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Accelerated Corrosion Test Method Development for Protective Coatings and Materials

ASETSDefense 23 August, 2018

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Introduction

Introduction to Project:

- Evaluation of protective coatings to predict service life of metal-based structures in corrosive environments has long relied on atmospheric exposure test sites.
- Due to new environmental requirements on heavy metal, toxic waste, hazardous air pollutants and volatile organic compounds, ARL and NASA is continually working on new coating technologies, which including cleaners, pretreatments, primers and topcoats.
- The US Army requires a specified corrosion program to be established on their assets.
- ARL requirements have been a minimum of 2-3 years of outdoor exposure at CCAFS. NASA's coatings have a 5-year atmospheric testing requirement.
- Current accelerated corrosion tests often provide false positives and negatives for coating performance, do not correlate to atmospheric corrosion exposure results, and do not correlate with atmospheric exposure timescales for lifetime prediction.
- A new more accurate and reliable accelerated corrosion test method will shorten the time needed to select corrosion protective coatings and will provide a new tool to evaluate and optimize new corrosion protection technologies.

Objectives

Objectives of Program:

- The objective of this project is to develop a new accelerated corrosion test method that predicts the long-term corrosion protection performance of protective coatings as accurately and reliably as current long-term atmospheric exposure tests.
- This new accelerated test method will shorten the time needed to evaluate the corrosion protection performance of coatings for both the U.S. Department of Defense (DoD) and TACOM's critical assets. NASA expects the same benefits.
- Results from this program to relate to aviation assets, as well as other services, such as NAVAIR.
- Corrosion mechanisms that occur during accelerated corrosion testing will be investigated using surface analytical techniques, electrochemistry, and visual inspection.
- Currently available long-term atmospheric exposure data from NASA's library will be used to validate the new accelerated method's accuracy and reliability.
- The effects of combinations of corrosion-relevant parameters will be used, such as temperature, relative humidity, ultraviolet radiation, and salts on the corrosion protective properties of coatings and corrosion of substrates.

Objectives

Objective Parameters:

- Baseline stack-up system will be used for correlation
- New test method will be evaluated for a variety of coatings and substrates
- Coordination with NAVAIR on their test method development and with PPG Industries on Corrosion under Coating effort with TARDEC
- Correlation with Army Test Center (ATC) corrosion testing on TACOM assets

Anticipated Results:

- Lifetime prediction of materials is a crucial step in the selection of methodologies to protect ground support and aviation DoD assets.
- No accelerated corrosion test method is currently available to provide accurate life cycle data. This new accelerated test method will:
  - Reduce the DoD's current corrosion prevention coatings qualification timeline from 3 years to less than half a year (estimated).
  - Improve the development of new materials by providing expedient corrosion/degradation performance data during the technology development process.
  - Allow new materials to be tested and expedited into end use for DoD applications at a much higher and more reliable rate.

Review of Previous NASA KSC Work

Study 1 (2010-2013): Understanding Correlations Between Accelerated Test Methods and Real-Time Data/Atmospheric Exposure

- Do any of our accelerated corrosion testing techniques correlate with atmospheric exposure?
- Extensive literature review found no satisfactory correlations or legitimate models.
- Understand initial corrosion product formation for each corrosion condition/technique.
- Does the initial corrosion product formation difference matter after extensive corrosion occurs?
- What about differences in the way corrosion forms during each corrosion test method?

Study 2 (2014-2015): New Accelerated Test Method Development for Corrosion Protective Coatings

- Determination and analysis of driving factors for corrosion of select coatings and bare metals for test method by analyzing results from the variable-isolating test methods.
- Design of new accelerated corrosion test method with high potential of AE correlation. Validation stage began, but not finalized.

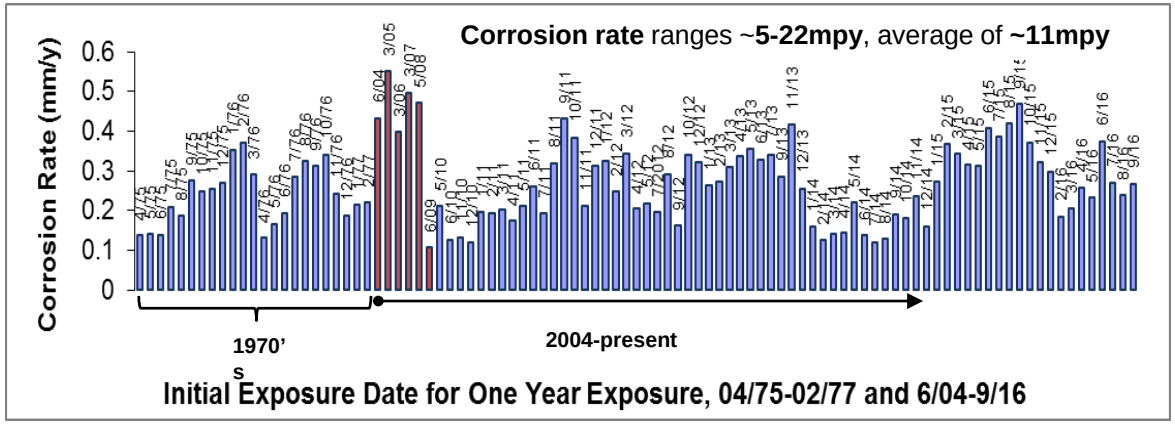
Study 3 (2016-present): Test Method Refinement and Collaboration with ARL/TARDEC

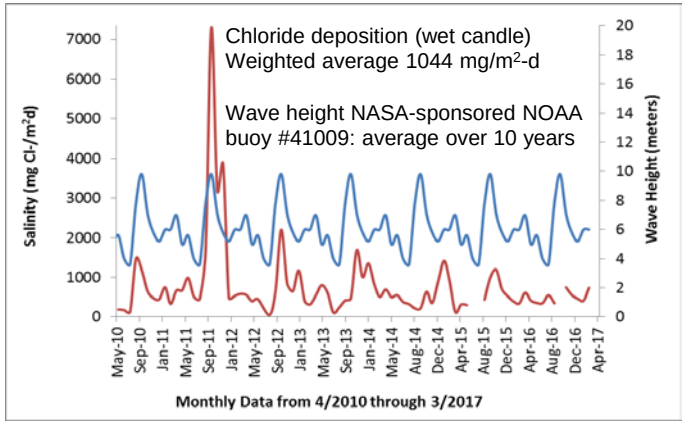
- Longer-scale testing times and more test iterations to fine-tune the new test method
- Test redesigned for collaboration.

