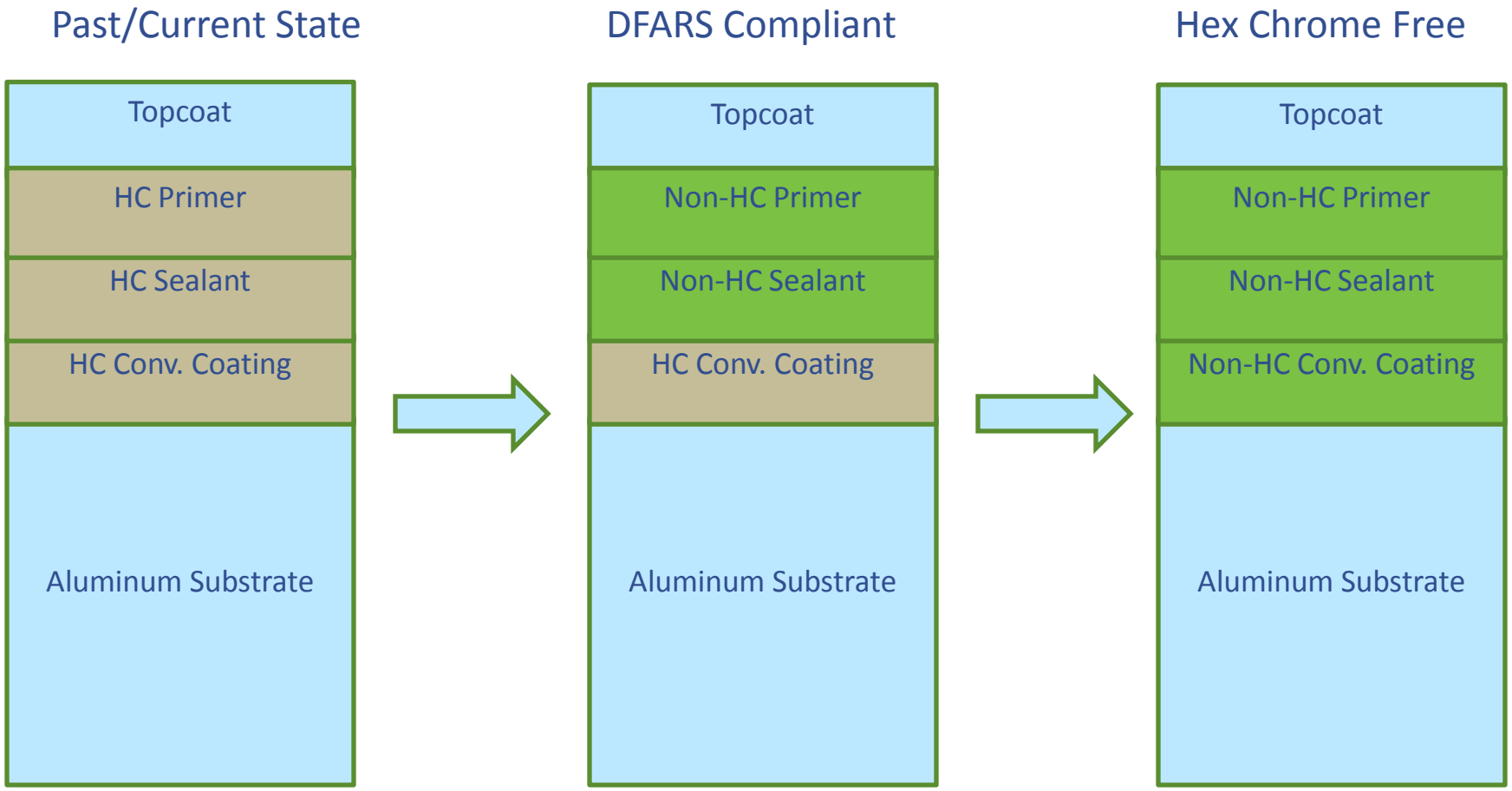
Phase II Research Results for Hex Chrome Free Sealant Alternatives

Greg Morose
Toxics Use Reduction Institute
University of Massachusetts Lowell

April 30, 2014

TURI
TOXICS USE REDUCTION INSTITUTE
UMASS LOWELL

Hexavalent Chromium (HC)



Sealant Research Overview

Research Phase	Timeframe	Purpose	Materials Evaluated
Phase I	2012 - 2013	Screening level research of the key factors for sealant performance	4 sealants 2 conversion coatings 2 aluminum alloys 2 primers 2 fastener types With & without topcoat
Phase II	2013 - 2014	• DFARs compliance for use of sealants • Sealant removal evaluation	6 sealants
Phase III ??	2014 – 2015??	Totally hex chrome free stack-up: conversion coating, sealant, primer, & topcoat ?????	To be determined

Phase II Research Project Objectives

- Conduct technical performance testing to evaluate the corrosion resistance of six types of sealants for four different types of sealant applications used in the aerospace/defense industry.
- The research results should provide significant statistical data to justify the use of DFARS-compliant assembly including hex chrome free sealants.
- Continue the working relationship with research participants as a basis for continued collaborative research.

Phase II Sealant Evaluation Team

Government

Aviation & Missile Command Safety Office

NAVAIR Naval Air Systems Command

NASA

U.S. Air Force

Industry

Lockheed Martin

Bombardier the evolution of mobility

Northrop Grumman

Raytheon

Academia

UMass Lowell

TURI Toxics Use Reduction Institute UMass Lowell

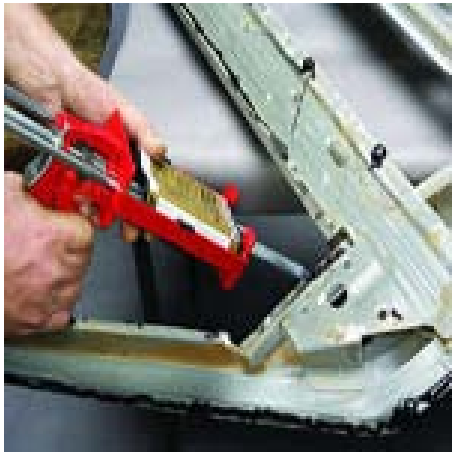
Sealant Applications

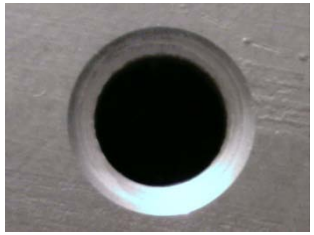
1. Sealant applied to the threads of a fastener (wet installation)

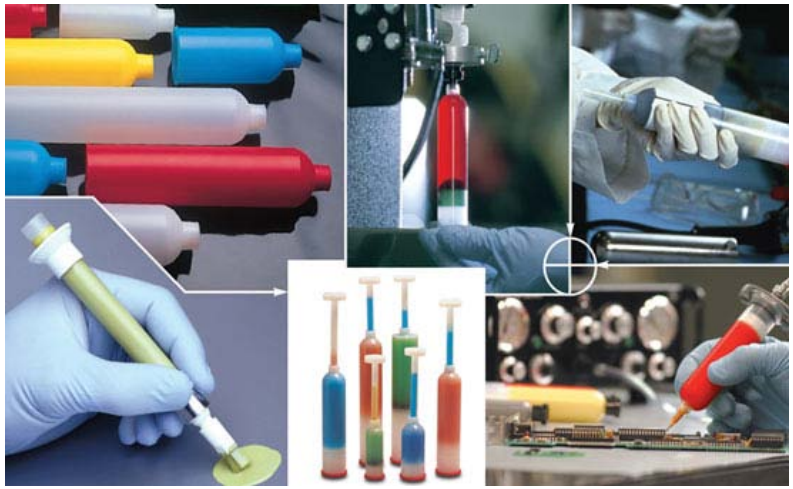
2. Sealant applied to the ends of a fastener

3. Sealant applied to butt joint (for example a ¼ inch gap between materials)

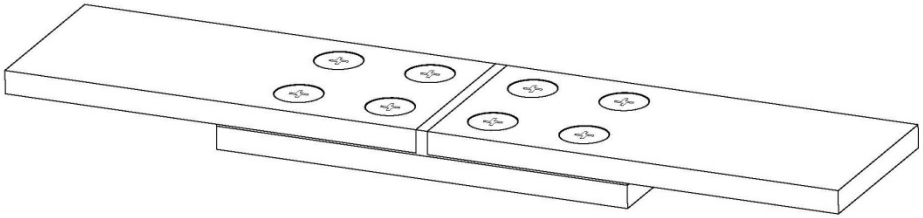
4. Sealant applied to faying surfaces (the surfaces of materials in contact with each other and joined together)





