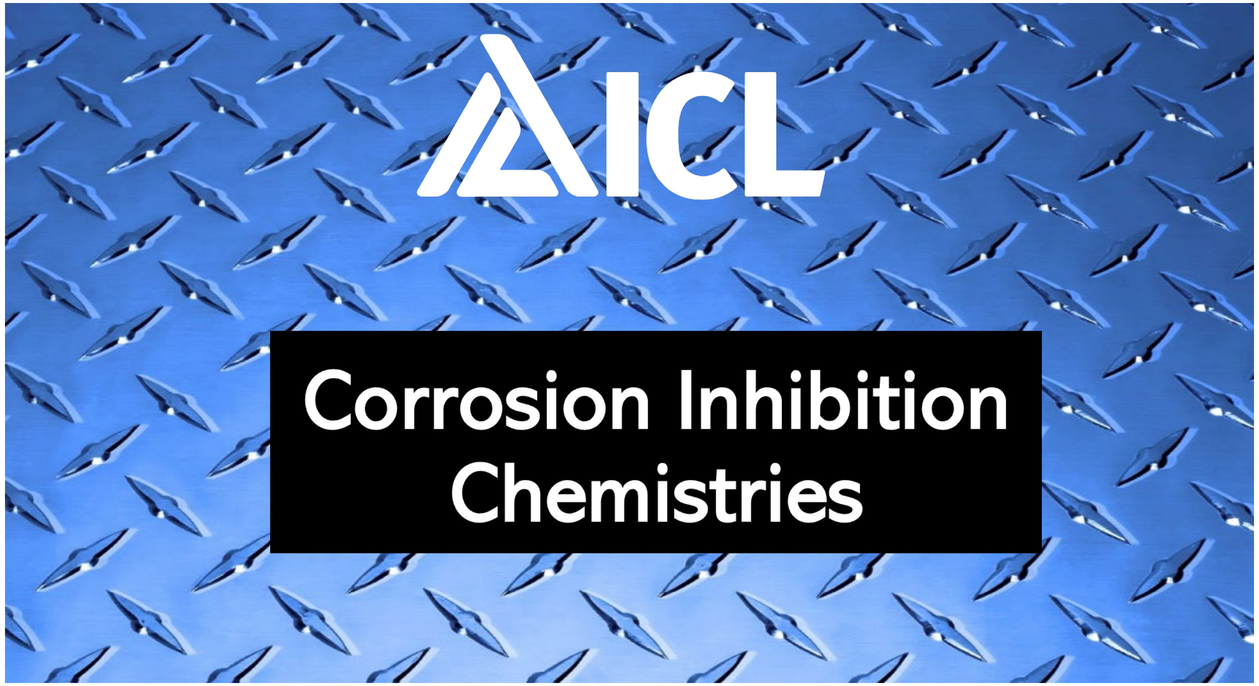
ICL Phosphate Specialty

Zinc Content – Hazardous Labeling

ADR/GHS Classification Rules	100 - 2.5% Zinc Compounds	< 2.5 - 0.25% Zinc Compounds	< 0.25% Zinc Compounds
GHS Pictogram		No pictogram	No pictogram
GHS Signal Word	WARNING (if Aquatic Chronic 1) or No signal word (if Aquatic Chronic 2)	No signal word	No signal word
Hazard Statement	Aquatic Chronic 1 H410 Very toxic to aquatic life with long lasting effects. or Aquatic Chronic 2 H411 Toxic to aquatic life with long lasting effects.	Aquatic Chronic 3 H412 Harmful to aquatic life with long lasting effects	Not classified by GHS
ADR Classification	UN3077 ENVIRONMENTALLY HAZARDOUS SUBSTANCE, SOLID, N.O.S. (Trizinc bis(orthophosphate), Zinc oxide)	Not classified as dangerous goods for transport	Not classified as dangerous goods for transport

ICL Phosphate Specialty





Corrosion Inhibition Chemistries

Corrosion Types

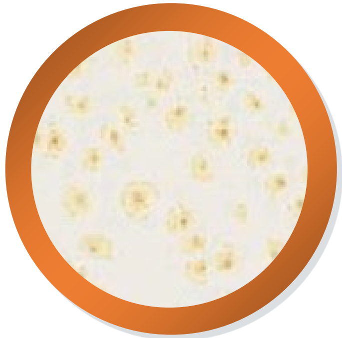
Of concern in coatings…

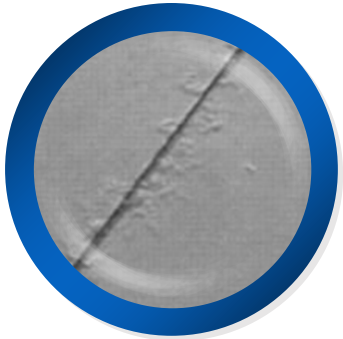
Flash Rust – Rapid, widespread corrosion seen during initial application.

Galvanic – Contact between two alloys which promotes oxidation of the less noble metal.

Filiform – Differential aeration promotes this unique form of corrosion.

Uniform – Metal degradation due to shifting anodic and cathodic positions.

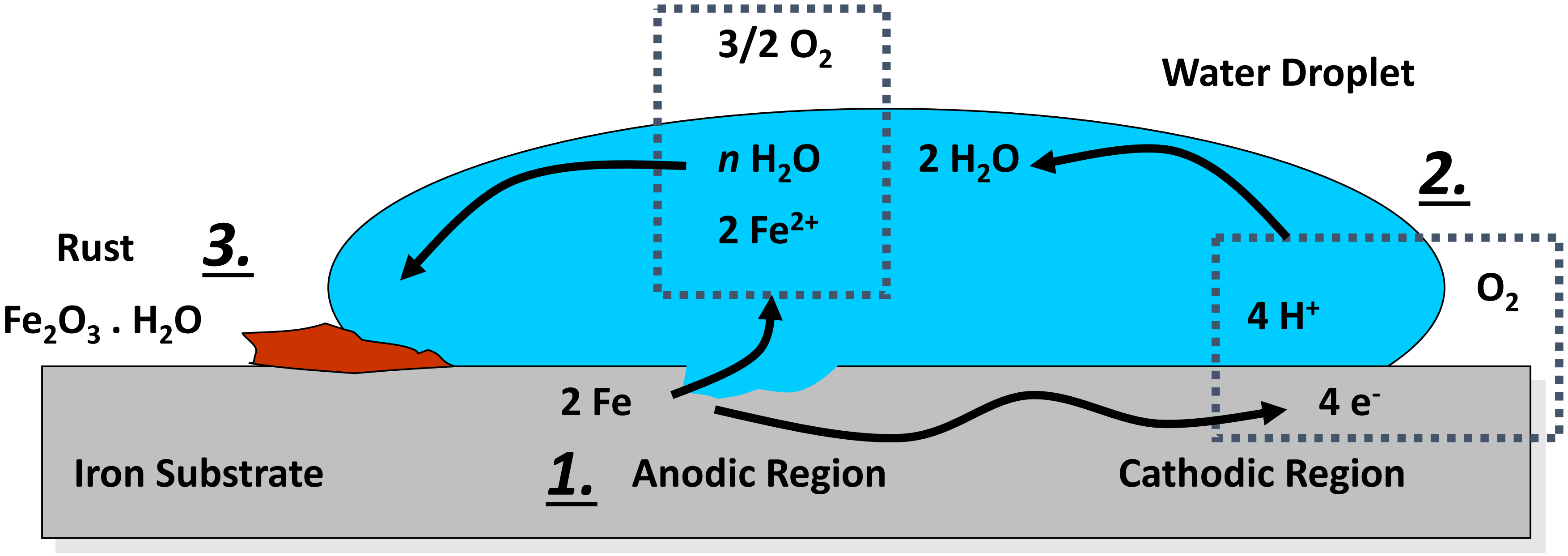




ICL Phosphate Specialty

Lambourne, R. (1999); *Paint and Surface Coatings: Theory and Practice,* 2 ed. (Lambourne, R. and Strivens, T.) England: William Andrew Publishing

Uniform Corrosion Mechanism



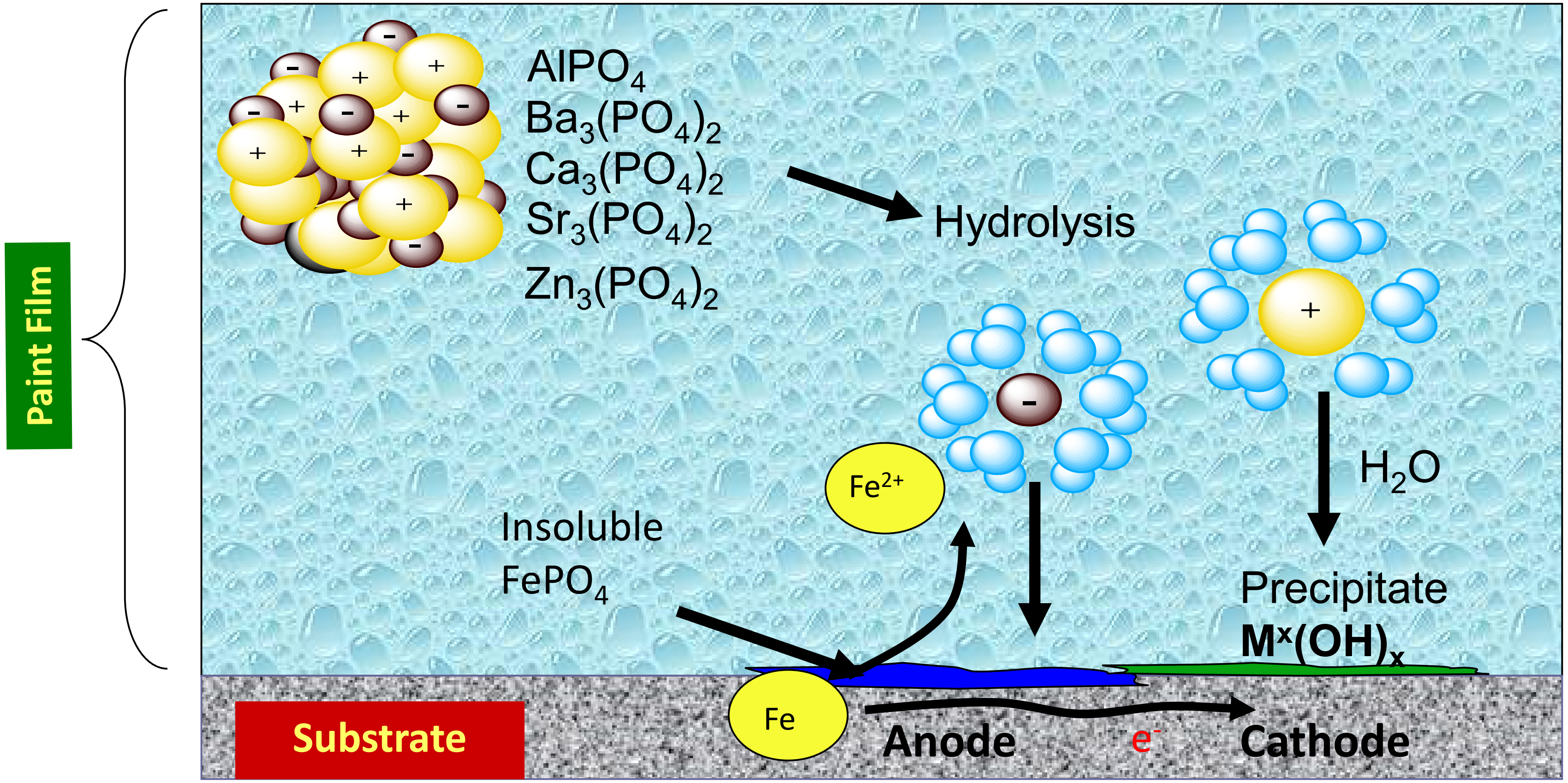
1. Oxidation of Fe yields electrons which travel through the metal.
2. Electrons at the Fe cathode reduce O_2 to H_2O.
3. The Fe^{2+} migrates through the drop and reacts with O^{2-} and H_2O to form rust.