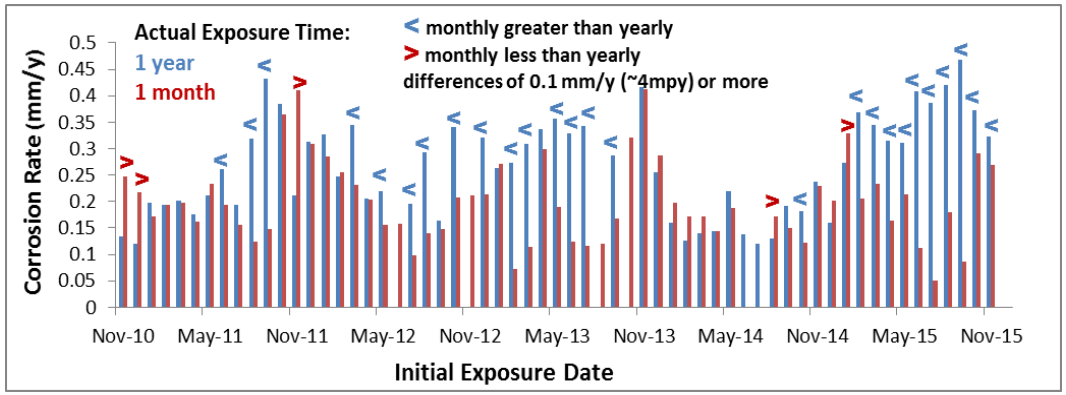
Study 1:
Corrosion Method Correlation (2010-2013)

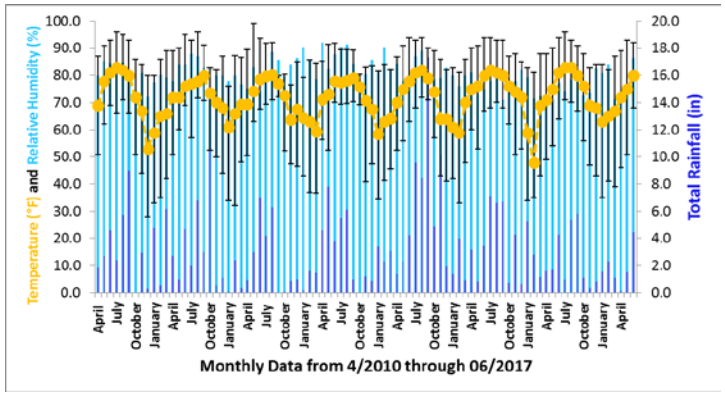
Technical Approach:

- Full Characterization of KSC Atmospheric Corrosion Test Site (data shown updated to present)
- Long-term atmospheric exposure to monitor seasonal effects per month/year.
- Accelerated corrosion methods: Alternative Seawater Spray Test (ASST) and neutral salt fog.
- Weight loss at varying timescales in correlation with atmospheric corrosion values.
- Monthly vs yearly corrosion rate extrapolations (data shown updated until Dec 2015)
- Sulfur deposition NADP FL99: 1-2 mg/m^2-d (very low)



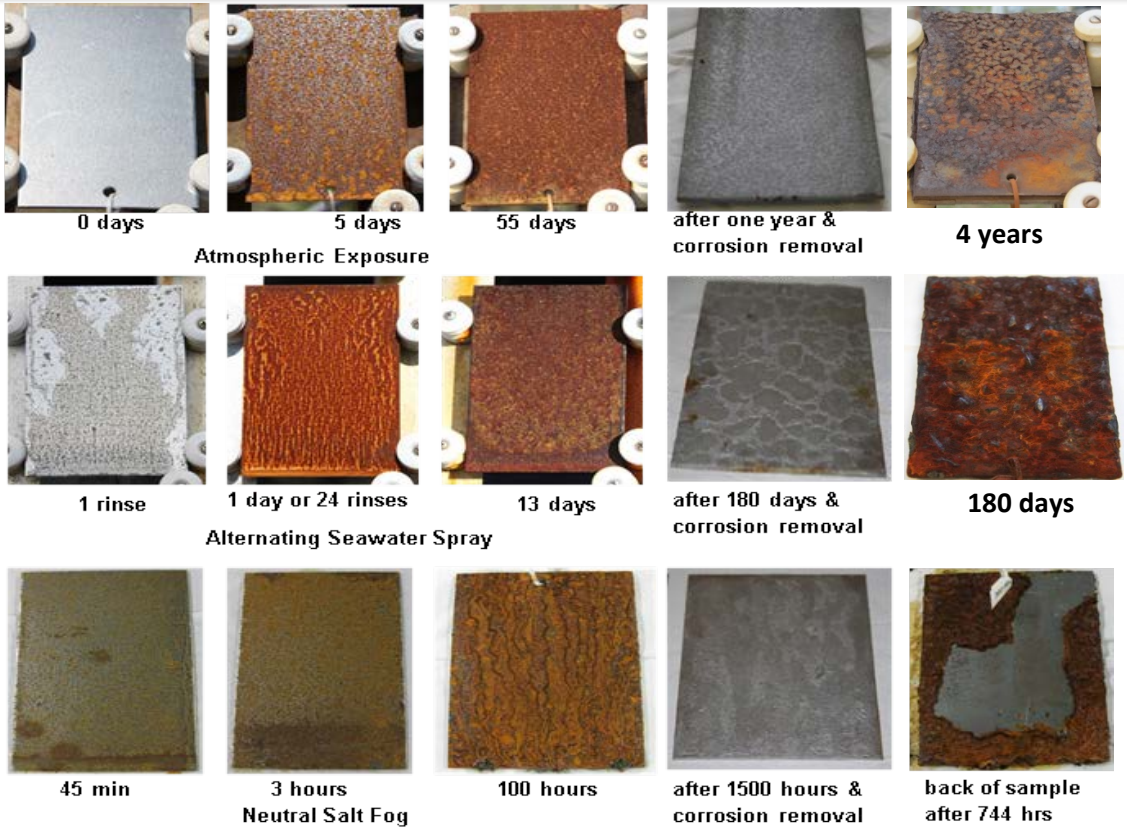


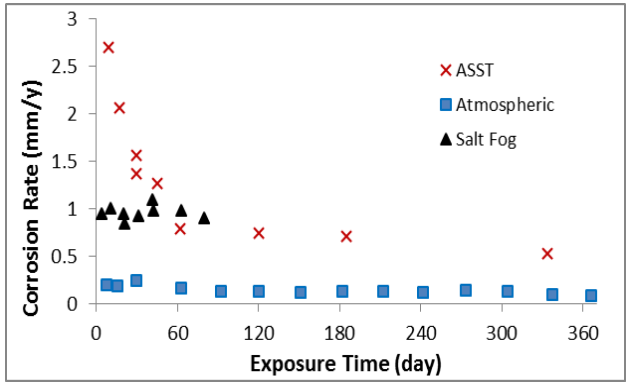


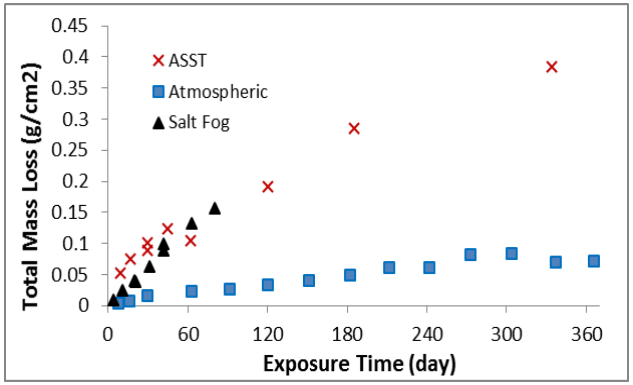


Study 1:
Corrosion Method Correlation (2010-2013)

- Obvious physical differences between corrosion test methods on identical metal samples, carbon steel example.
- Salt Fog Chamber results inconsistent with loosely adhered corrosion product and extreme cathodic (bare metal) and anodic areas (corroded areas). Results incomparable to atmospheric corrosion timescales and modes of corrosion failure.
- Alternating Seawater Spray is more closely related to Atmospheric Exposure, but too aggressive at settings of 10min/hr.
- Relying on mass loss/corrosion rate data alone is not legitimate for correlations.