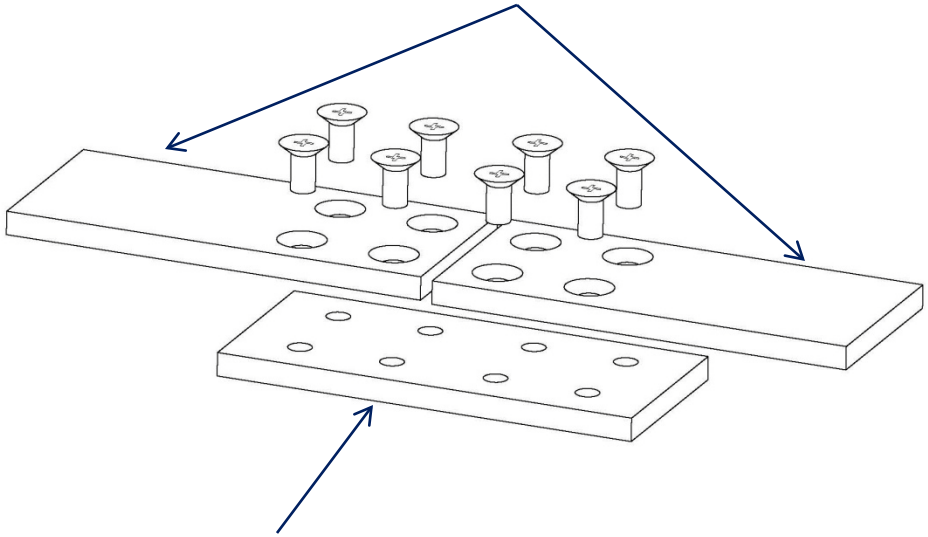


Test Vehicle Assembly Drawing



Three aluminum plates: 2” x 4.5” x 0.25” (alloy 7075 only)

2 top plates



1 bottom plate

8 stainless steel fasteners with 100 degree countersunk heads

Phase II Sealant Selection

Vendor	Vendor PN	Specification	Purpose	Chemical Class	Corrosion Inhibitor
PPG Aerospace	PS-870	MIL-PRF-81733 Type II Class 1 Grade A	Baseline	Polysulfide	Hexavalent chromium
3M	AC-735	MIL-PRF-81733 Type II Class 1 Grade B and AMS 3265 Class B	Alternative Sealant	Polysulfide	Zinc phosphate
PPG Aerospace	PR-1775	AMS 3265 Class B	Alternative Sealant	Polysulfide	Phosphite salt Second chemical TBD
PPG Aerospace	PR-2870 (RW-6040-71)	MIL-PRF-81733 Type II Class 2 Grade B	Alternative Sealant	Polythioether	Chemical ID TBD
Flame Master	CS 5500N CI	Not yet qualified	Alternative Sealant	Polysulfide	Molybdates
PPG Aerospace	PR-1440	AMS-S-8802 Type 2 Class B	Negative Control	Polysulfide	None

Priming and Painting of Test Vehicles

Vendor	Model	Primer/ Topcoat	Specification	Hexavalent Chromium Containing
PPG Aerospace (Deft Inc.)	44GN098	Primer	MIL-PRF-85582 Type 1 Class N	No
PPG Aerospace (PRC-Desoto)	Kit Code 8211F37886MPY22K Base - CA 8211/F37886 Activator - CA 8200B M&D	Topcoat	MIL-PRF-85285 Type 1	No

Phase II Design of Experiments

Number	Alloy	Sealant	Conversion Coating	Secondary Finish	Test
1	7075	PPG PS-870	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
2	7075	PPG PS-870	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
3	7075	PPG PS-870	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
4	7075	PPG PS-870	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
5	7075	PPG PS-870	Iridite 14-2	HCF Primer & Topcoat	Beachfront
6	7075	3M AC-735	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
7	7075	3M AC-735	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
8	7075	3M AC-735	Iridite 14-2	HCF Primer & Topcoat	Beachfront
9	7075	3M AC-735	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
10	7075	3M AC-735	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
11	7075	PPG PR-1775	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
12	7075	PPG PR-1775	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
13	7075	PPG PR-1775	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
14	7075	PPG PR-1775	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
15	7075	PPG PR-1775	Iridite 14-2	HCF Primer & Topcoat	Beachfront

Phase II Design of Experiments

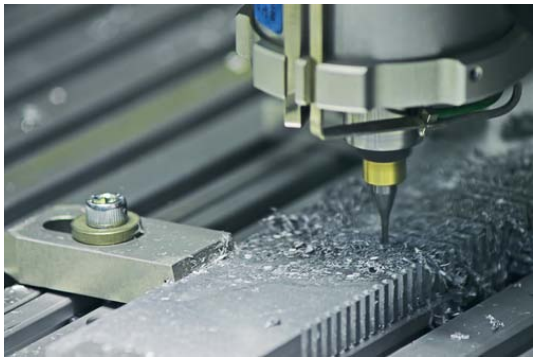
*Test vehicles # 16, and #18 are spares.

Number	Alloy	Sealant	Conversion Coating	Secondary Finish	Test
*17	7075	PPG RW-6040-71	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
19	7075	PPG RW-6040-71	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
20	7075	PPG RW-6040-71	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
21	7075	PPG RW-6040-71	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
22	7075	PPG RW-6040-71	Iridite 14-2	HCF Primer & Topcoat	Beachfront
23	7075	FM CS 5500N CI	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
24	7075	FM CS 5500N CI	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
25	7075	FM CS 5500N CI	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
26	7075	FM CS 5500N CI	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,008 hrs
27	7075	FM CS 5500N CI	Iridite 14-2	HCF Primer & Topcoat	Beachfront
28	7075	PPG PR-1440	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
29	7075	PPG PR-1440	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
30	7075	PPG PR-1440	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
31	7075	PPG PR-1440	Iridite 14-2	HCF Primer & Topcoat	Salt fog 1,000 hrs
32	7075	PPG PR-1440	Iridite 14-2	HCF Primer & Topcoat	Beachfront

Phase II Research Process

Test plan development
All participants

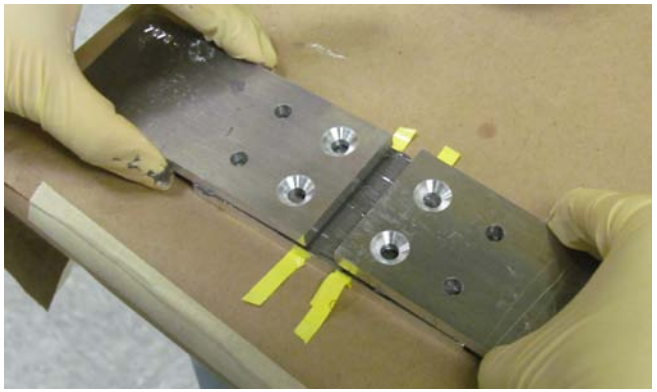
Test vehicle CAD design
Raytheon



Aluminum plate machining
NASA

Research Process

Conversion Coating
(MacDermid Iridite 14-2)
Northrop Grumman



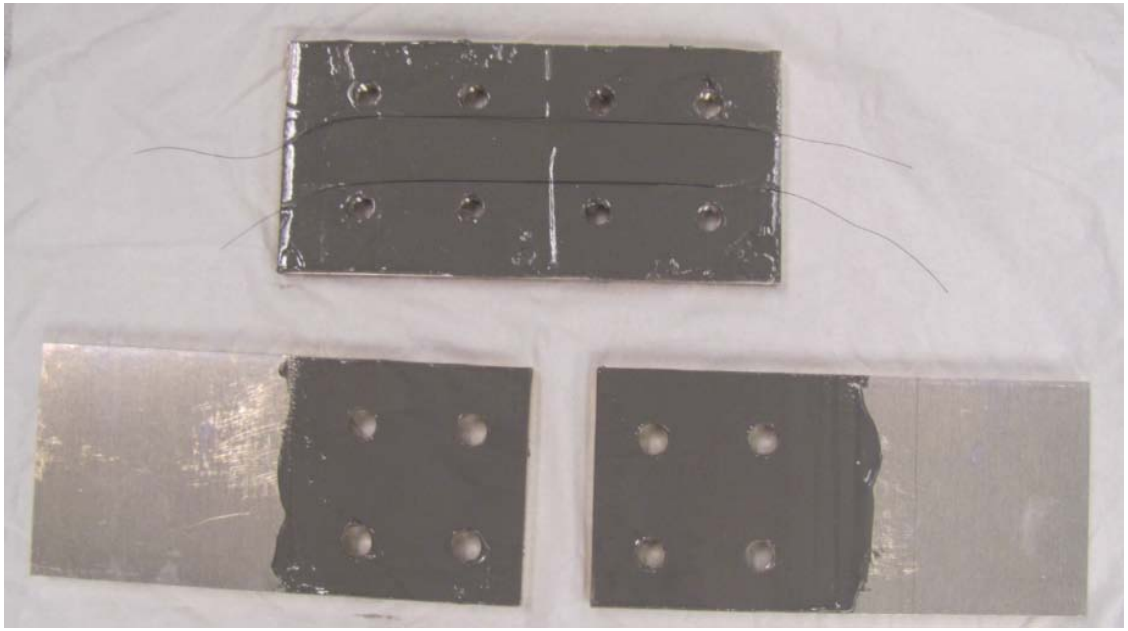
Test Vehicle Assembly*
Raytheon

Test Vehicle Preconditioning
(MIL-PRF-81733D, Section 4.8.9.3.1 Cyclic Loading for Class 1 Materials)
U.S. Navy