ICL Phosphate Specialty

Passivation

Inorganic Inhibitor Mechanism

- Anodic Reaction
  - Slow the reaction rate of anodic dissolution.
  - Produce reaction products which form a thin film over anode.
- Cathodic Reaction
  - Disrupt the flow of electrons from the anode to the cathode.
  - Produce reaction products which precipitate selectively at cathodic sites.
- Barrier Properties

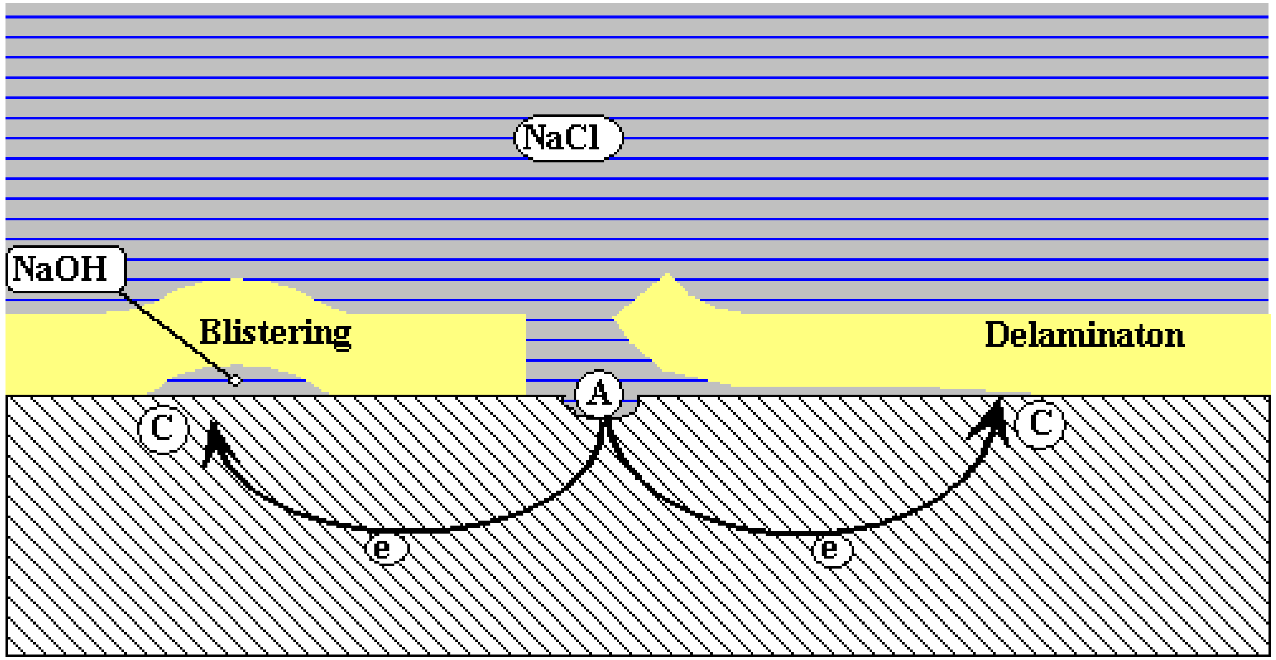


	$AlPO_4$	$Ba_3(PO_4)_2$	$Ca_3(PO_4)_2$	$Sr_3(PO_4)_2$	$Zn_3(PO_4)_2$
K_{sp}	**10×10^{-21}**	**3×10^{-23}**	**1×10^{-26}**	**1×10^{-31}**	**9×10^{-33}**

Olmsted, J & Williams, G; *CRC Handbook of Chemistry and Physics: 5° ed., 2007.*
Excerpt from ICL\ Advanced Additives HALOX® promotional materials, ICL Performance Products, LP., 2015.

ICL Phosphate Specialty

Adhesion Failures



REACTIONS:

Anodic.........$Fe \rightarrow Fe^{++} + 2e$

$Fe^{++} + O_2 + H_2O \rightarrow Fe_xO_y + H_2O$

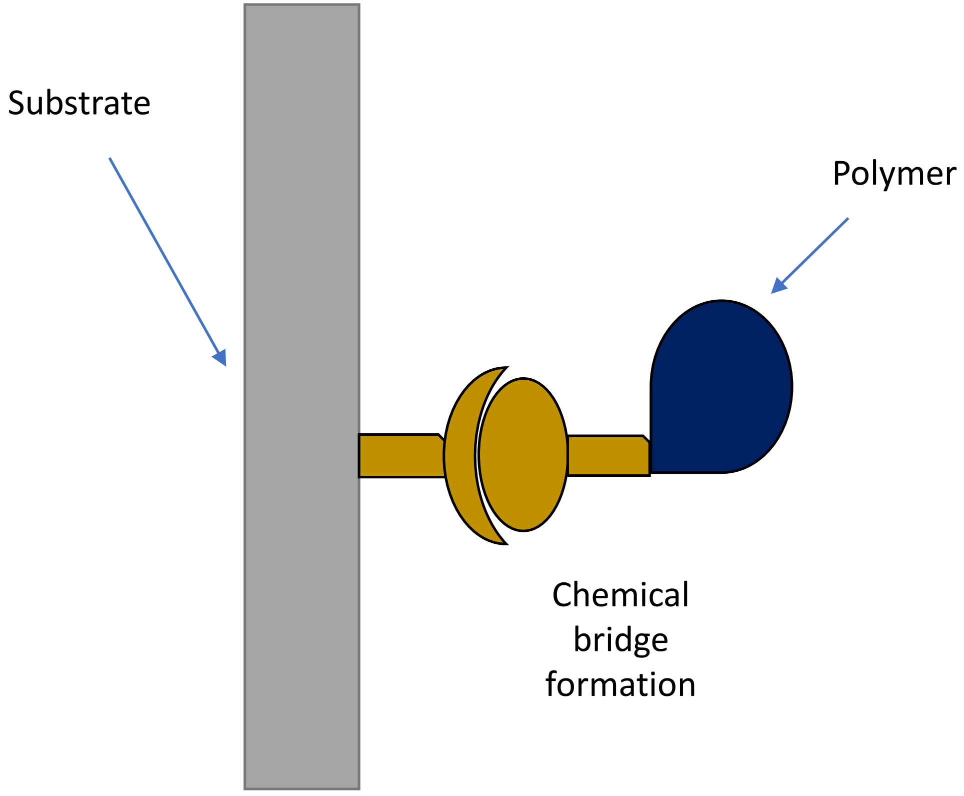
Cathodic......$H_2O + 1/2\ O_2 + 2e \rightarrow 2OH$

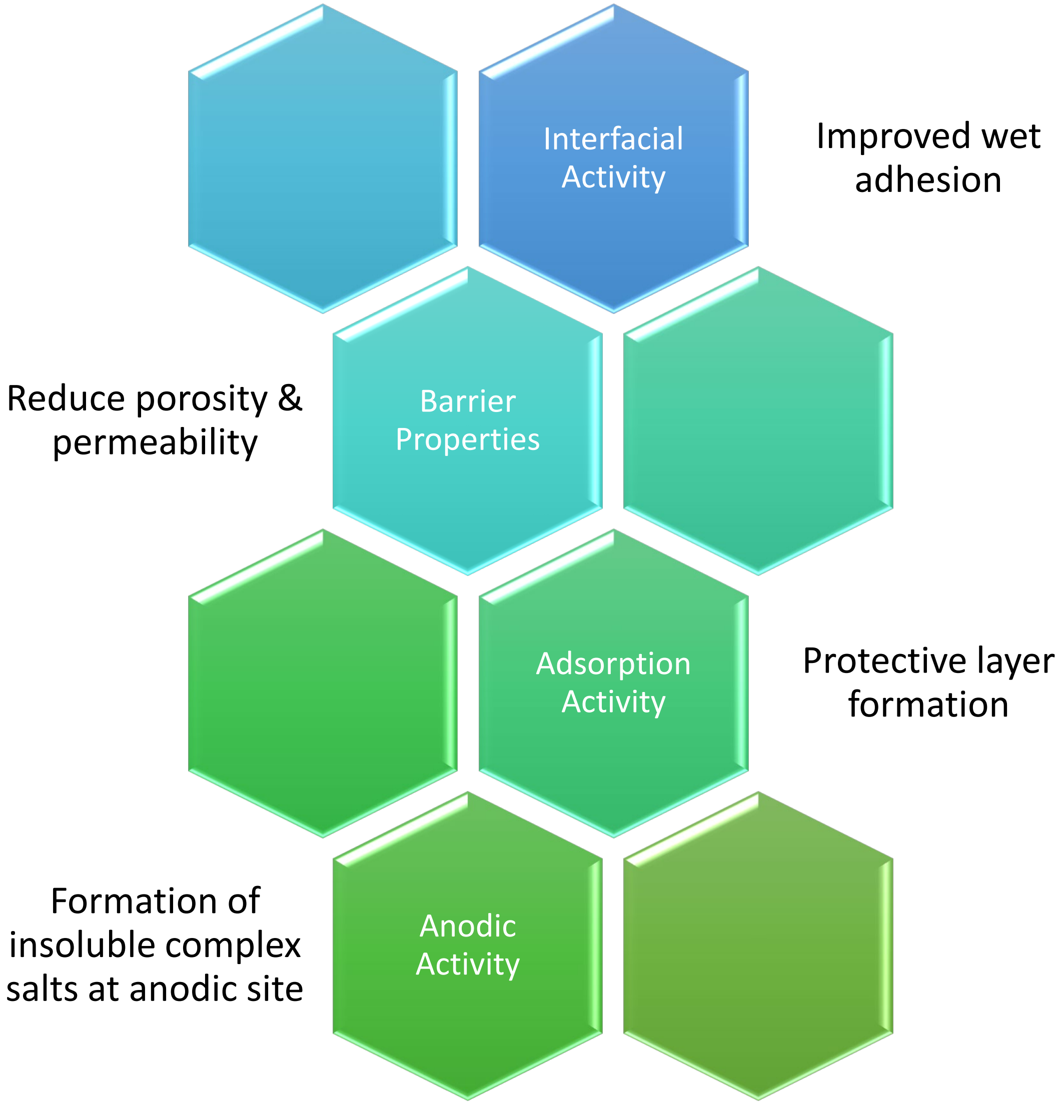
$2Na^{+} + 2OH^{-} \rightarrow 2NaOH$

Phosphate Specialty

Greenfield, D. & Scantlebury, D.; JCSE: Vol.3 Paper 5, 2000.