Study 2:
New Accelerated Test Method (2014-2015)

- Driving factors for corrosion determined by controlling variables with uncoated 1010CS example

- **NIST SPHERE (RH, T, UV):** Corrosion product formation: UV is a driving factor in combination with a higher RH (75%) as compared to no UV.

- **NIST Dark Chamber (RH, T)**: No corrosion, RH (75%) and T alone are not strong corrosion driving factors.

- **UV Chamber (UV, T)**: No corrosion: UV and T alone are not strong driving factors for corrosion.

- **Salt Fog Chamber (100% RH, T, NaCl)**: Corrosion product formation: the presence of salts in a moist environment is a very strong driving factor for corrosion. Applying only salt and moisture to samples in a chamber DOES NOT result in comparable results to atmospheric exposure

- **Alternating Seawater Spray Test (atmospheric conditions plus additional seawater):** Corrosion product formation similar to long-term atmospheric exposure in a marine environment.

RH, T

NIST dark chamber
(1000 hrs)

UV, RH, T

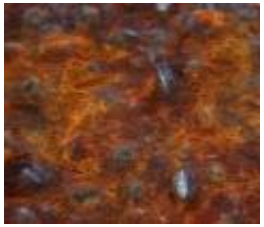
NIST SPHERE
(1000 hrs)

UV, T

NASA UV chamber
(1000 hrs)

unexposed carbon steel metal

Atmospheric conditions, accelerated salts and moisture



New Test Method Alternating Seawater Spray Test (ASST)
(4 months)

NASA beachside atmospheric exposure (1 year)

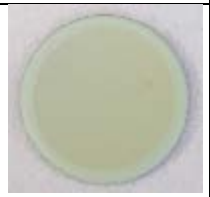
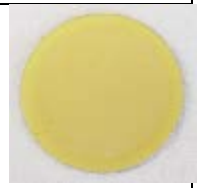
NASA salt fog chamber (144 hrs)

accelerated salts, RH, T

Study 2:
New Accelerated Test Method (2014-2015)

Have additional data for:

- Al2024-T3 bare
- 304SS bare
- Al5052 coated with the following configurations:
  - SurTec 650V
  - 650V / Deft 084
  - 650V / Hentzen 16708
  - Deft 084
  - Hentzen 16708
- 1010CS and Al2024-T3 coated with CPCs:
  - Bio-Medium Preservative
  - Fluid Film
  - VpCI 368

Corrosion Test Method	SurTec 650V	650V/Deft 084	Deft 084	650V/ Hentzen	Hentzen
Unexposed					
Beachside Atmospheric Exposure, 1 year					
NIST SPHERE, 1000 hrs					
Salt Fog Chamber, 2000 hrs					

Clear differences in corrosion protection "results" based on test method

Study 2:
New Accelerated Test Method (2014-2015)

Prototype apparatus combined natural and artificially induced conditions

- Most successful formation of corrosion comparable to atmospheric exposure
- Acceleration of the most important driving factors for corrosion: cyclic time-of-wetness & salts

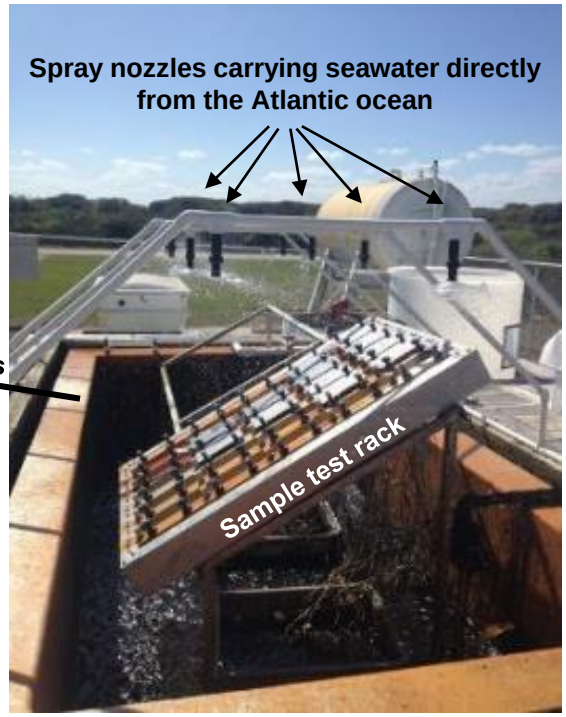
Natural Conditions

Samples **continuously exposed to atmospheric conditions** included variables that induce corrosion with a combined effect:
- Temperature, UV, wind, wetting from natural precipitation
- Hydroscopic salts, new and those left on the surface that reactivate corrosion reactions during re-wetting
- Cyclic wetting and drying due to natural condensation and day and night cycles

Artificial Conditions

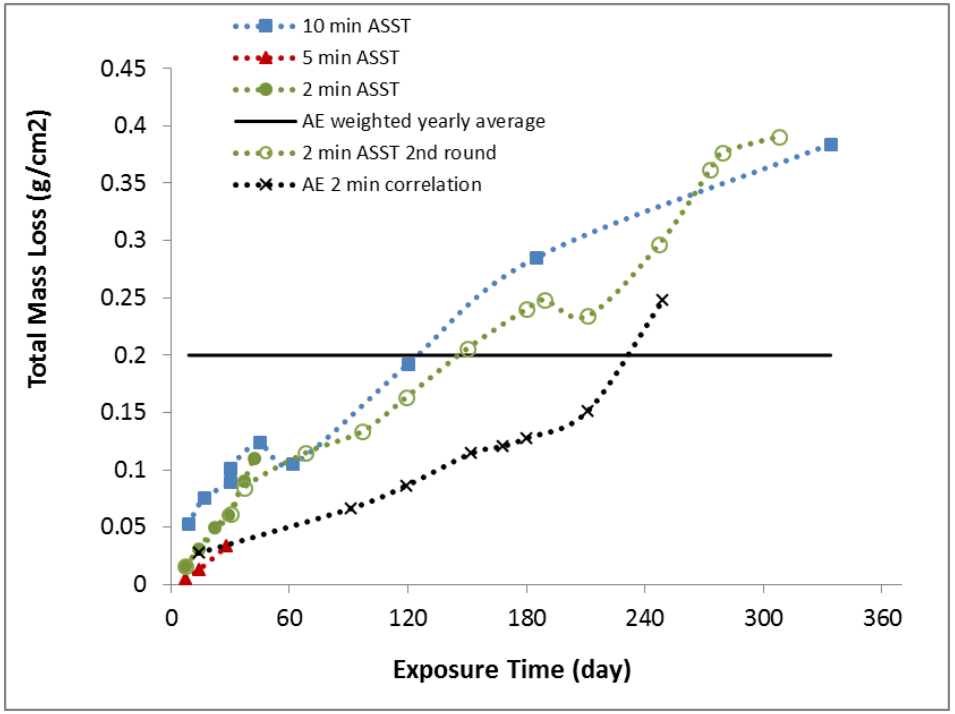
Alternating spray of seawater onto samples: Iterations of 10, 5, and 2 minutes per hour, 24-hours each day