*Fasteners for the test vehicle provided by **Bombardier.**

Phase II Test Vehicle Assembly Process

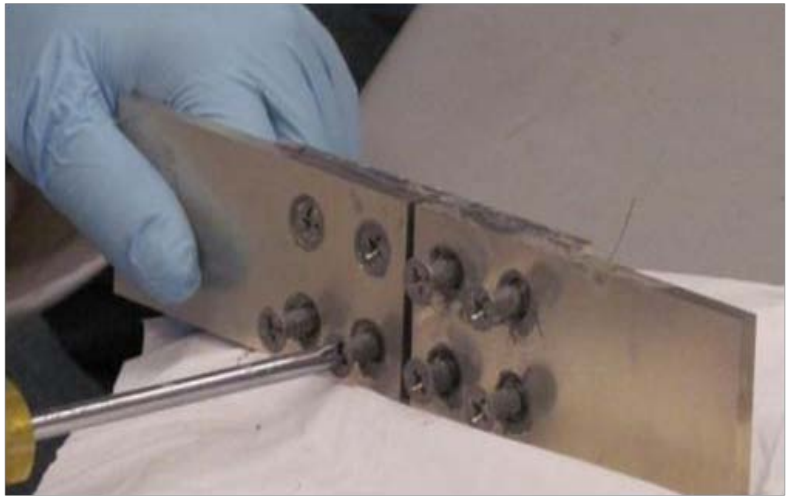
1. Cleaning: All plates were solvent wiped with Acetone.
2. Butt Joint Scribe: Scribed the top side of the bottom plate with an “X”.
3. Faying Surface: Applied approximately 0.005 inch of sealing compound to one side of each of the 3 mating TV panels with an orange stick or glass rod. Add 0.005 inch bond wires to control the sealant thickness.

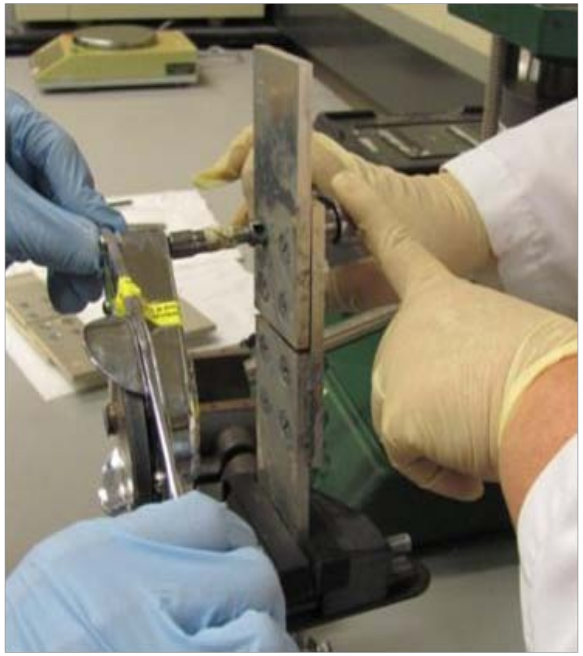


Phase II Test Vehicle Assembly Process

4. Application of Sealant to Fasteners: Fasteners were cleaned with acetone prior to installation. All 8 fasteners were evenly coated with sealant using an orange stick or gloved finger.

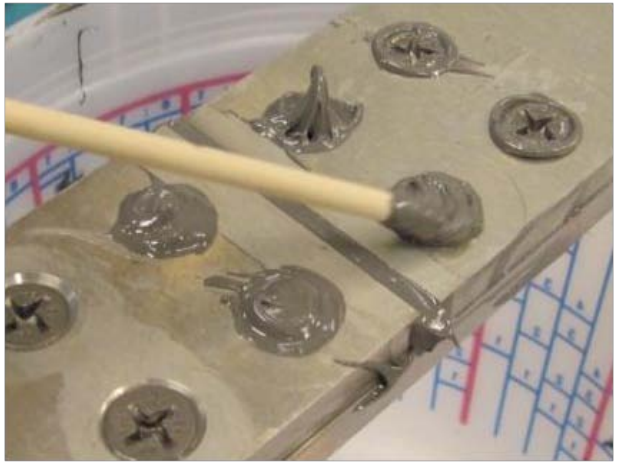
5. Installation of Fasteners. Fasteners were inserted into the holes of the freshly mated panels and nuts were installed. All fasteners were hand tightened with a screwdriver. Then the plate was held in a vice and all eight fasteners were torqued to 40 in-lbs .





Phase II Test Vehicle Assembly Process

6. Butt Joint: Sealing compound was applied to the butt joint to completely fill the gap using an orange stick or glass rod.
7. Clean: Excess sealant was wiped from the entire test vehicle with cotton swab and acetone to remove the majority of the sealant from the exterior
8. Fastener Heads: An orange stick or glass rod was used to apply sealant to completely cover over and around six fastener heads, as well as the corresponding six nuts.
9. Excess Sealant Removal: All the residual sealant from the processing of the test vehicle was removed.

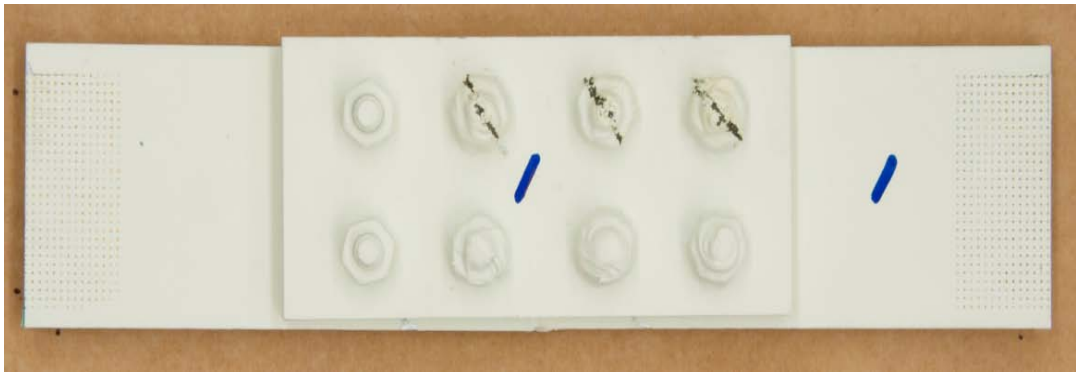


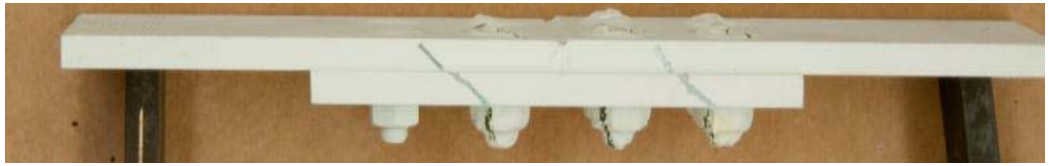
Phase II Test Vehicle Assembly Process

10. Curing: The assembly cured for 48 hours at ambient laboratory temperature with the relative humidity between 35 and 48%.

11. Prime and Paint: Following a surface wipe with acetone, primer and topcoat were applied to the test vehicles according to manufacturer instructions. Test vehicles were allowed to cure for a minimum of 48 hours prior to scribing.