Organic Inhibitor Mechanism



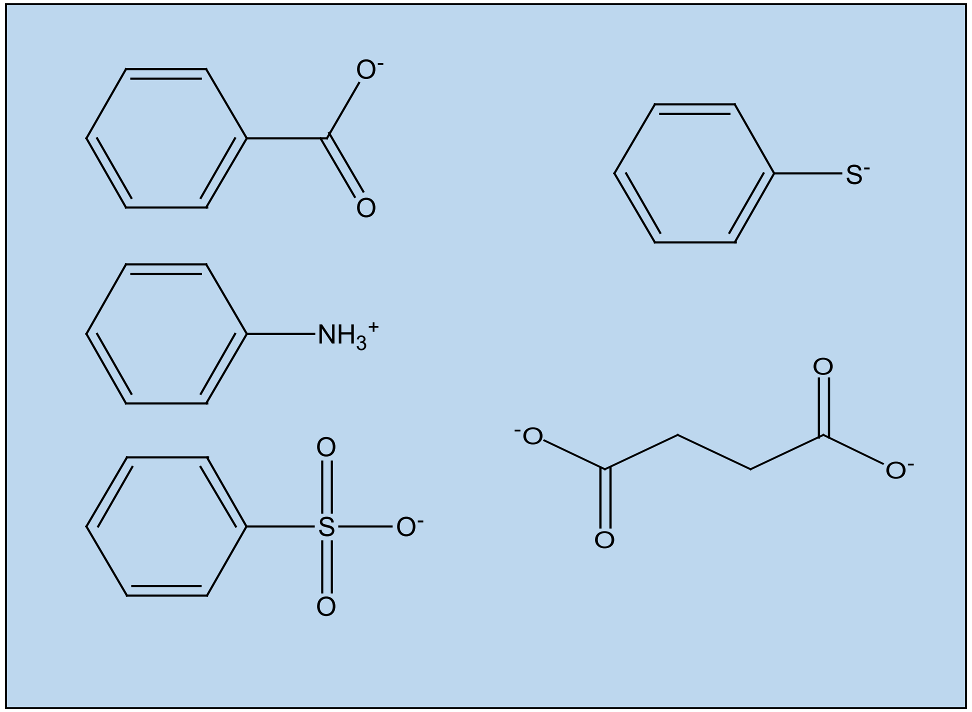


Organic Inhibitor Chemistries

Mechanism: Hydrophobic Film Formers

Slow both anodic and cathodic reactions

- **Benzoates**
- **Amines**
- **Sulfonates**
- **Thiols**
- **Di-acids**



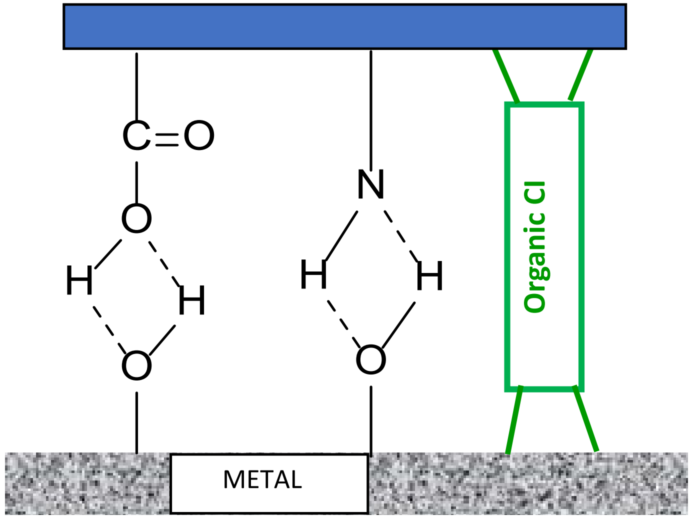
Phosphate Specialty

Organic Inhibitor – Mechanism

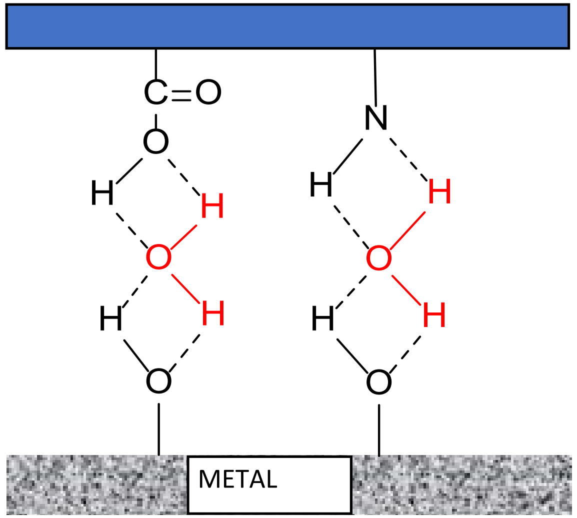
Water and corrosion products can cause:

Adhesion Loss, Delamination, Blistering

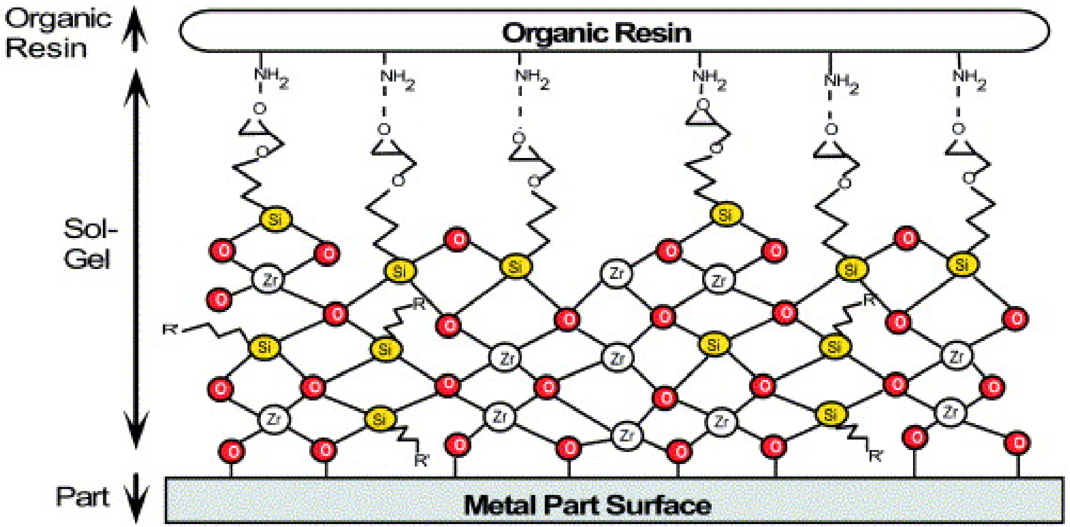
(Cathodic Reactions)



ABSENCE OF WATER



SMALL QUANTITIES OF WATER



Coatings adhere by mechanical AND polar interactions (e.g. hydrogen bonding). These can be displaced by water.

ICL Phosphate Specialty

Flash Rust Prevention

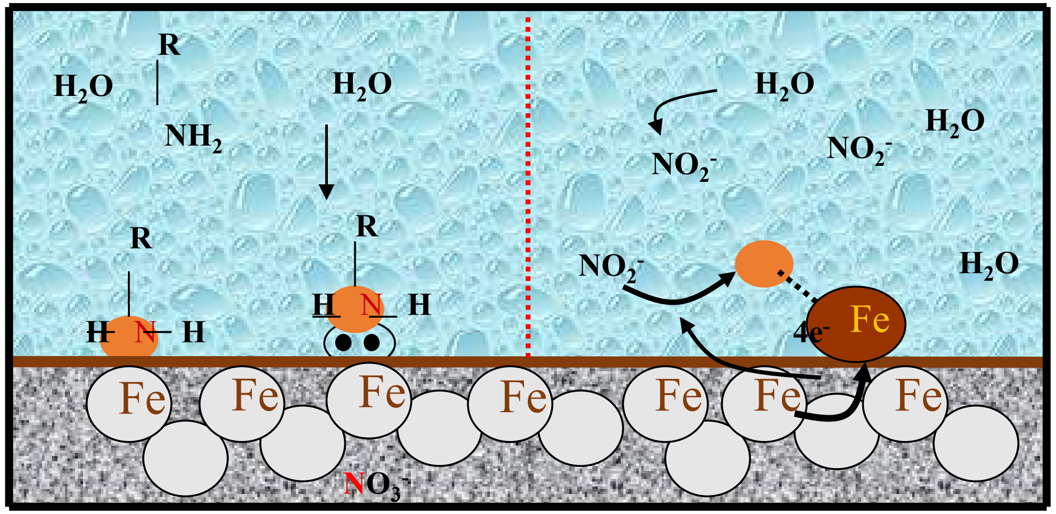
Flash rust occurs during the drying process of water-based coatings. It results in the rapid formation of a metal oxide.

Most prone substrates:

- Blasted steel (high profile)
- Welded seams
- Cold rolled steel

Common Chemistries:

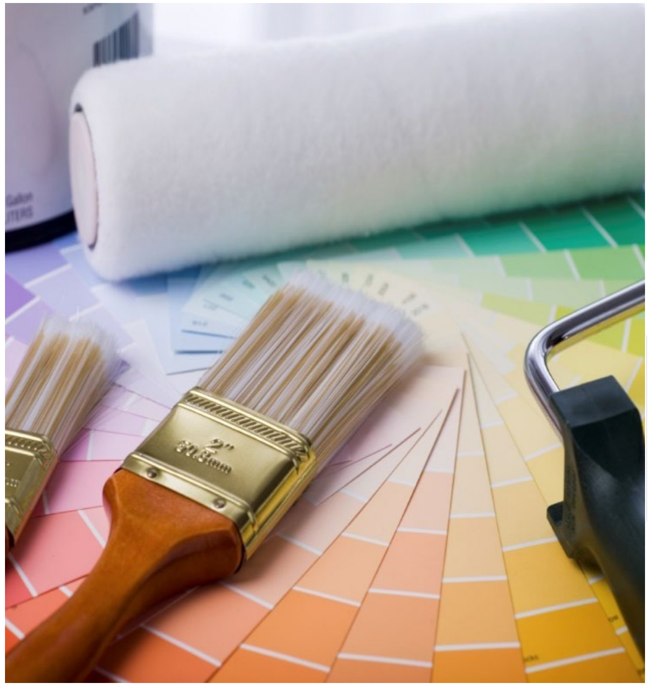
- Sodium Nitrite
- Ammonium Benzoate
- Borates
- Amines