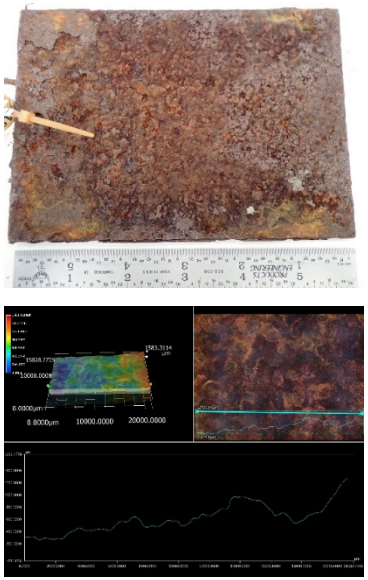
Location of prototype apparatus



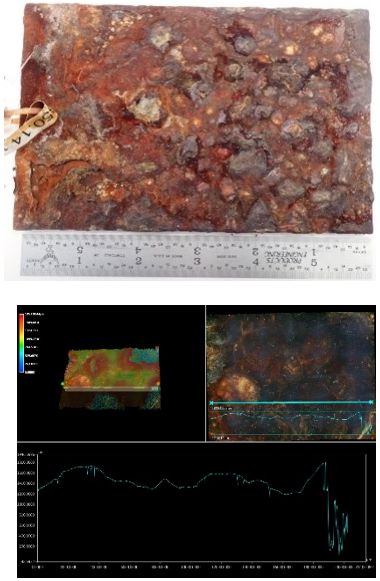
Study 3:
New Accelerated Test Method (2016-present)

- ASST for a 2 min/hr spray time for one year to determine acceleration rate of test method.
- Carbon steel samples only pulled at varying exposure times.
- Tandem samples in long-term atmospheric exposure.
- Record mass loss, visual/physical characteristics, and general surface roughness/topography.
- Cross reference mass loss values from new test method to atmospheric exposure values as a function of exposure time





Long-Term Atmospheric Exposure 365 days



ASST 150 days

Current Effort Test Plan

Phase 1:

- Compare test coupons from selected accelerated test methods to determine how/when degradation begins and the mode of degradation of the coating systems for each test method.
- Develop new accelerated test method parameters at KSC and perform first round of correlation testing on select coatings.
- Perform analysis of first round of test panels for correlation validation.

Phase 2:

- Based on data from Phase 1 work, the test plan will further develop the accelerated test method and incorporate more complicated test articles, such as c-rings and c-channel panels for test method validation.
- Fundamental coatings degradation analysis correlation will occur to determine how the coatings failure mechanisms correlate to long-term atmospheric testing at KSC and ARL.
- Aircraft-related and weapons systems coatings will be included in the test sets.

Current Effort: Phase 1

Accelerated Corrosion Test Method Validation:

- Five test methods to investigate the effects of combinations of corrosion-relevant parameters such as temperature, relative humidity, ultraviolet radiation, and salts on the corrosion protective properties of coatings and corrosion of substrates.
- Test methods chosen based on likelihood that they will provide meaningful data to long-term atmospheric corrosion data.
- Long-term atmospheric exposure data from NASA available and used to validate accuracy and reliability of new test method.

Accelerated Seawater Spray Test (ASST) System

NASA KSC beachside atmospheric corrosion test site

ARL atmospheric corrosion test site at CCAFS

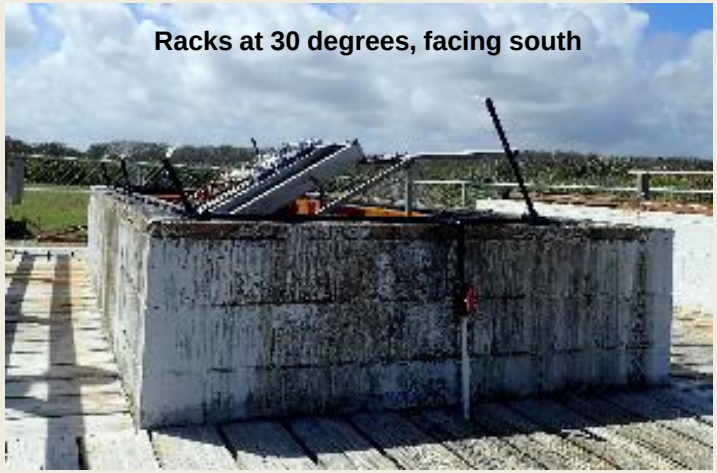
Neutral salt fog chamber, ASTM B117

Chamber running GMW14872

Phase 1: Accelerated Test Method

Alternating Seawater Spray Test Redesign:

- Natural beachside marine conditions at NASA KSC plus accelerated seawater spray at 2 min/hr, for 24 hours each day.
- Spray nozzles spray up towards the samples with adjustable spray heads to cover larger areas than previous test.
- Two test beds, 4 racks per test bed. 200-280 sample size capacity.



Phase 1: Materials Matrix

Objective Parameters:

- Smaller subset of approved mil-spec and NASA coating systems applied to 1010 carbon steel, 4130 carbon steel, and 2024 aluminum panels.
- Flat panels, nominally 4” x 6”, both scribed and non-scribed panels.