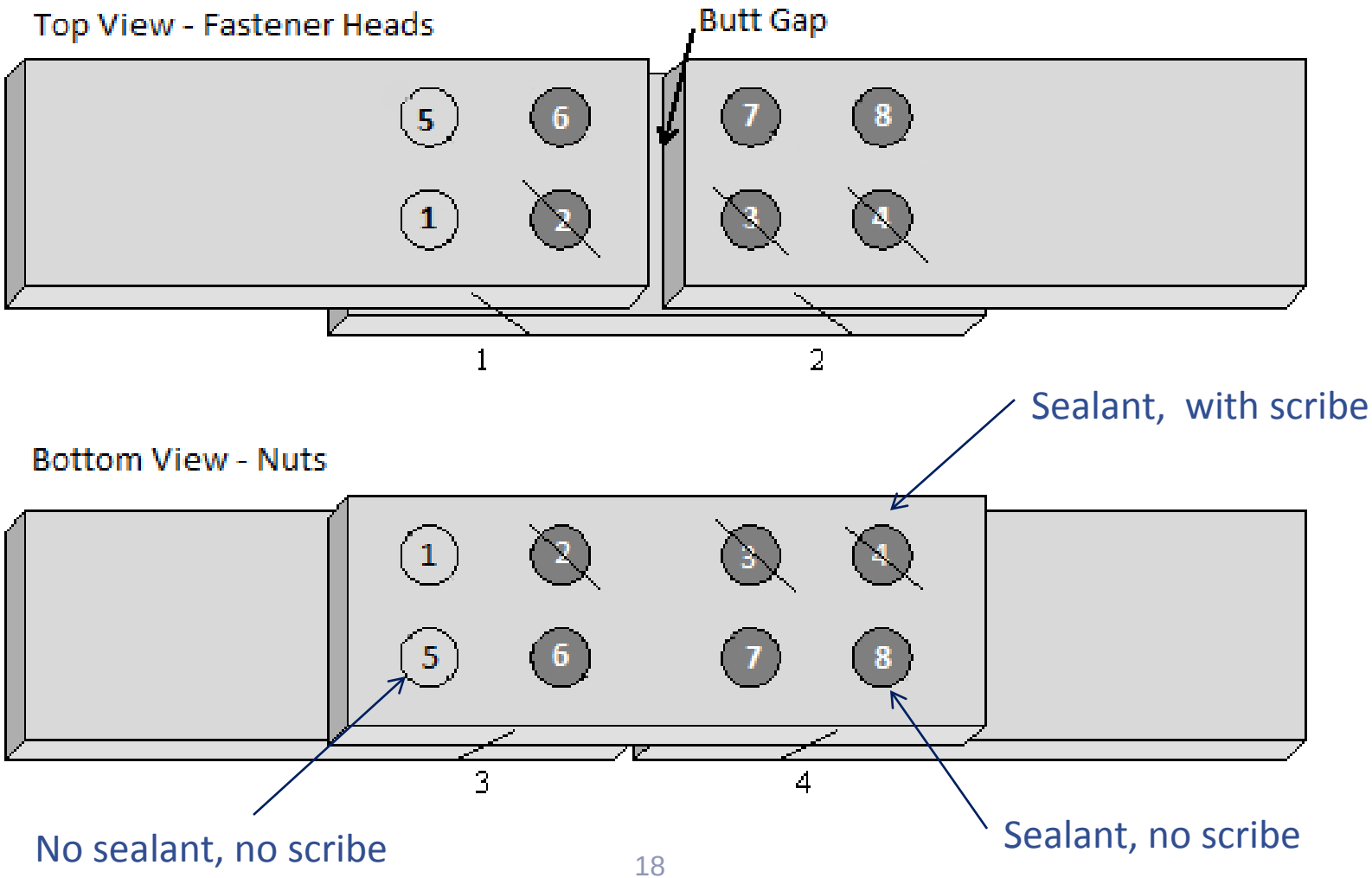
12. Additional Scribes: Additional scribing was done through the primer/topcoat across the edges of the test vehicle in four locations and on fastener heads and nuts





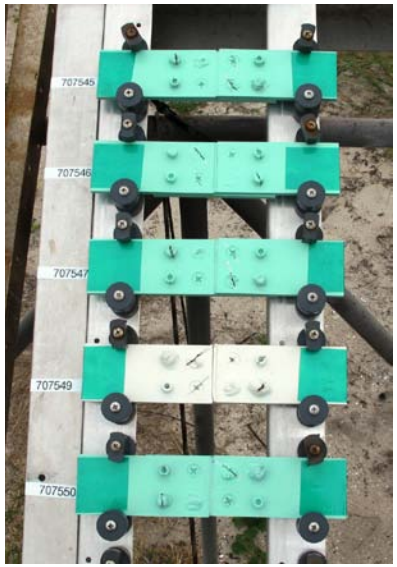
Sealant Application on Fasteners

All eight fasteners are wet installed.



Research Process

Accelerated Corrosion Test
1,000 hours
SO_2 Salt Fog, ASTM G85 Annex 4
(24 Test Vehicles)
Lockheed Martin



Long-term Corrosion Test
1 year duration
(6 Test Vehicles)
NASA

Research Process

Sealant Removal
TURI, UMass Lowell

Corrosion Inspection & Analysis
Lockheed Martin

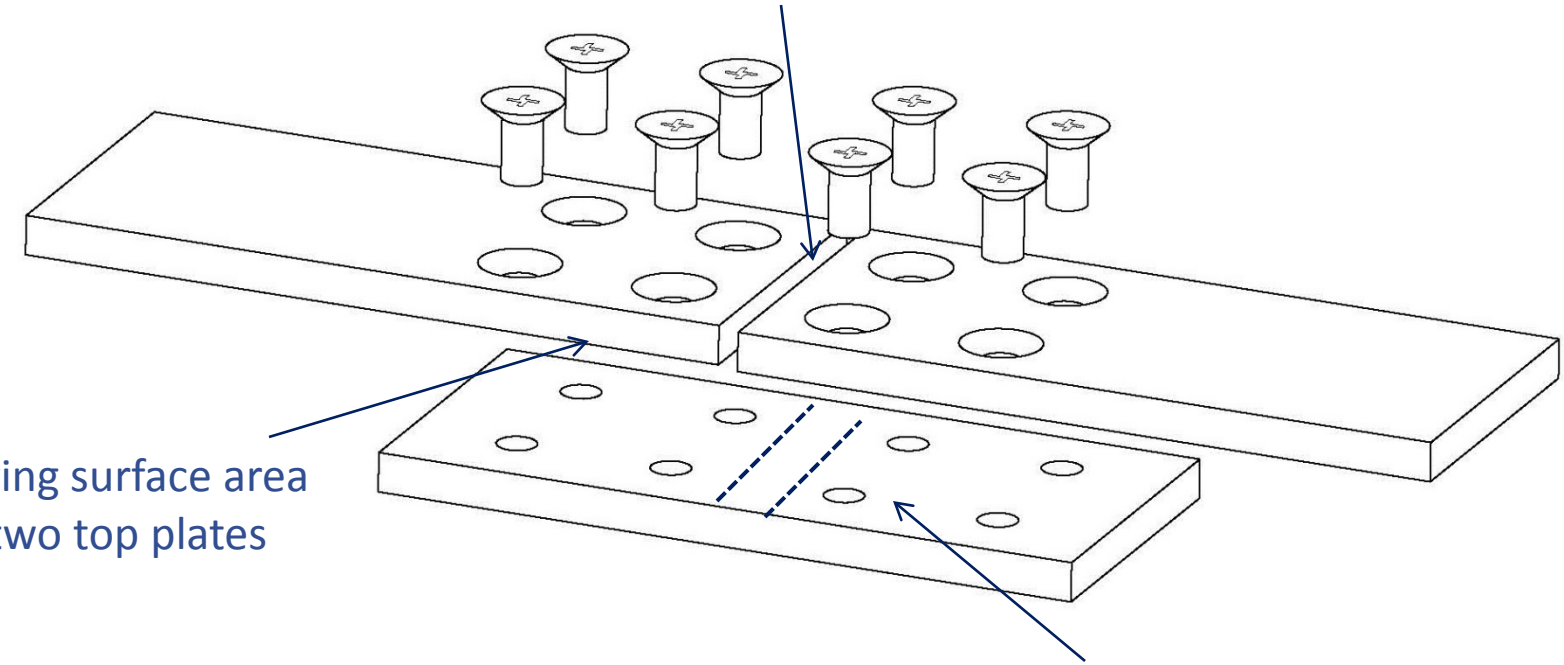
Statistical Analysis & Write Paper
TURI, UMass Lowell

Percent Corrosion Inspection Areas

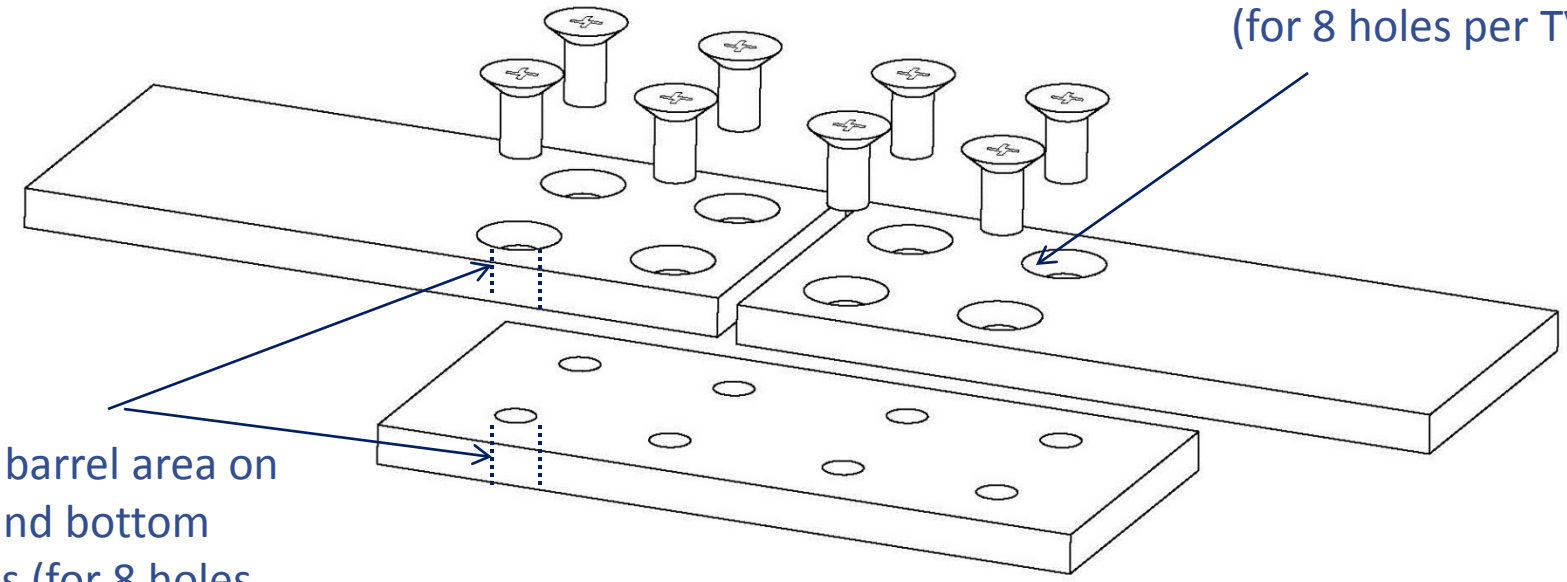
Area of Inspection for Percent Corrosion	Relevant Sealant Application
1) Faying Surface & Butt Joint Areas	• Faying surface • Butt joint
2) Fastener Hole Area: includes countersink and hole barrel areas	• Fastener threads • Fastener stems
3) Exterior Surface: Ring around fastener holes covered with sealant (top and bottom plates)	• Fastener heads and nuts