Chemisorption **Oxidation**

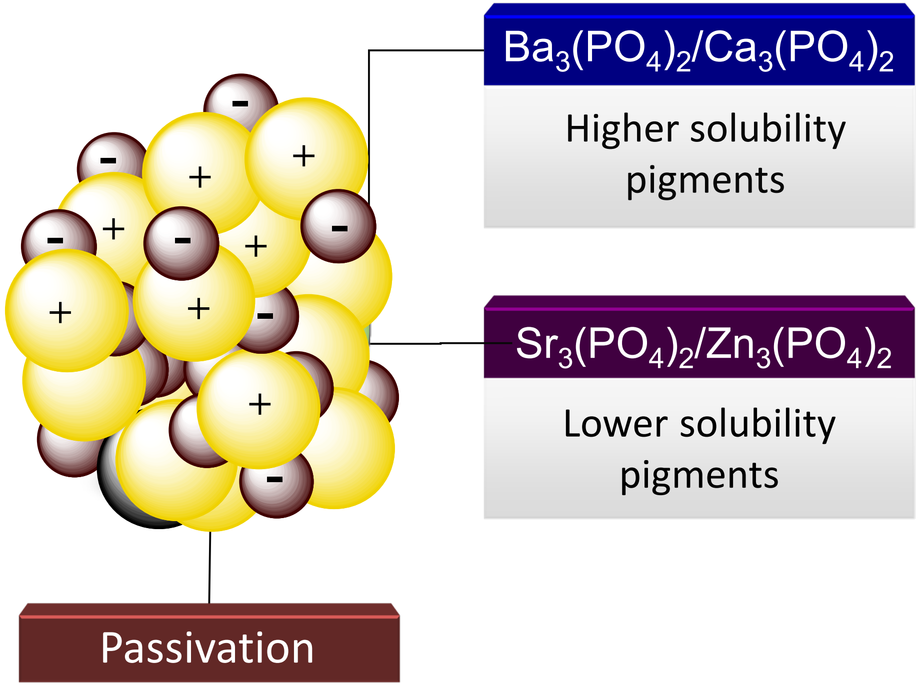
Conditions which increase flash rust:

- High Humidity
- Chloride Contamination
- Low pH
- High O_2 Concentrations



Corrosion Inhibitor Synergies

Improving Coating Performance



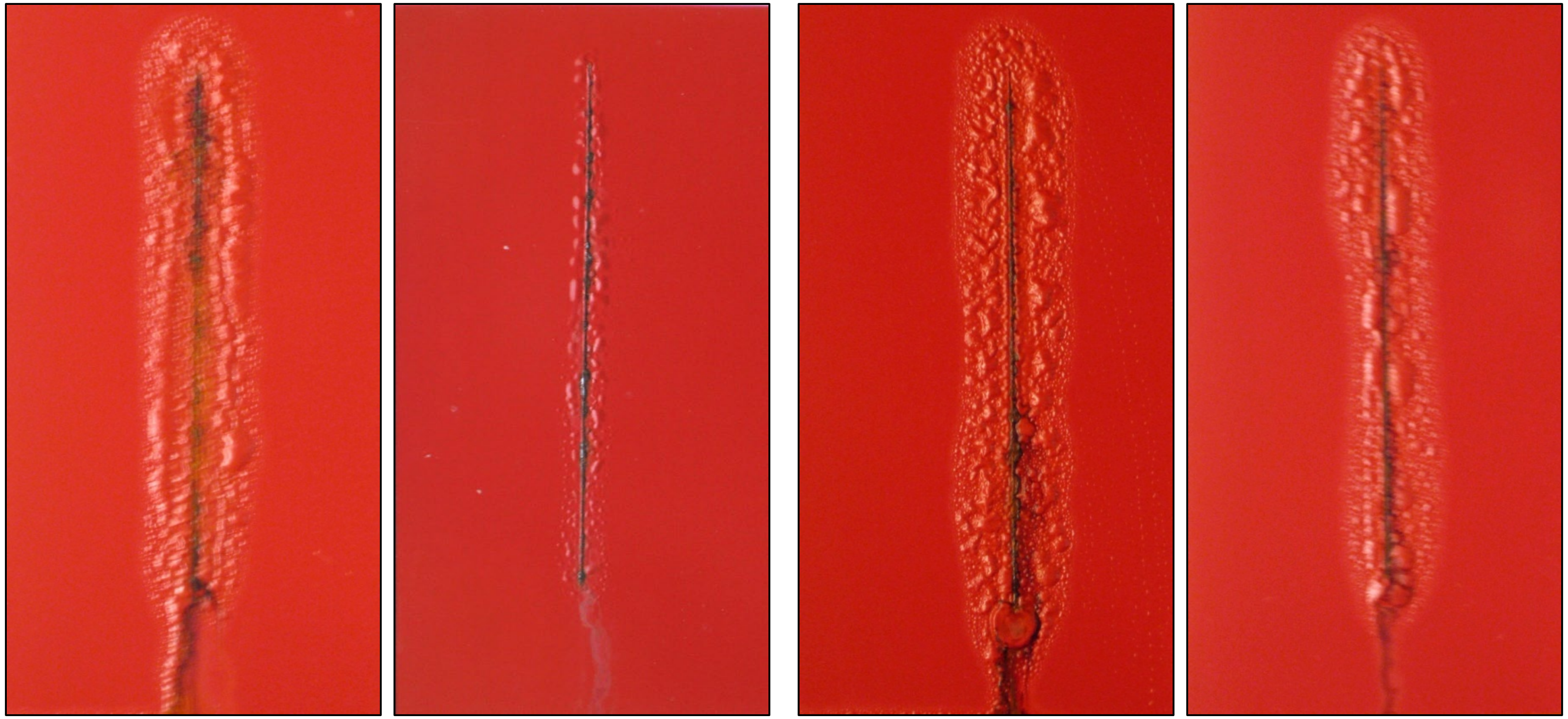
	$AlPO_4$	$Ba_3(PO_4)_2$	$Ca_3(PO_4)_2$	$Sr_3(PO_4)_2$	$Zn_3(PO_4)_2$
K_{sp}	**10×10^{-21}**	**3×10^{-23}**	**1×10^{-26}**	**1×10^{-31}**	**9×10^{-33}**

Olmsted, J & Williams, G; *CRC Handbook of Chemistry and Physics: 5° ed., 2007.*

Blended Inorganics

200 hours
ASTM B117

Solvent-borne Alkyd
CRS – 2 mils DFT



Strontium Zinc Phosphosilicate

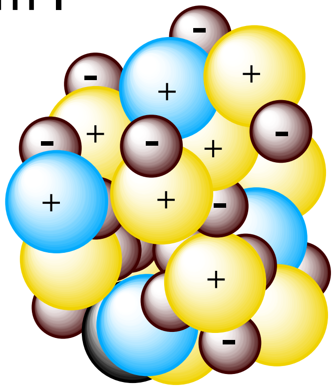
Barium Phosphosilicate

Best performance found with
75% Barium Phosphosilicate **+** 25% Strontium Zinc Phosphosilicate

Phosphate Specialty

Improving Coating Performance

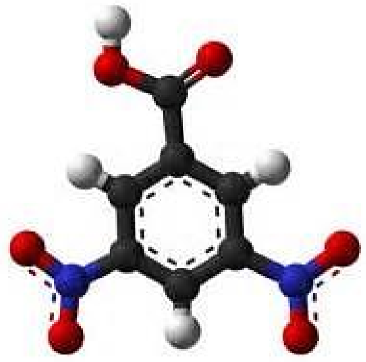
Mechanism I



Inorganic

Anodic Passivation

Ion Scavenging



Organic

Adhesion

Hydrophobicity

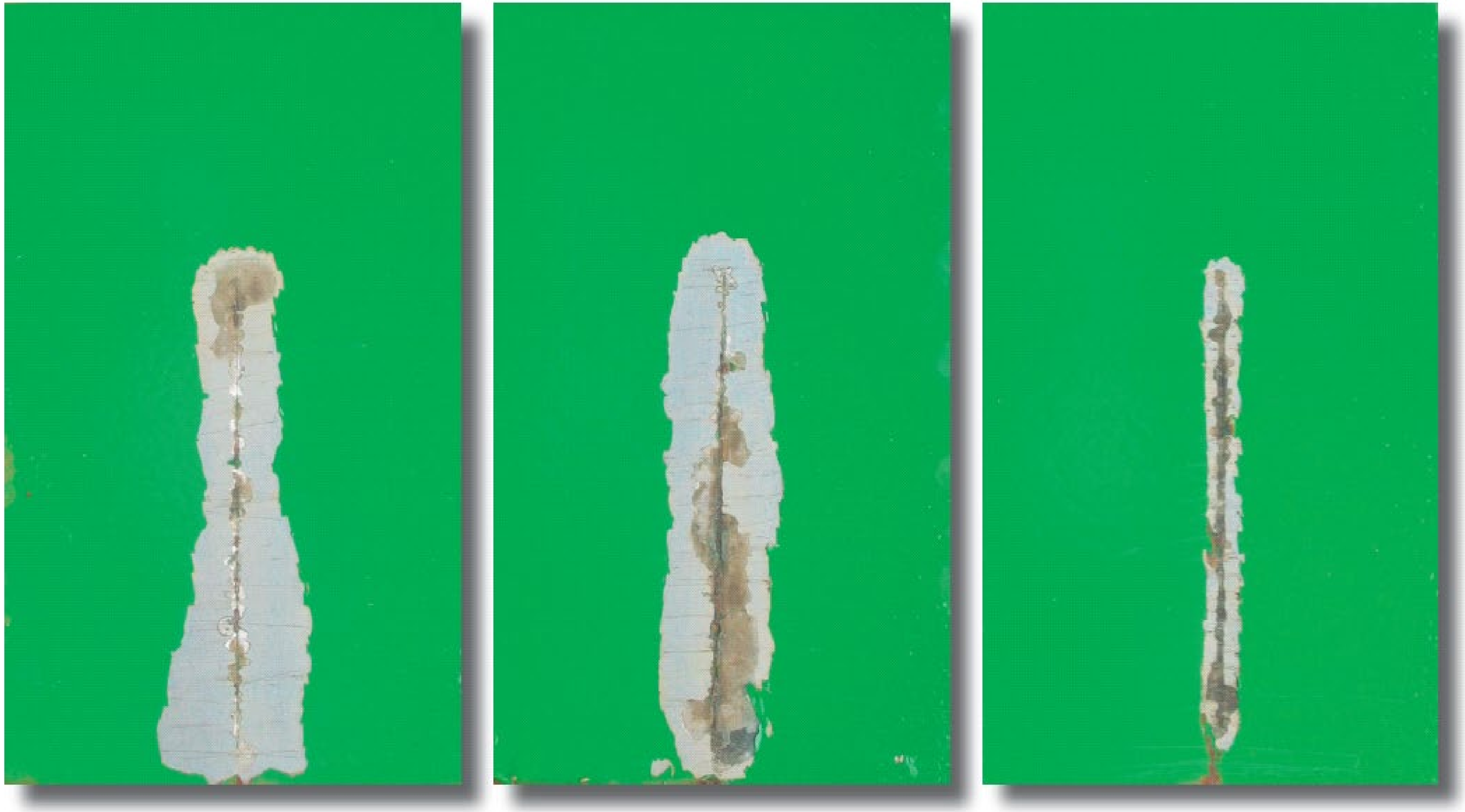
Mechanism II

Synergy

Product Combinations

504 hours SALT SPRAY

5% Zinc Phosphate + 2.5% Calcium Borosilicate	5% Zinc Phosphate + 2.5% Calcium Borosilicate + 1% Alkyl Ammonium Salt	5% Zinc Phosphate + 2.5% Calcium Borosilicate + 3% Alkyl Ammonium Salt