Coating Systems Selected for Phase 1

System	Substrate	Pretreatment	Primer	Mid-coat	Topcoat
1	1010 CS	Zn Phos	53022 Type II	n/a	53039 (tan)
2	1010 CS	Zn Phos	53022 Type IV	n/a	53039 (tan)
3	4130 CS	Bare (1 mil profile)	Organic zinc	53022 Type IV	53039 (tan)
4	4130 CS	Bare (1-3 mil profile)	Inorganic zinc	53022 Type IV	53039 (tan)
5	Al 2024	hex chrome	53022 Type II	n/a	53039 (tan)
6	Al 2024	hex chrome	53022 Type IV	n/a	53039 (tan)
7	4130 CS	Bare (1-3 mil profile)	Inorganic zinc	n/a	n/a
8	4130 CS	Bare (1-3 mil profile)	Inorganic zinc	n/a	Poly-siloxane
9	4130 CS	Bare (1-3 mil profile)	Epoxy Mastic	n/a	n/a
10	1010 CS	Bare	n/a	n/a	n/a
11	Al 2024	Bare	n/a	n/a	n/a

Phase 1: Analysis Strategy

- To obtain an objective view of the mechanism of corrosion and the corrosion products present on the substrate surface.
- By measuring the corrosion severity from the ASST test and pulling panels from the other test methods at a point in time when they reach the corrosion severity similar to that found in the ASST test.
- Analysis of these panels will evaluated by lab personnel who do not know origin of each test panel except for the panels that have been exposed at the KSC beach. This breath of work will be completed by PPG.

Roles and Responsibilities for Phase 1 Testing

- ARL: Provide project guidance and supply test coupons and coatings.
- KSC: Provide test plan, apply coatings, complete testing using long-term atmospheric and accelerated corrosion test methods, perform physical analysis of corrosion of coatings (color, gloss, adhesion) and substrates as a function of time on each test method.
- PPG: Provide blind analysis of corrosion mechanisms for select Phase 1 test sets using fundamental analysis techniques at their analytical facilities.

PPG's Global Analytical Network

Our mission is to:

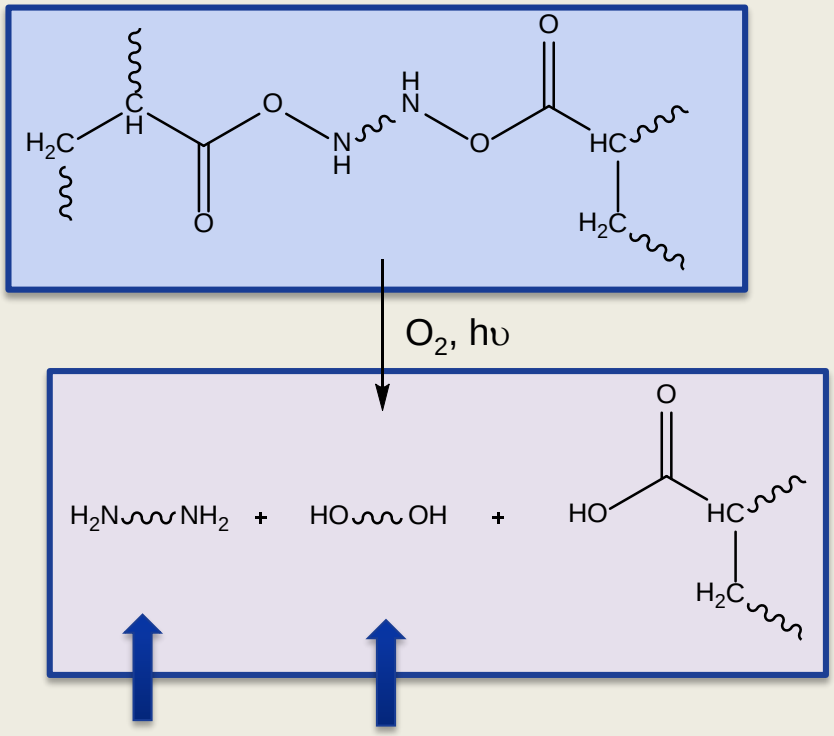
- Provide quality, state-of-the-art analytical services
- Provide tailored, cost-effective, and timely solutions in the areas of customer and production support, research and development, regulatory affairs, raw material validation, and deformulation analysis

PPG Analytical Team Overview

- Regulatory & Wet Chemistry
- Chromatography
- External Customer Support (Field)
- Atomic Spectroscopy
- Molecular Characterization (Photo-oxidation values)
- Materials Characterization (Corrosion analysis)

What is photo-oxidation

- Paint degrades due to introduction of oxygen into the polymer matrix and exposure to ultraviolet light
- Various weathering conditions (WOM, QUV, Florida Exposure) can be used to accelerate the oxidation process



Degradation generates OH, NH functional groups

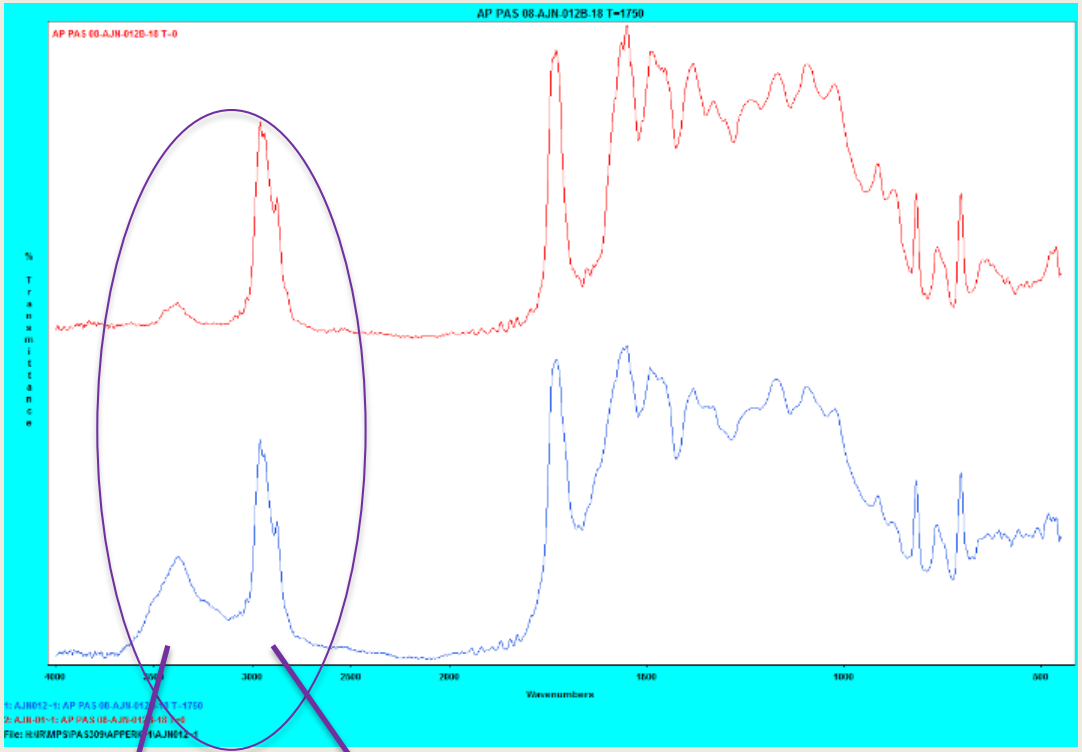
Quantifying Photo-oxidation

IR spectroscopy is sensitive to changes in functional groups

Increases in OH and NH groups are a useful measure of the degree of degradation

Technique developed in partnership with Ford Motor Company to address coating clearcoat delamination in late 80's