Test vehicle inspection conducted by Curtis Lemieux and Kent DeFranco from Lockheed Martin.

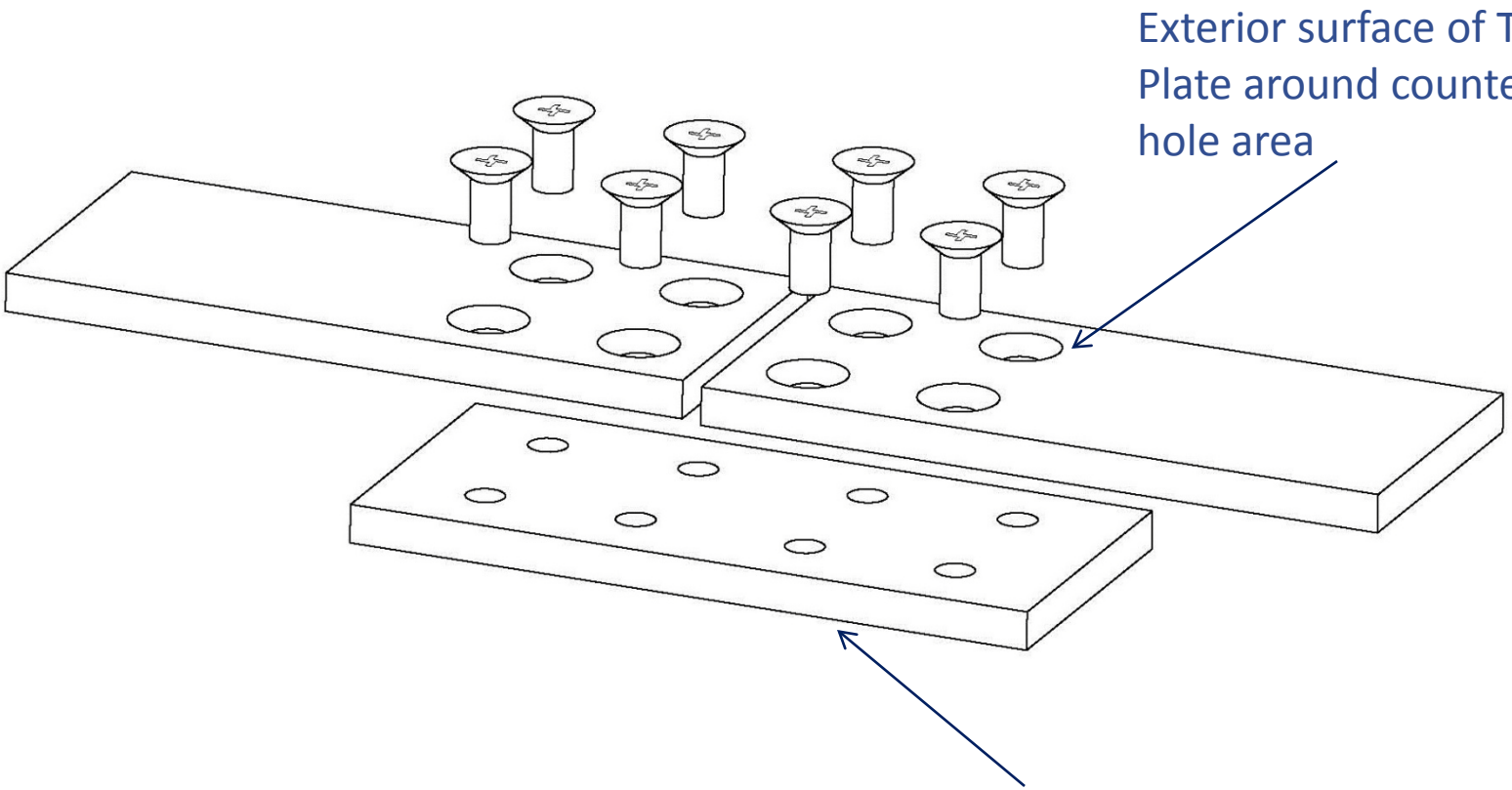
Areas of Inspection:
1) Butt Joint & Faying Surface



Areas of Inspection:
2) Fastener Hole Areas

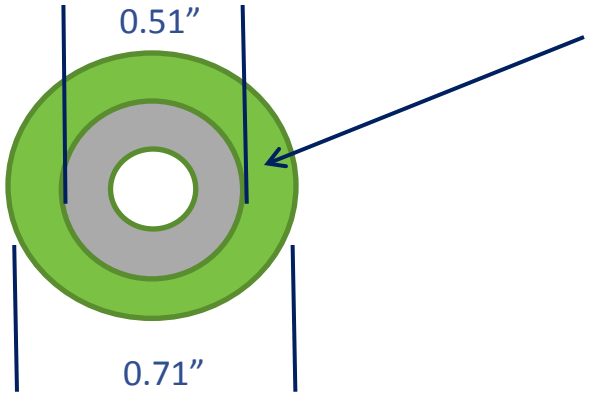


Areas of Inspection:
3) Ring Area Around Fastener Holes



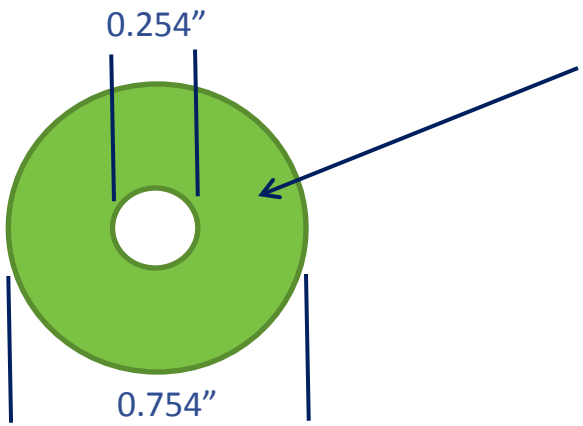
Ring Area on Exterior Surface Around Fastener Holes

Top Plate Inspection Area around Countersunk Hole



Inspection area (0.1” wide around countersink)

Bottom Plate Inspection Area around Fastener Hole



Inspection area (0.25” wide around hole)