Inorganic/Organic Synergy

2000 hrs.
ASTM B117

2K Water-Based Polyurethane
on Bare Aluminum 3003
Dry Film Thickness: 75 µm

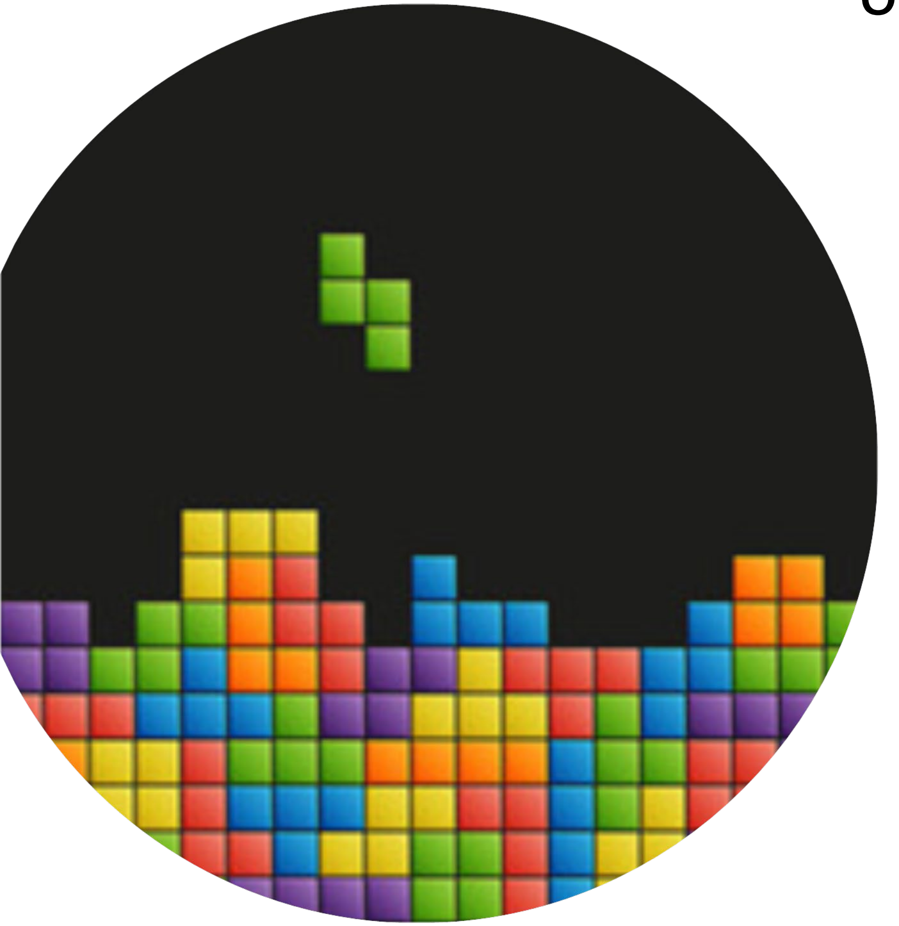
Blank

Competitor

2% - Calcium Phosphate
0.5% - Organosilane

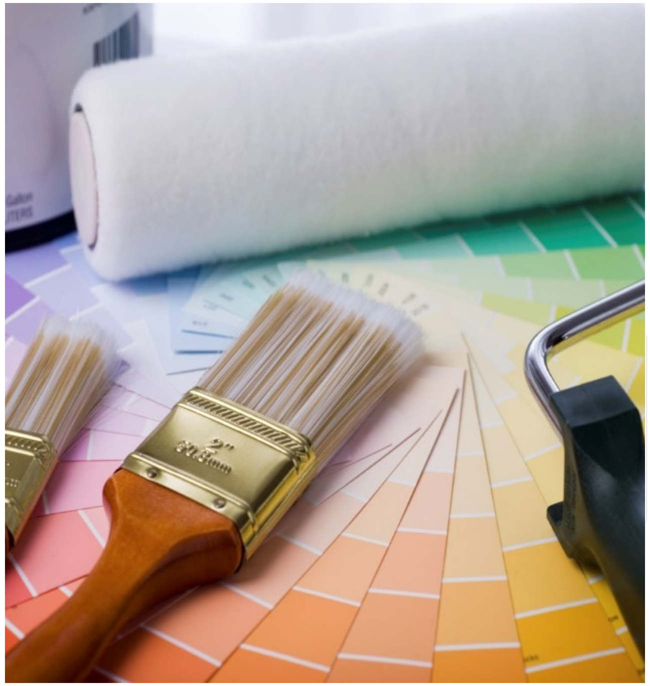
2% - Calcium Phosphate
1% - Organosilane

Formulating success depends on selection and optimization of ALL formulation components.



- Resin System
- Extender Pigments
- Dispersants
- Surfactants
- Co-solvents
- Rheology Additives
- Corrosion Inhibitors

ICL Phosphate Specialty



Corrosion Test Methods

Background

Real World Data

Not always reproducible

Geographic variability

Data gathering is slow

Long-term planning required

Experimenter Requires

Rapid information

Reproducible data

Accurate data

Multiple variables tested

Accelerated Devices

Artificial light

Salt fog chambers

Humidity cabinets

Screening of many samples

Quicker results

Exterior Exposure Variables

- UV Radiation
- Temperature
- Moisture – dew, rain, vapor
- Freeze-thaw cycles
- Oxygen permeation
- Pollutants e.g. volcanic ash, acid, SO_2
- Microbial growth
- Surface preparation
- Applicator Variability
- Dry film thickness
- Marine environments, wind, mechanical damage, and the list goes on…

Controlled Test Variables

- Location – Worst Case Environments
  - South Florida
    - high-intensity sunlight
    - high annual UV
    - high year round temperatures
    - frequent rainfall
    - high humidity
    - marine conditions
- Type of test rack
  - unbacked, backed, under glass
- Orientation of test sample
  - angle to horizon (30, 45 or 90°)
  - directional face (north or south)

Accelerated Test Methods

STATIC TESTS

- Salt Spray (ASTM B117)
- Humidity Testing (ASTM D2247)
- Immersion Test (ASTM D870)
- Electrochemical Impedance (ASTM G106)

CYCLIC TESTS

- Prohesion (ASTM G85)
- Cyclic Weathering (ASTM D5894)
- Cosmetic Corrosion (SAE J2334)
- Filiform Corrosion Test (ASTM D2803)

Neutral Salt Spray: ASTM B-117

Method:

- Samples at 15-30°angle.
- 5% NaCl solution.
  - pH 6.50-7.20
  - Mixed with humidified air
- Temperature at 35°C.
- Continuous fog.
- Panels are typically scribed.

Positives:

- **Widely used in many industries.**
- Can be used as a QC method.
- Low cost.
- **Severe, quick test.**
- Can be used for screening.

Negatives:

- High concentration of salt.
- **Cabinet to cabinet reproducibility.**
- Static fog and temperature.
- Variance between replicates.
- No UV light exposure.
- **Does not correlate to real world results.**

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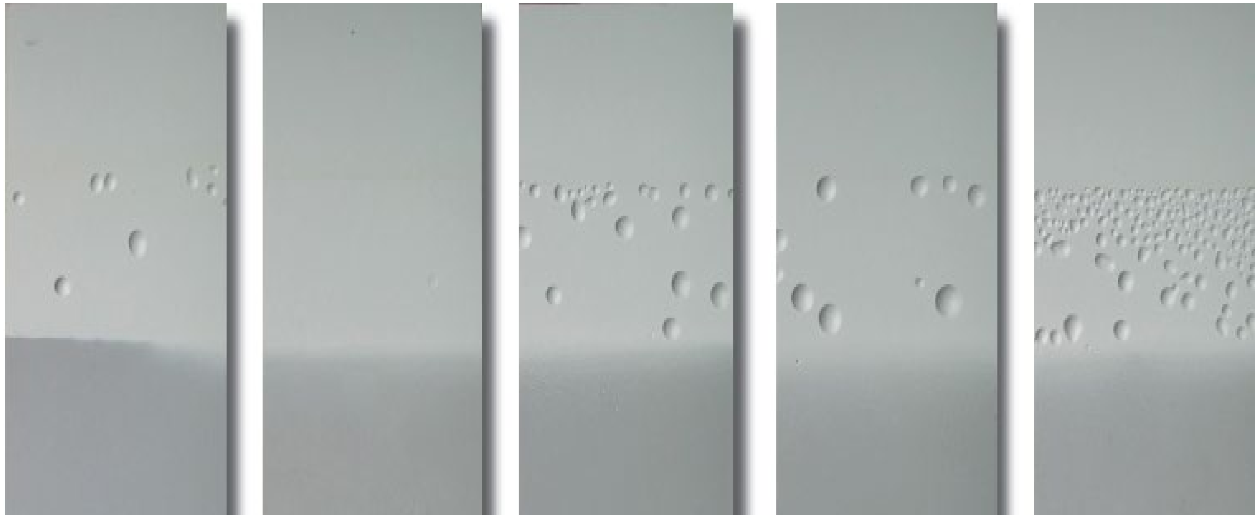
Humidity Test (ASTM D2247)

- Samples are exposed to 100% relative humidity.
- Chamber maintained at 100° F.
- Water vapor condenses on surface.
- No scribe.
- Failure can occur in many forms.