Top, red: Unexposed
Bottom, blue: WOM Exposed



OH/NH region increases with oxidation

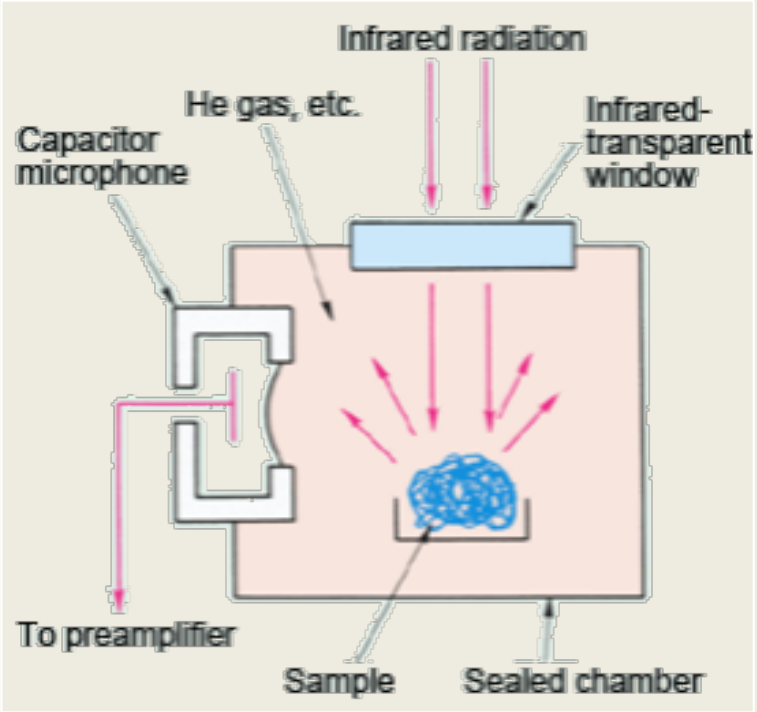
CH stretch used as standard

Quantifying Photo-oxidation

How do we measure photo-oxidation values at PPG?

Photoacoustic Spectroscopy Technique (PAS)

1. Sample placed in sealed chamber with IR window
2. IR radiatiation heats sample
3. Chemical bonds respond by various stretching or bending mechanisms specific to their composition
4. Vibrations are captured by sensitive detectors as sound waves
5. Computer decodes and calculates spectrum

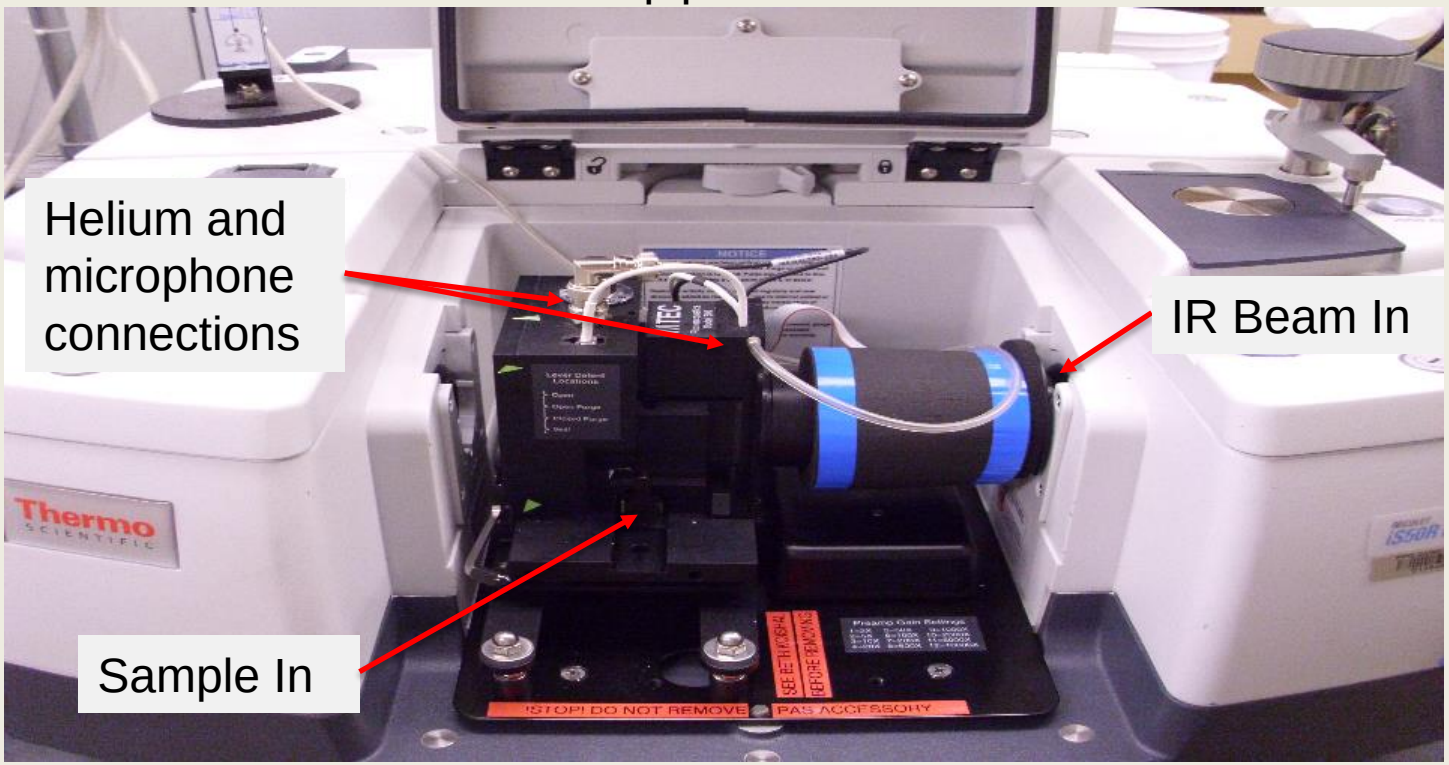


https://www.shimadzu.com/an/ftir/support/ftirtalk/talk7/intro.html

Quantifying Photo-oxidation

How do we measure photo-oxidation values at PPG?

Equipment



Quantifying Photo-oxidation

How do we measure photo-oxidation values (POV)?