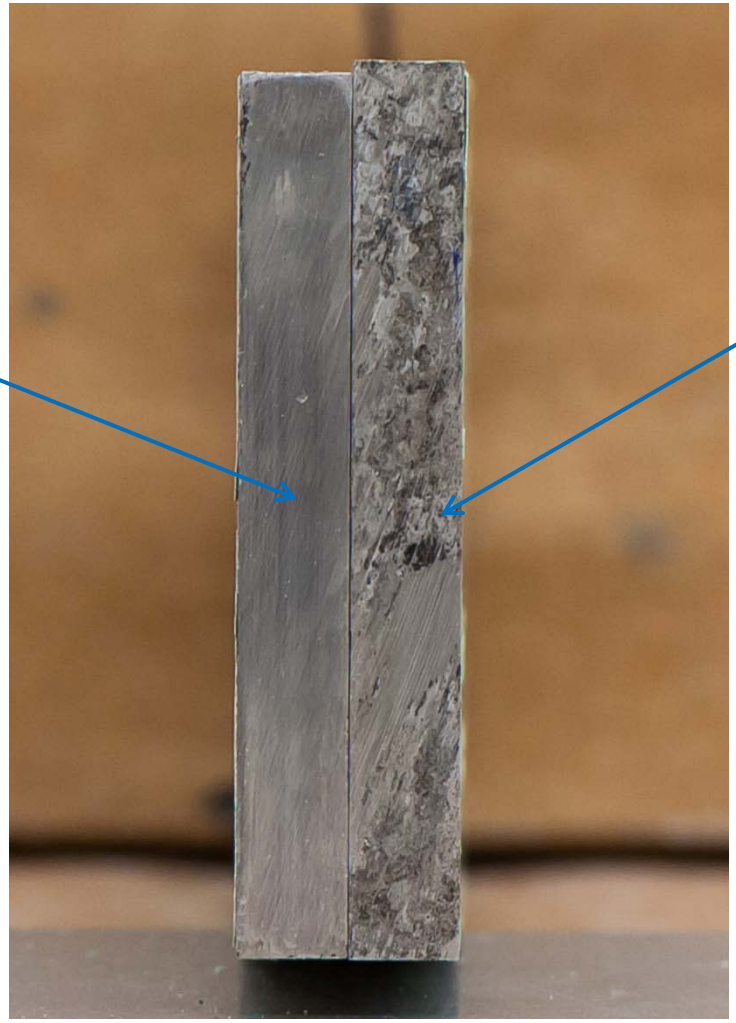
Phase II Corrosion: Countersunk Hole

TV 19, Fastener Hole 2

Phase II Corrosion: Butt Joint

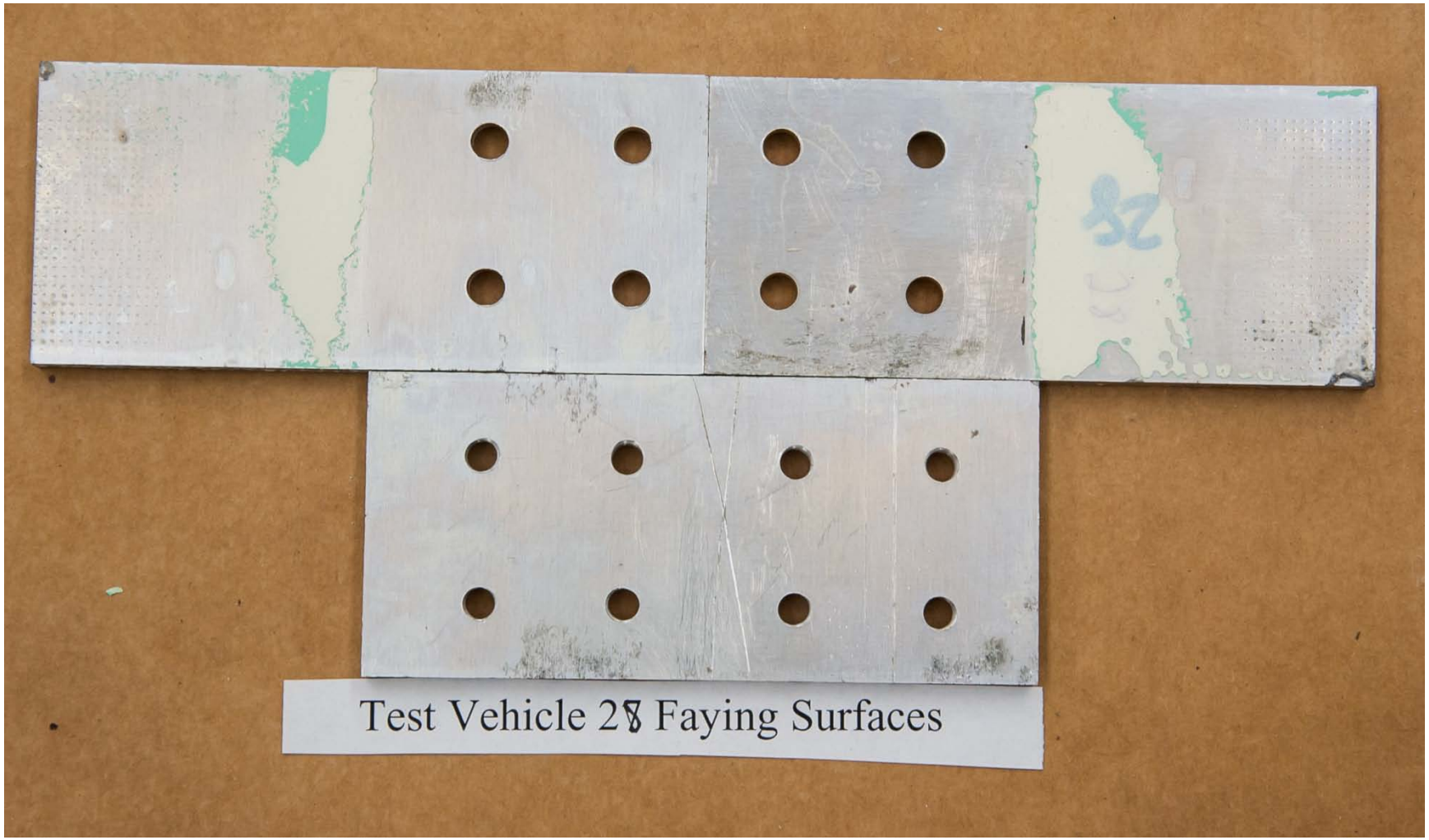
0% corrosion

55% corrosion



TV 19, Butt Joint

Phase II Corrosion: Faying Surface



TV 28, Faying Surface

Statistical Analysis

The Analysis of Variance (ANOVA) method was used for hypothesis testing. The null hypothesis used for this research is that the corrosion values for different factor/level combinations within the design of experiments are the same for each combination. The alternative hypothesis is that the corrosion values for different factor/level combinations are not the same.

Alpha risk is the probability of rejecting the null hypothesis when it is actually true, resulting in a Type 1 error.

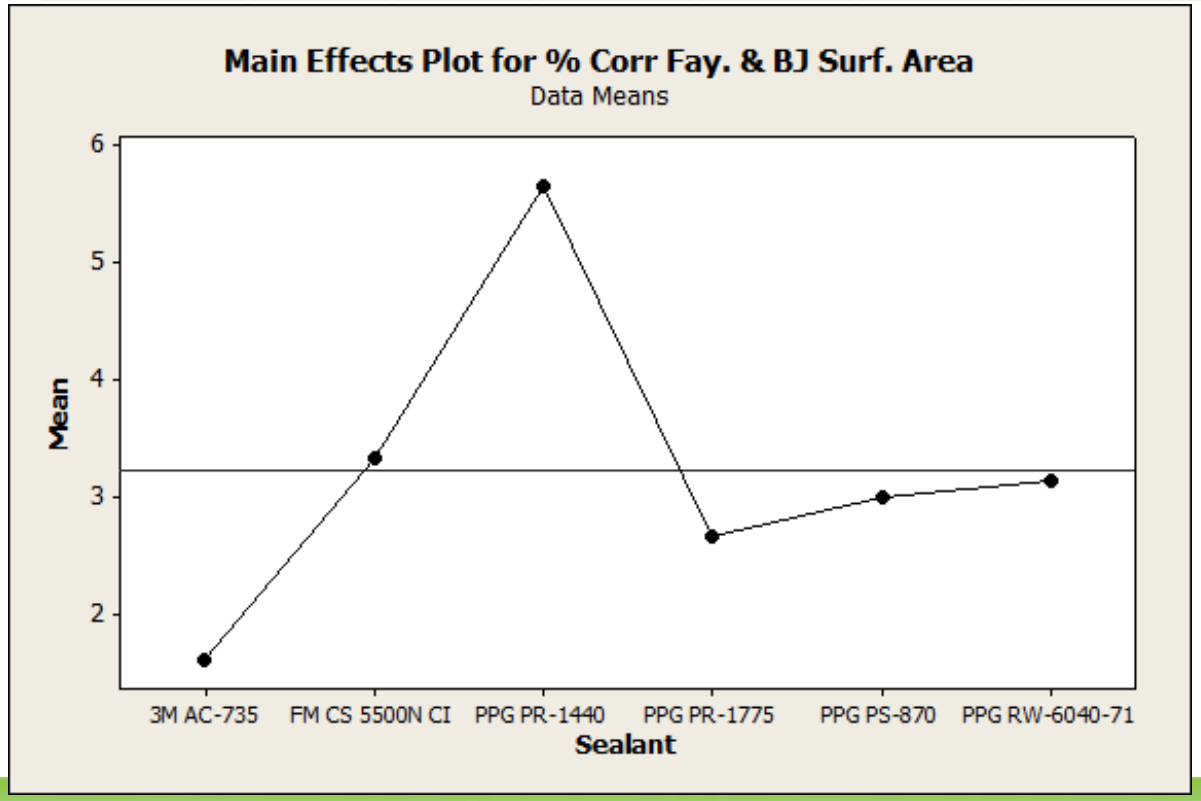
Confidence level = 1 - alpha risk

For the purposes of this research, we will consider the results to be statistically significant if the Confidence Level is at least 90%, with a corresponding alpha risk of 10%.