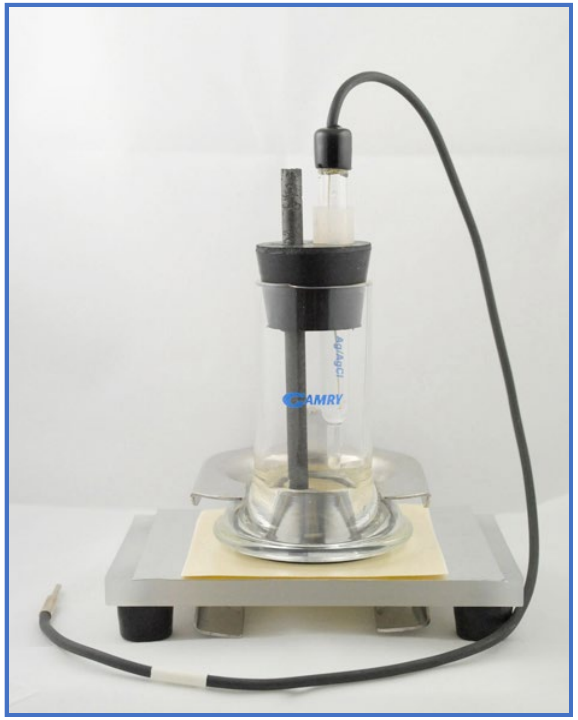


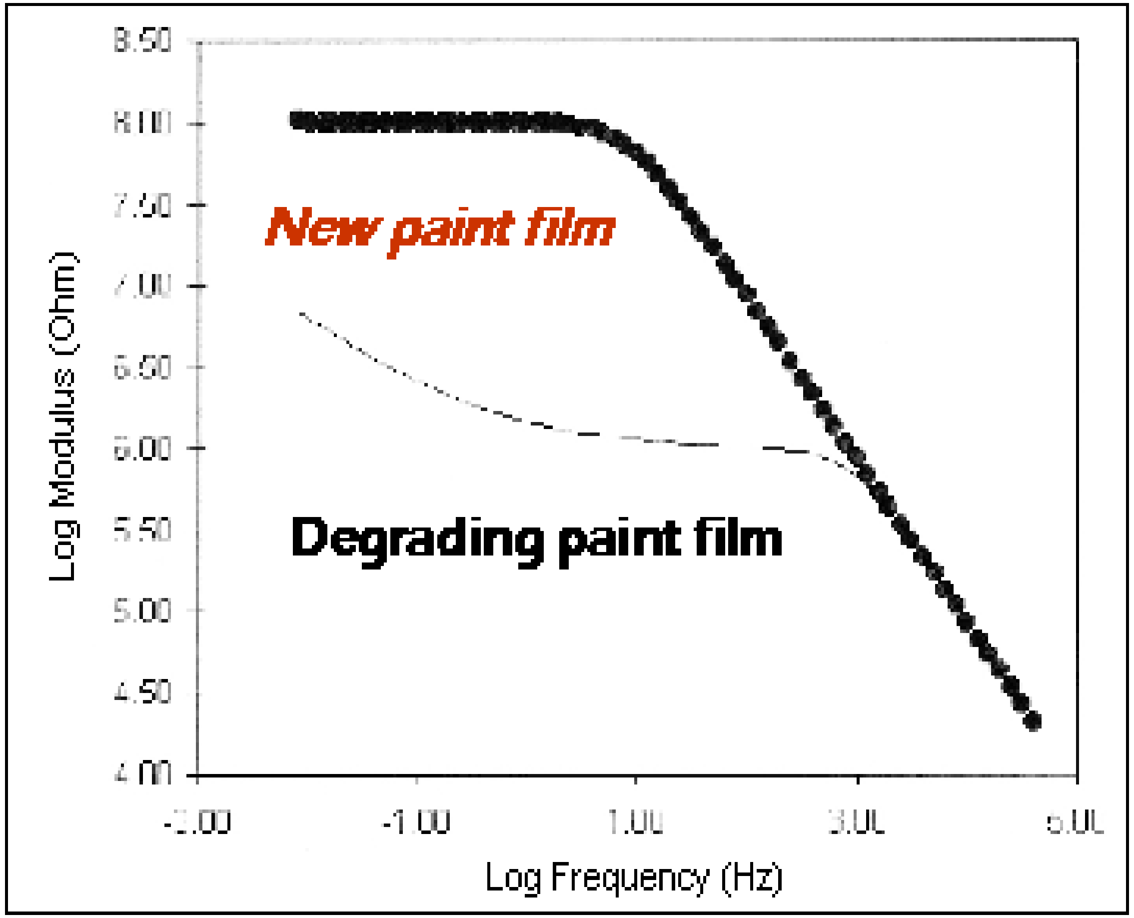
Long Oil Alkyd – CRS – 2 mils DFT
336 hours

2K High Solids Epoxy – BHRS – 3 mil DFT
500 hours

Electrochemical Impedance Spectroscopy (EIS)

- Non-destructive test.
  - No scribe
- Measures the breakdown of a coating due to electrolyte attack.
- Measures the resistance (charge transfer) and capacitance (how the coating behaves when exposed to an electrolyte).





Prohesion Cycle (ASTM G85-A5)

- Cyclic salt fog.
- Mixed electrolyte solution.
  - 0.05% NaCl
  - 0.35% ammonium sulfate
  - pH 5.0-5.4
- Salt fog for one hour at 25°C.
- One-hour dry period at 35°C.
- Steps are repeated continuously.

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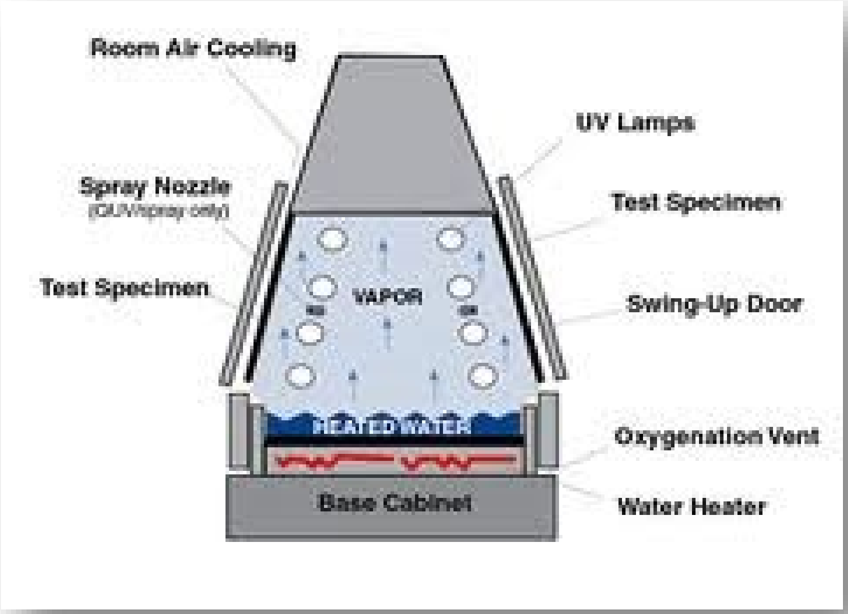
Cyclic Weathering (ASTM D5894)

- Cyclic corrosion test consisting of one week in QUV and one week in Prohesion.
- Cyclic, panels exposure to wet/dry periods.
- UV exposure.
- Better correlation to real world exposure.

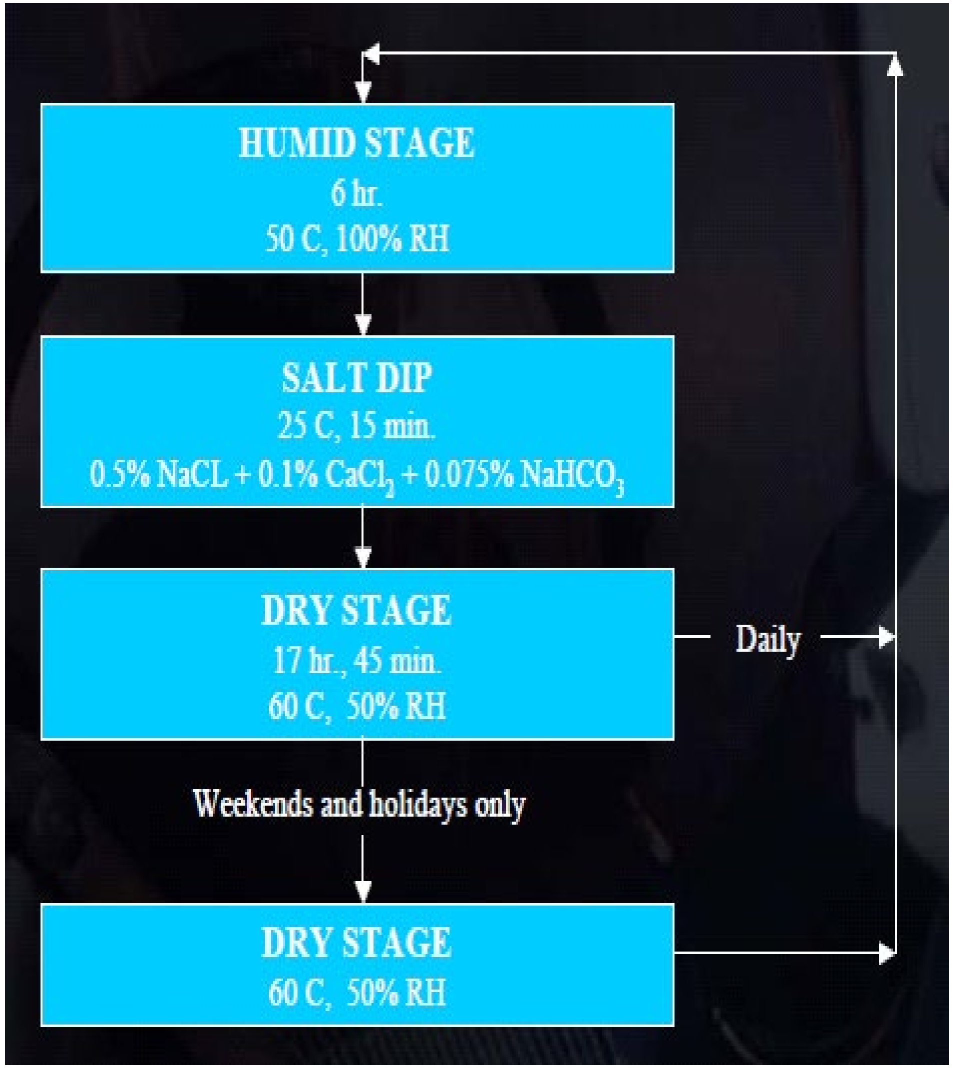


Phosphate Specialty

SAE J2334

- Developed by Society of Automobile Engineers.
- Cosmetic corrosion lab test.
- Field correlated test method.
  - Can be used for coating validation.
- 60-cycle minimum for automotive system.