Calculating Photo-oxidation values:

1) Integration of OH/NH/CH region (3700-2200 cm^{-1})

2) Integration of CH region (3125-2750 cm^{-1})

3) Figure of Merit (FOM) = $\frac{(OH/NH/CH)-(CH)}{(CH)}$

4) POV = $FOM_{exposed}$ - $FOM_{unexposed}$

*Calculating POVs always requires an unexposed sample to compare to the weathered sample of the same make-up (chemistry and layer composition)

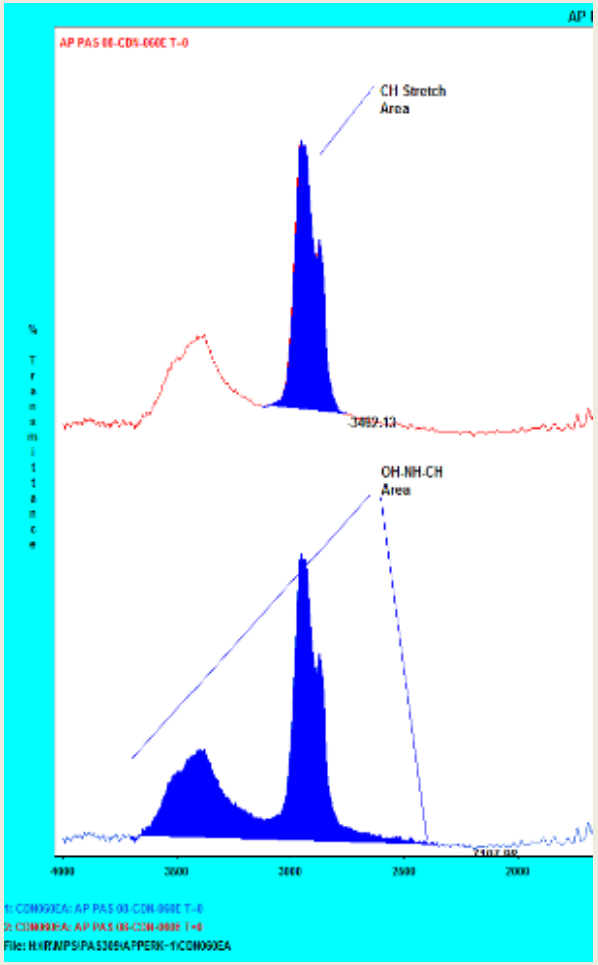
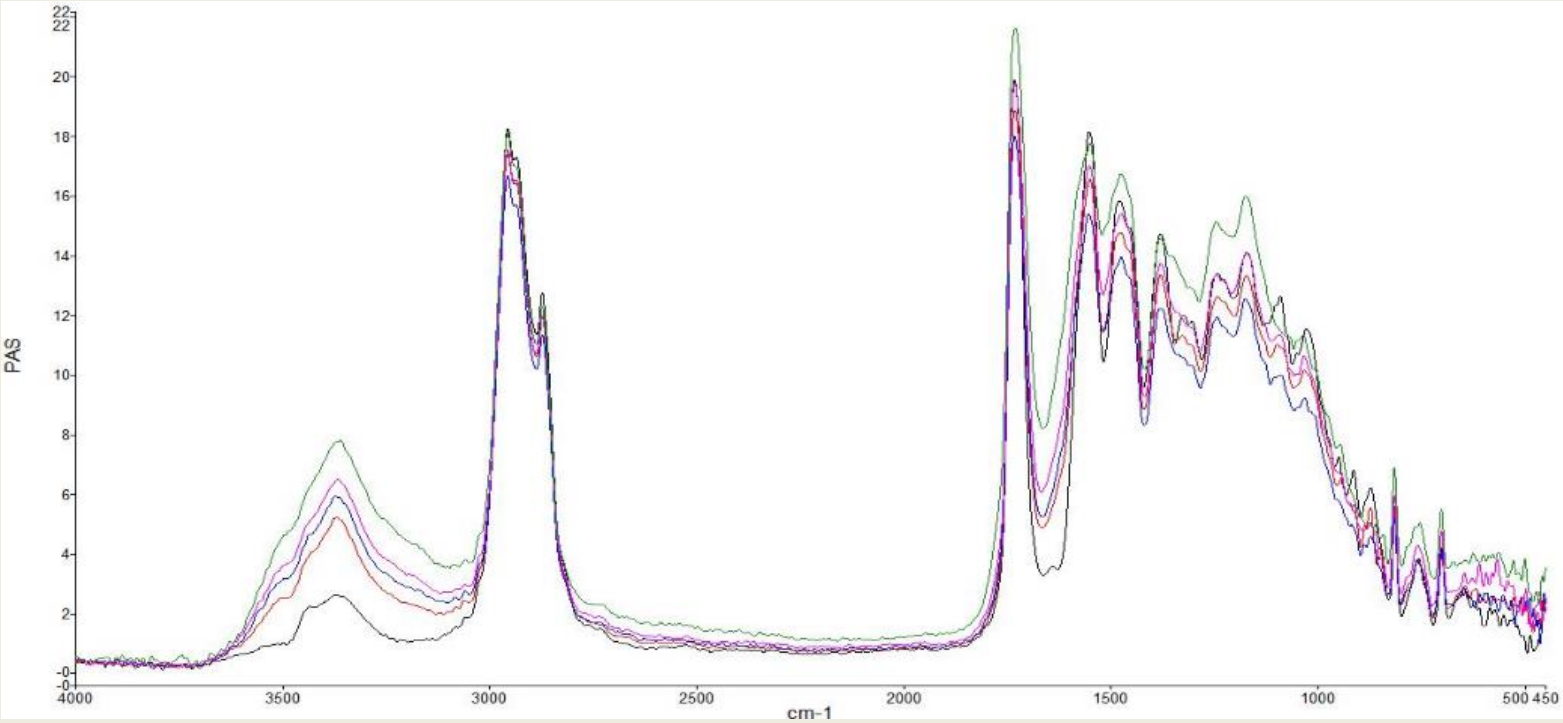


Photo-oxidation Example

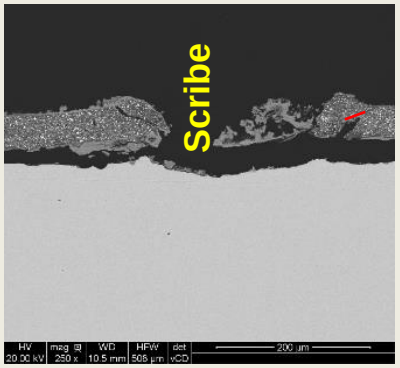
Coating Sample from 0 through 5000 hours exposure testing