Minitab software was used for the statistical analysis. The ANOVA method was used along with the Tukey Method for comparisons between individual sealant performance.

1) Butt Joint and Faying Surface Areas

Surface Area	PS-870	AC-735	PR-1775	RW-6040	CS 5500N CI	PR-1440	All Sealants	Results
Faying Surface & Butt Joint	3.0%	1.6%	2.7%	3.1%	3.3%	5.7%	3.2%	Statistical Difference 90% Confidence Level



The percent corrosion for PR-1440 is higher than the AC-735 sealant.

No statistical difference (< 90% confidence) for the percent corrosion for AC-735, CS 5500N CI, PR-1775, PS- 870, and RW-6040.

No stat. difference for the percent corrosion for PR-1440 , CS 5500N CI, PR-1775, PS- 870, and RW-6040.

2) Fastener Hole Area

The fastener hole area includes the countersunk area and the hole barrel area.

There was statistical difference identified for the following:

- Sealant protection method (Overcoating fastener heads and nuts)
- Fasteners with sealant overcoat and no scribe

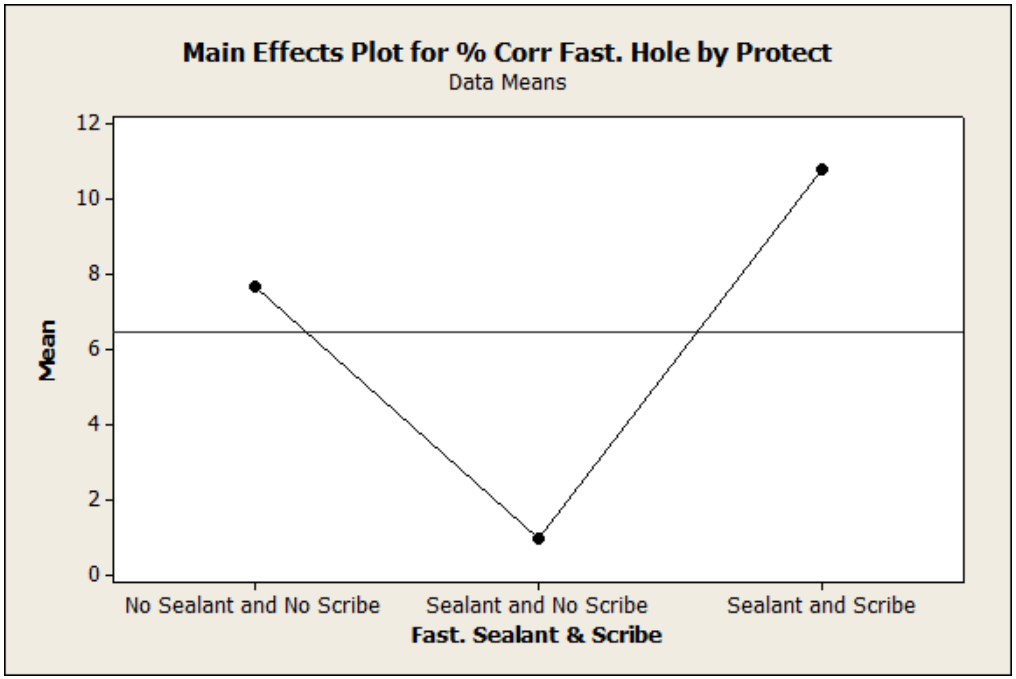
There was no statistical difference identified for the following:

- Fasteners with sealant overcoat and scribe
- Fasteners with no sealant overcoat
- All types of fasteners combined (overcoat and no overcoat)

This lack of statistical difference in some areas is primarily due to the high level of variation for percent corrosion values within each sealant type ("within group variance"). This variation was greater than the variation of corrosion values between sealant types ("between group variance").

Fastener Hole Area

Area	Fasteners with sealant overcoat and no scribe	Fasteners with sealant overcoat and scribes	Fasteners with no sealant overcoat and no scribes	Average for all Fasteners	Results
Fastener hole area (countersunk and barrel areas)	1.0%	10.8%	7.7%	7.1%	Statistical Difference 90% Confidence Level

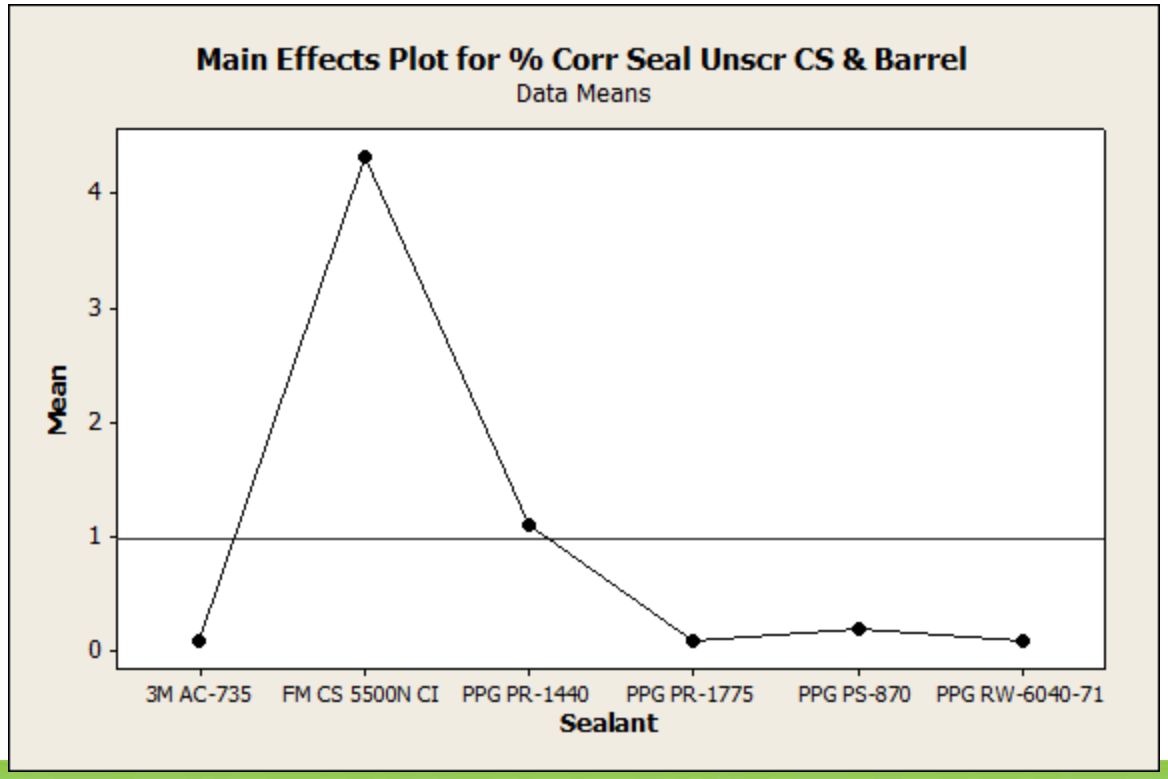


All fasteners were wet installed with sealant.

The fastener holes with sealant overcoat and no scribes provided better corrosion protection than fastener holes with either: 1) sealant overcoat and scribes or 2) no sealant overcoat.

Fastener Holes with Sealant Overcoat and No Scribes

Area	PS-870	AC-735	PR-1775	PR-2870 (RW-6040)	CS 5500N CI	PR-1440	All Sealants	Results
Fastener hole area (countersunk and barrel)	0.2%	0.1%	0.1%	0.1%	4.3%	1.1%	1.0%	Statistical Difference 90% Confidence Level