Salt solution:
- 0.5% NaCl
- 0.1% $CaCl_2$
- 0.075% $NaHCO_3$



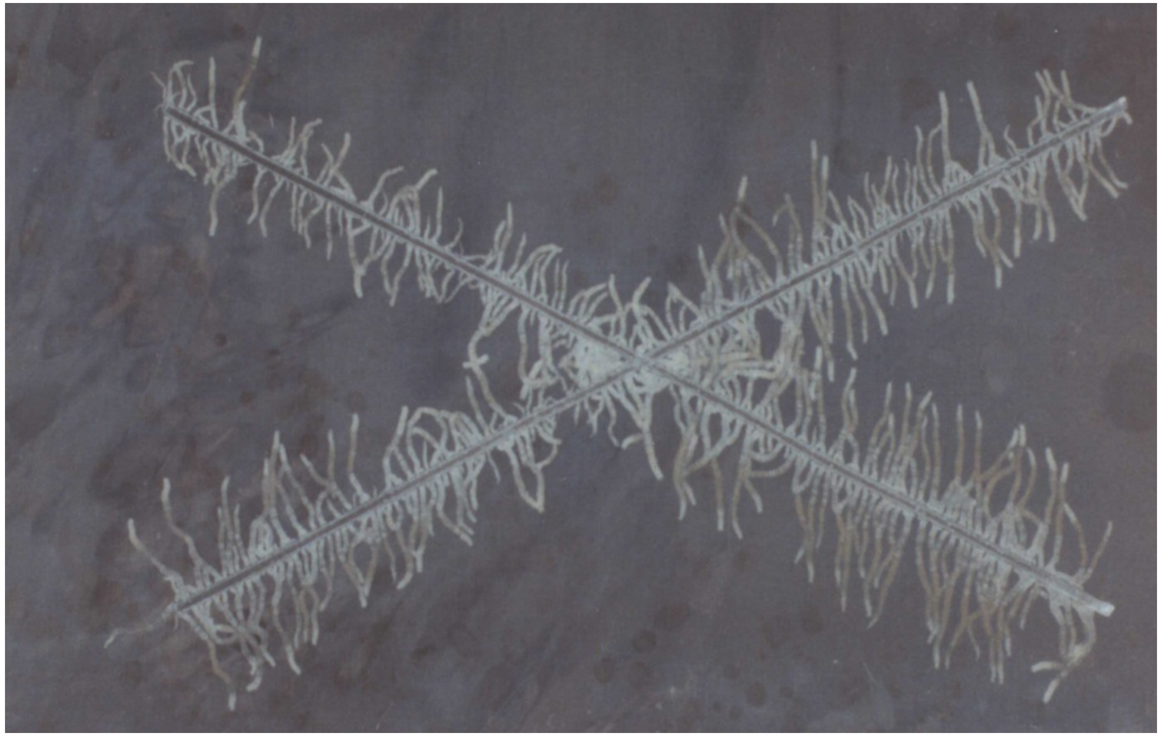
ICL Phosphate Specialty

http://www.ascott-analytical.com/SAEJ2334/saej2334testconditions.htm and
http://www.leymanlift.com/images/Army_Corrosion_Summit_SAEJ2334.pdf

Filiform Corrosion (ASTM D2803)

- Unique differential oxygen cell occurring on coated substrates.
- Development of thin thread-like filaments beneath the coating.
- Occurs on aluminum, steel, magnesium and others, generally not zinc-coated substrates.
- Filaments grow by anodic propagation or undermining.
- The head is anodic and tail cathodic.

- Scribed panels placed in corrosive atmosphere (ASTM B117 for 4 to 24 hours) or immersed in a NaCl solution.
- Panels exposed to 85% humidity at 77^{o}F.

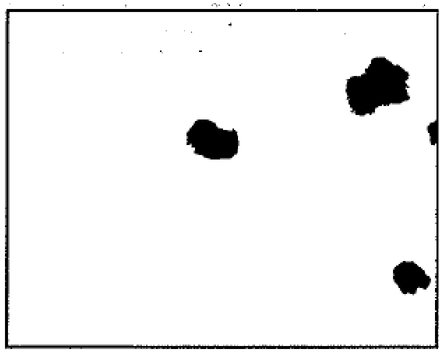


ICL Phosphate Specialty

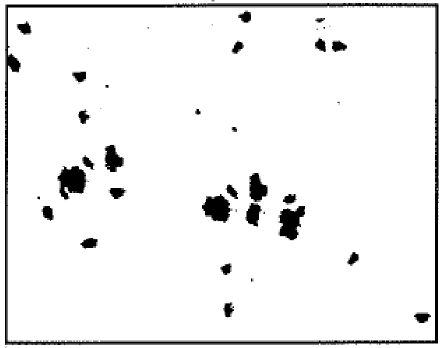
Performance Measurements

Within each test method, measurements are used to access performance.

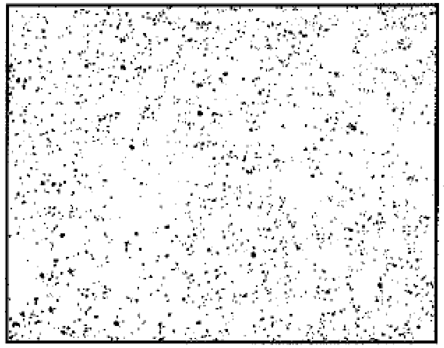
- Scribe Creep
  - Spatula Scrape
  - Air Blow-off
  - Visual to Extent of Blistering
- Blistering
  - Size
  - Frequency
- Field Corrosion
  - Type
    - Spot
    - General
    - Pinpoint
  - Frequency