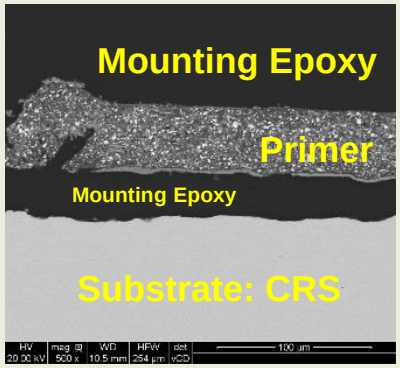


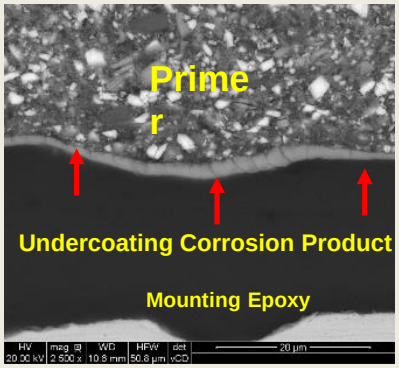
Additional Techniques

Cross-sectional SEM can provide valuable insights about corrosion morphology

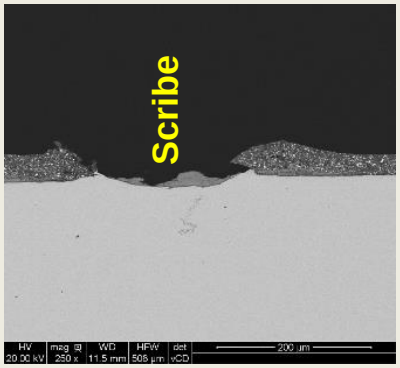
No Inhibitor

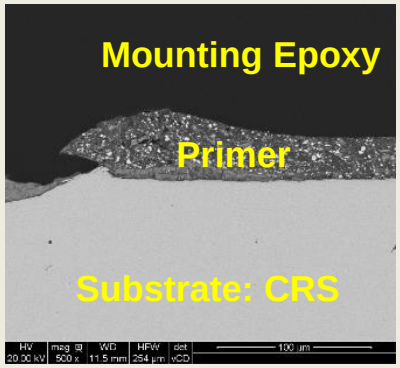


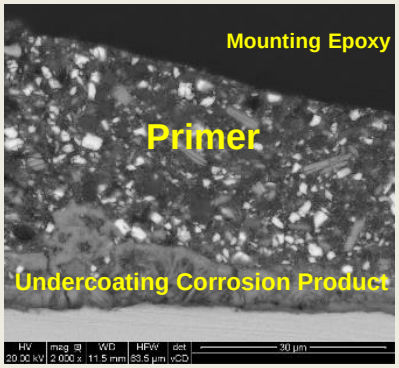




With Inhibitor



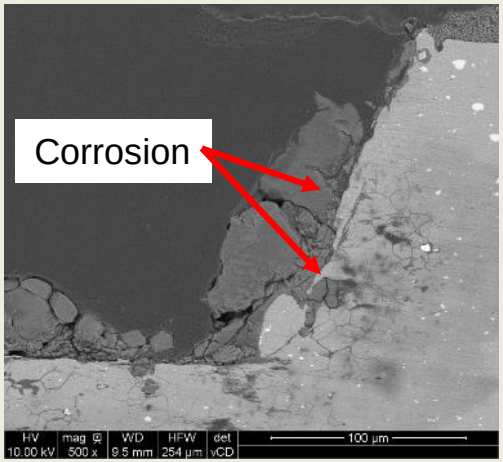




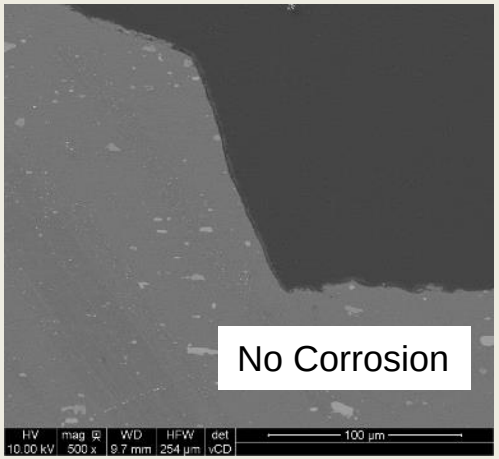
Additional Techniques

SEM Coupled with Energy Dispersive X-Ray Spectroscopy provides detailed elemental mapping which can inform about specific corrosion products and migration of corrosion inhibitors

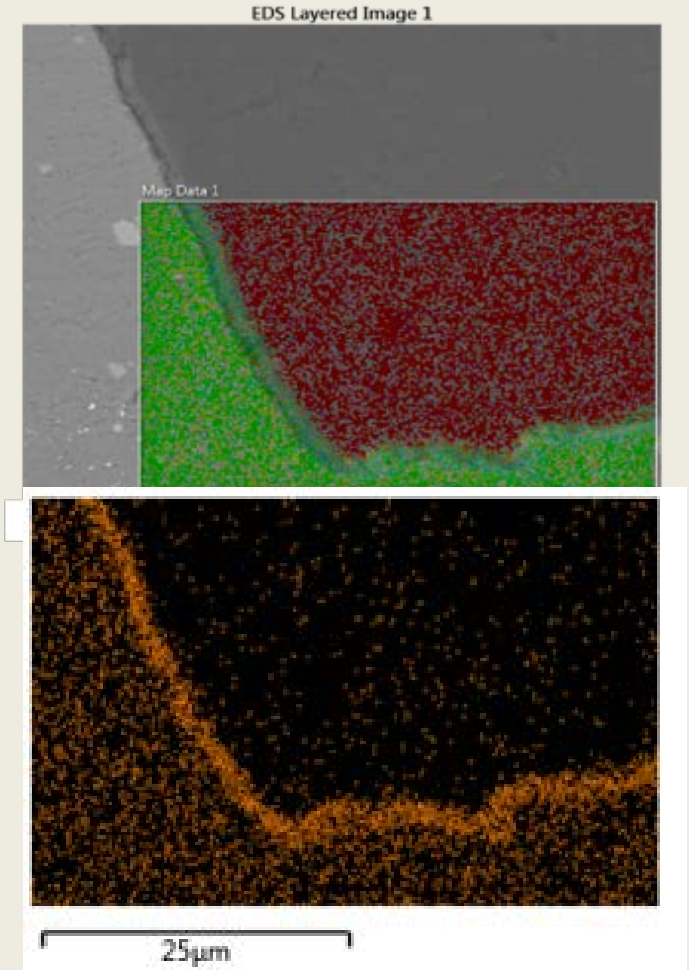
w/o corrosion inhibitor



with corrosion inhibitor



SEM Cross-sectional Images after 100 hours salt spray



EDS Image showing inhibitor migration

Goals for Analytical Studies

Leverage PPG Analytical capabilities to answer…

- How does POV compare for samples exposed in the accelerated method vs. standard exposure?
- What is the role of topcoat oxidation in corrosion processes?
- Can POV be used to increase our confidence in results obtained from accelerated exposure testing?
- Can advanced imaging and elemental analysis confirm corrosion products are similar in both accelerated and standard exposure methods?

Summary of Objectives

- Develop a new accelerated corrosion test method to predict the long-term corrosion protection performance of protective coatings as accurately and reliably as current long-term atmospheric exposure tests.
- Use a long-term atmospheric environment in combination with seawater spray to accelerate the evaluation time but ensure that the corrosion mechanisms are similar to long-term testing correlations.
- Perform analysis in a “blind” manner to verify corrosion mechanisms.
- Apply this test to both steel and aluminum-based substrates used in both ground and air assets to validate the test method.

Summary of Objectives

Special thanks to TARDEC for their assistance and supporting this program

Questions?