Rust Grade 5-S, 3% Rusted



Rust Grade 5-G, 3% Rusted

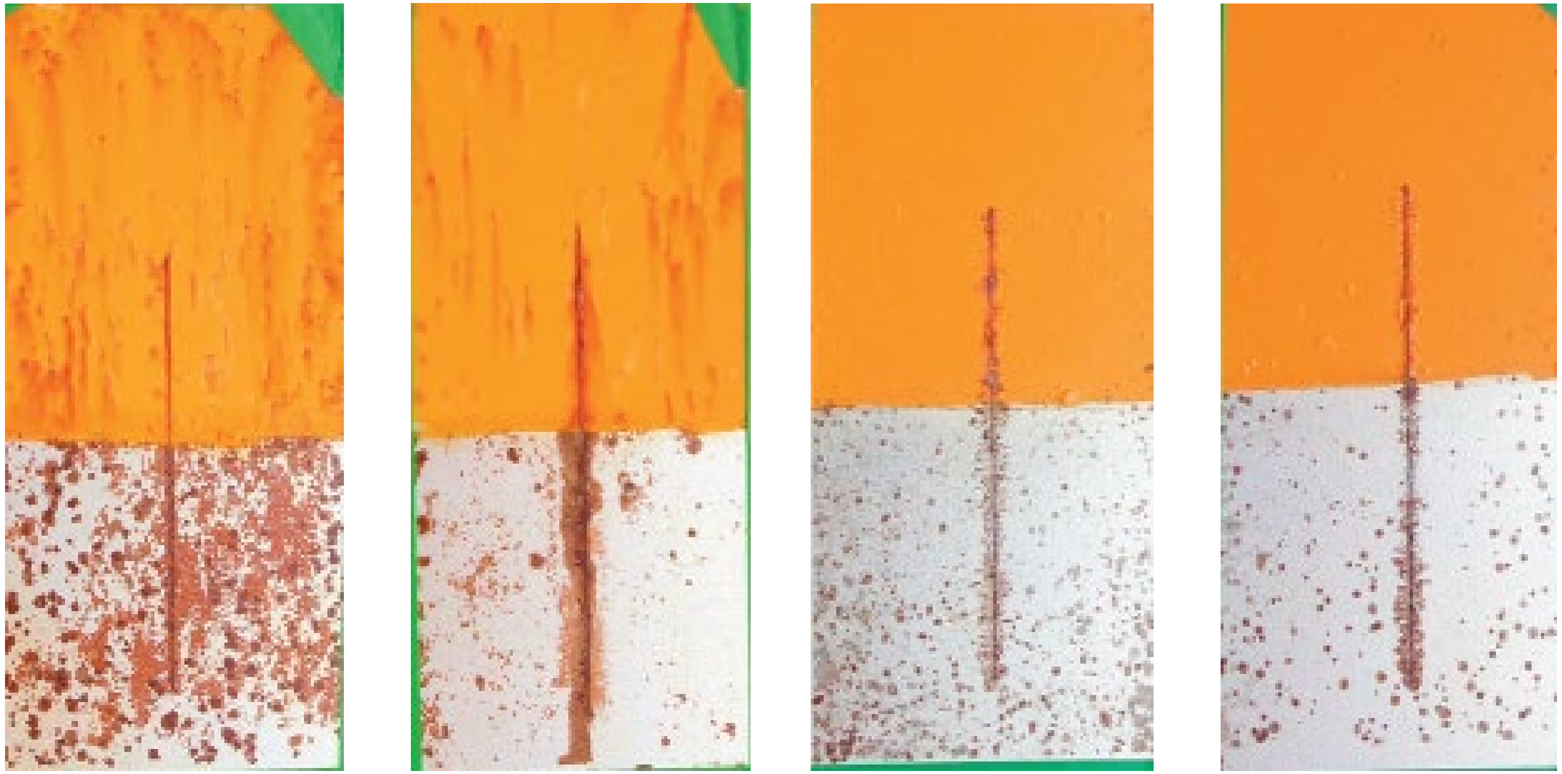


Rust Grade 5-P, 3% Rusted

ICL Phosphate Specialty

Test Comparisons

Salt Spray vs. Cyclic Weathering



336 Hours
Salt Spray

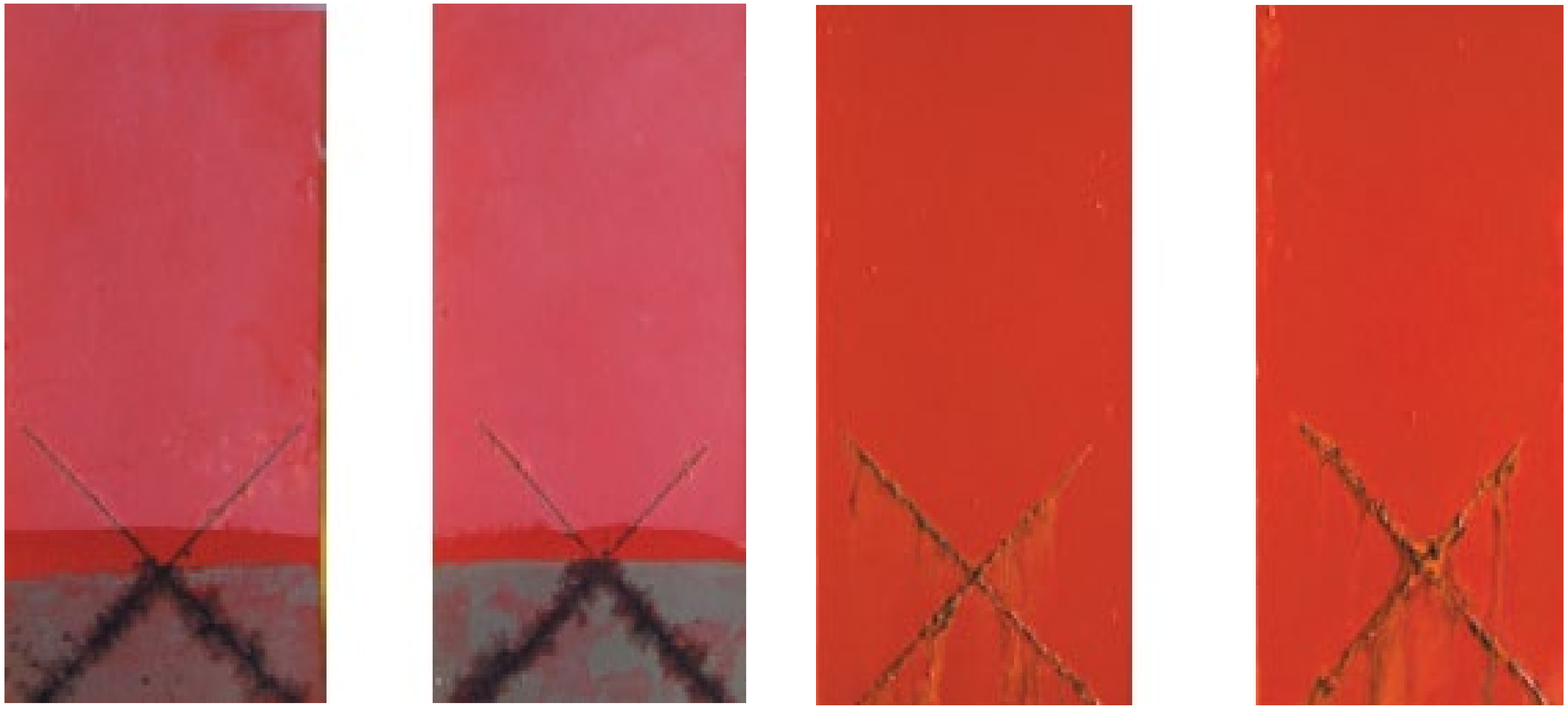
672 hours – 2 cycles
Cyclic Weathering

Waterborne Acrylic – CRS- 2.25 mils DFT

ICL Phosphate Specialty

Test Comparisons

Exterior Exposure vs. Salt Spray



2.5 years at Industrial Site **500 hours Salt Spray**

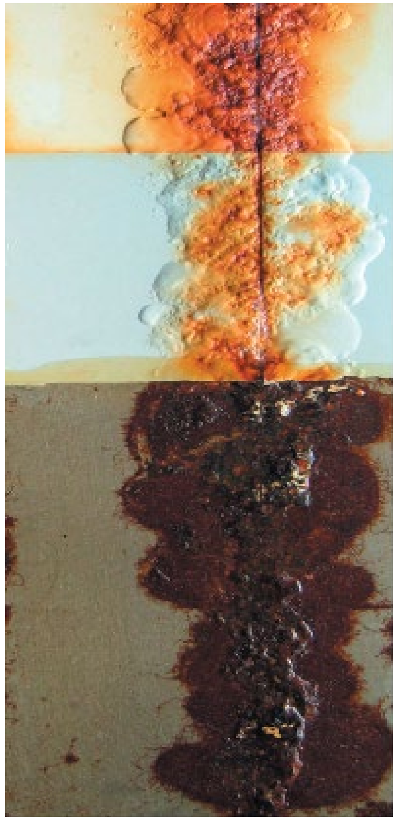
Phosphate Specialty

Test Comparisons

Solvent Based Polyurethane – CRS- 2.0 mils DFT

2K Hours Salt Spray

2K Hours Prohesion



2 Years
Ocean City, FL 45ºS

Phosphate Specialty

Corrosion Tests Stats

Perfect Correlation $C+R^2 = 2.00$

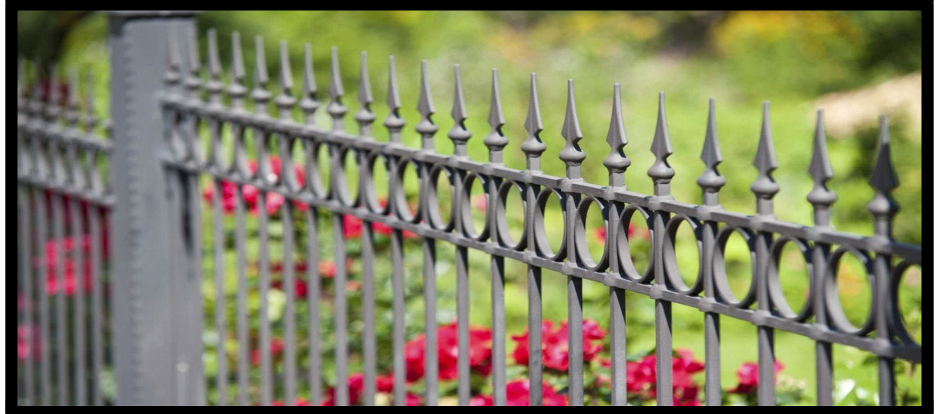
Test	Duration	C	R^2	$C+R^2$
SAE J2334	80 cycles	0.97	0.96	1.93
Acid Rain CCT	45 cycles	0.97	0.78	1.75
CCT-IV	35 cycles	0.86	0.74	1.6
GM9540P(B) (GM)	50 cycles	0.59	0.84	1.43
JASO M610	45 cycles	0.98	0.44	1.42
AISI-A	50 cycles	0.75	0.46	1.21
AISI-C	50 cycles	0.41	0.74	1.15
Michigan Suburban	24 months	0.51	0.61	1.12
GM9540P(B) (ACT)	50 cycles	0.67	0.44	1.11
B117 Salt Spray	4 weeks	0.05	0.19	0.24
QUV-Prohesion	12 weeks	0.2	0.62	0.82

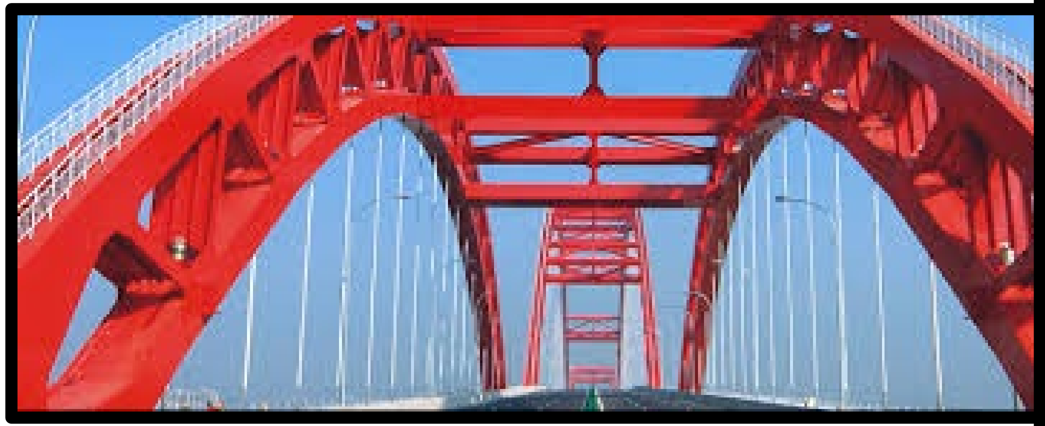
Reference: John Repp – Corrpro Companies, Inc - US Army Corrosion Summit 2002
Correlation Coefficient, C and r^2 Scribe creep compared for 5-yr exterior exposure data

ICL Phosphate Specialty

Which Test to Choose?

- Based on objective of project.
  - Raw material screening
  - Product validation
  - Quality Control
- Exposure correlation not always necessary.
- Controls should always be used.
- Test severity and length must match expectation of product performance.





ICL Phosphate Specialty

Review

MARKET TRENDS

Changing regulatory environment drives changes to formulations.

CORROSION INHIBITOR CHEMISTRIES

Inorganic & organic chemistries provide anodic and cathodic protection.

FORMULATING GUIDANCE

Inhibitor combinations provide best performance.

CORROSION TEST METHODS

Many static and cyclic test methods selected based on project type.

THANK YOU

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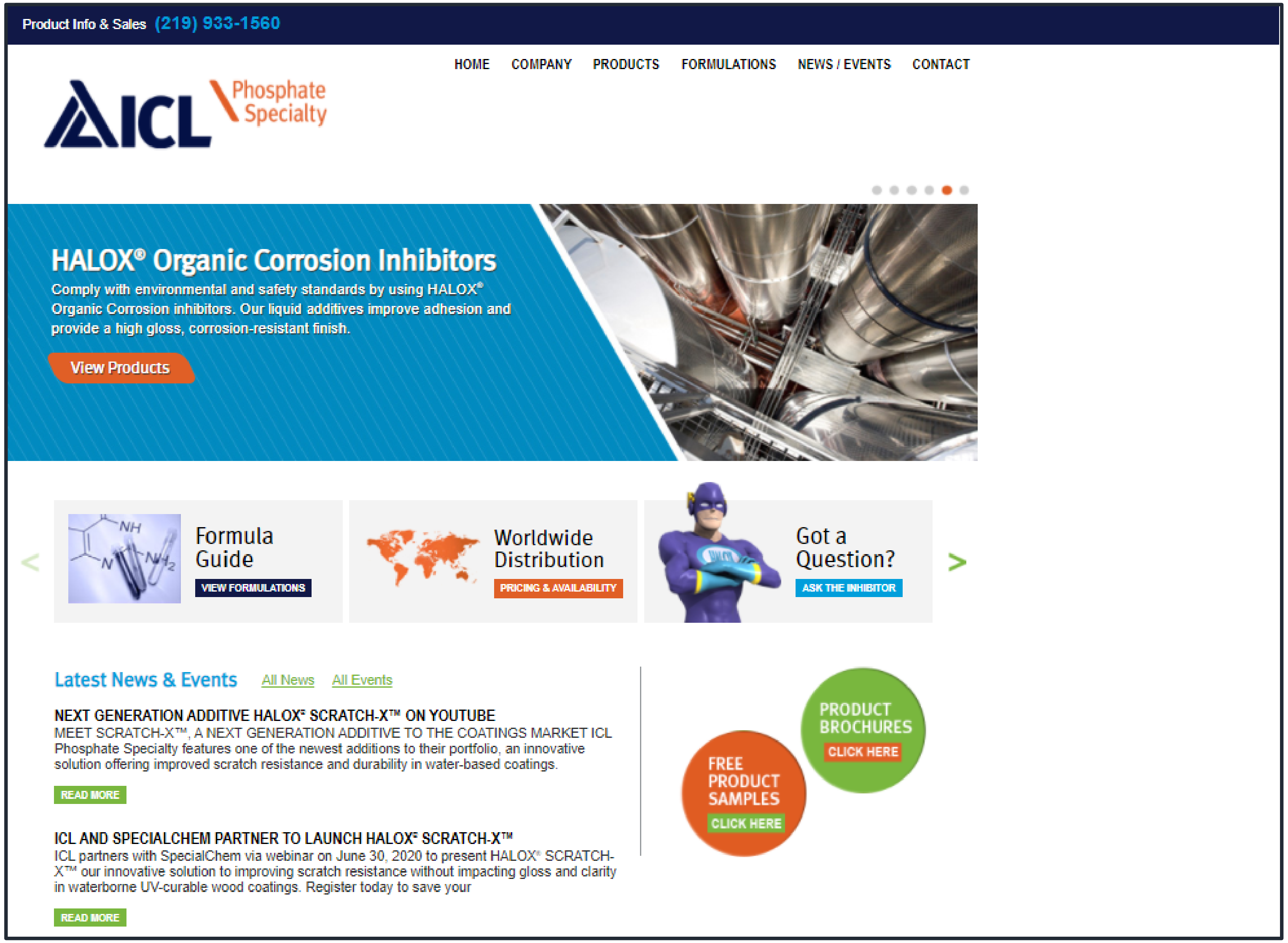

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