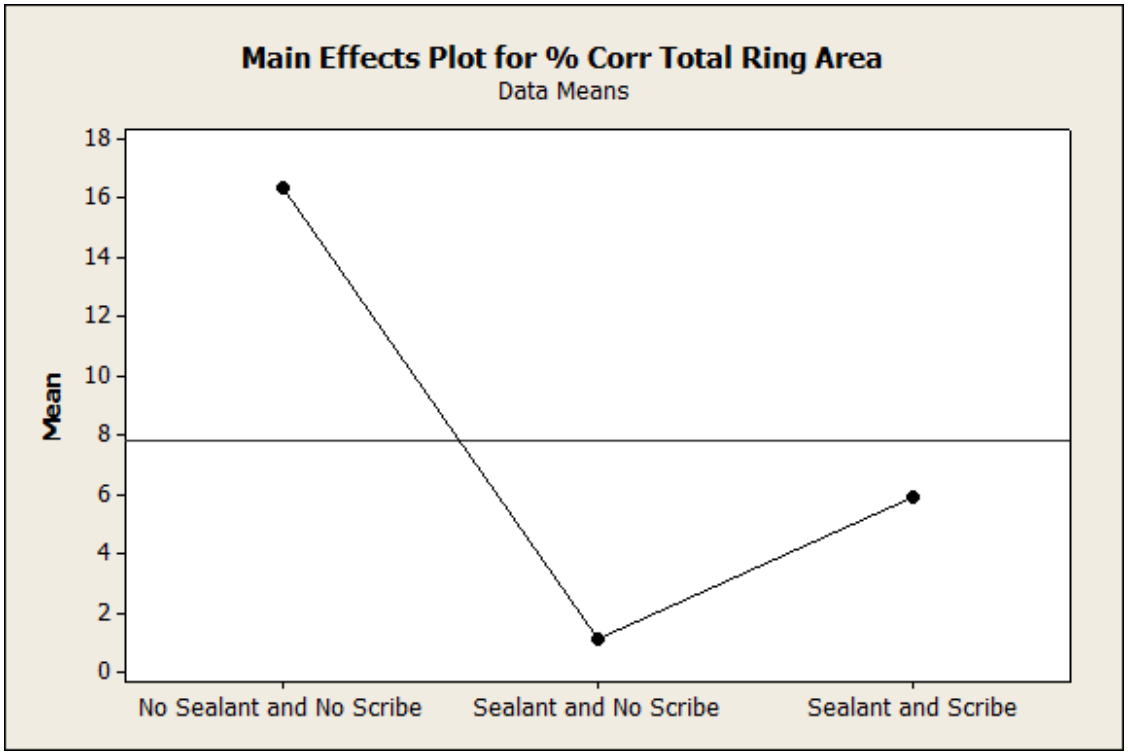


The percent corrosion for CS 5500N CI is higher than for the PS-870, AC-735, PR-1775, PR-1440, and PR-2870 sealants.

No statistical difference for the percent corrosion for AC-735, PR-1440, PR-1775, PS-870, and PR-2870.

3) Ring Around Fastener Hole Area

Area	Fasteners with sealant overcoat and no scribe	Fasteners with sealant overcoat and scribes	Fasteners with no sealant overcoat and no scribes	Average for all Fasteners	Results
Ring around fastener hole area (top & bottom)	1.1%	6.0%	16.3%	6.7%	Statistical Difference 90% Confidence Level

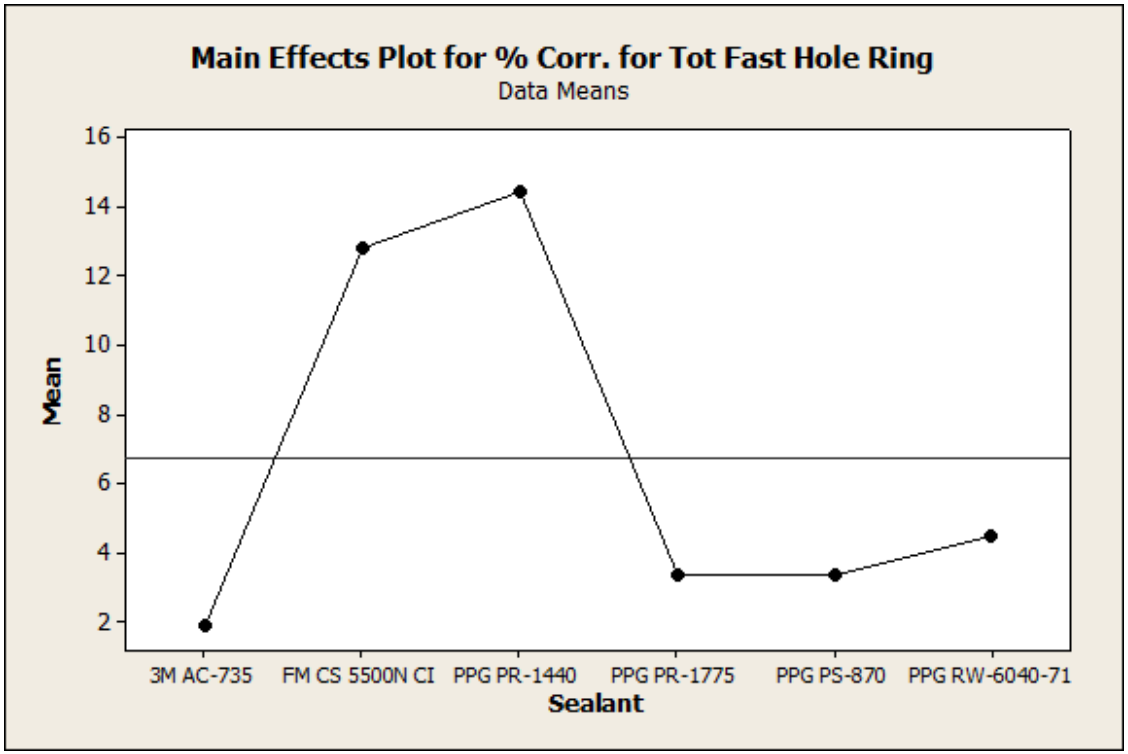


All fasteners were wet installed with sealant.

The fastener holes with a sealant overcoat (with and without scribes) provided better corrosion protection than fastener holes with no sealant overcoat.

Ring Around Fastener Hole Results

Area	PS-870	AC-735	PR-1775	PR-2870 (RW-6040)	CS 5500N CI	PR-1440	All Sealants	Results
Ring around fastener hole areas (top & bottom)	3.3%	1.9%	3.4%	4.5%	12.8%	14.4%	6.7%	Statistical Difference 90% Confidence Level



The percent corrosion for PR-1440 and CS 5500N CI is higher than for the PS-870, AC-735, PR-1775, and PR-2870 sealants.

No statistical difference for the percent corrosion for AC-735, PR-1775, PS-870, and PR-2870.

Possible variation in surface preparation is suspected to influence results.

Conclusions

The Phase II Design of Experiments appears robust for the following reasons:

Experiment Power: There were four replicates provided for each sealant type. This provided statistical differences for each of the three inspection areas.

Sealant Application Differentiation: There were differences in the corrosion results for the different sealant applications (e.g. butt joint, fastener holes, etc.)

Sealant Product Differentiation: There were statistical differences between the corrosion inhibiting performance of the various sealant products for each of the three inspection areas.

CI Additive: The sealant with no corrosion inhibitor additive had the lowest or second lowest corrosion protection for each of the three inspection areas.

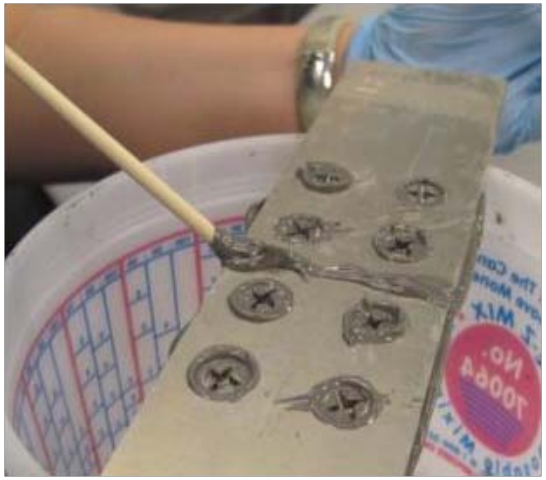
Induced Damage: The sealant overcoat and scribed areas had more corrosion than the sealant and un-scribed areas.

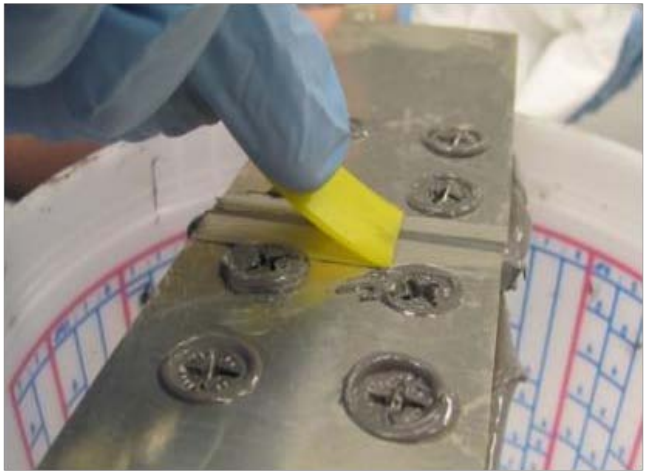
Sealant Protection: The areas with sealant overcoat and no scribes had less corrosion than areas with no sealant and no scribes.

Conclusions

For the faying surface/butt joint areas, four alternative sealants containing non-hex chrome corrosion inhibitors (AC-735, CS 5500N CI, PR-1775, and PR-2870) provided equivalent corrosion prevention performance to the baseline sealant PS-870.

For the fastener holes and ring around the fastener areas, three alternative sealants containing non-hex chrome corrosion inhibitors (AC-735, PR-1775, and PR-2870) provided equivalent corrosion prevention performance to the baseline sealant PS-870.





Phase II Results

Results to be presented at ACE meeting, May 6-7, 2014 in Cincinnati, OH

The complete results for Phase II sealant evaluation will be documented in a white paper and published (print & on-line) by Products Finishing in August 2014.

Thank you!

Backup Slides

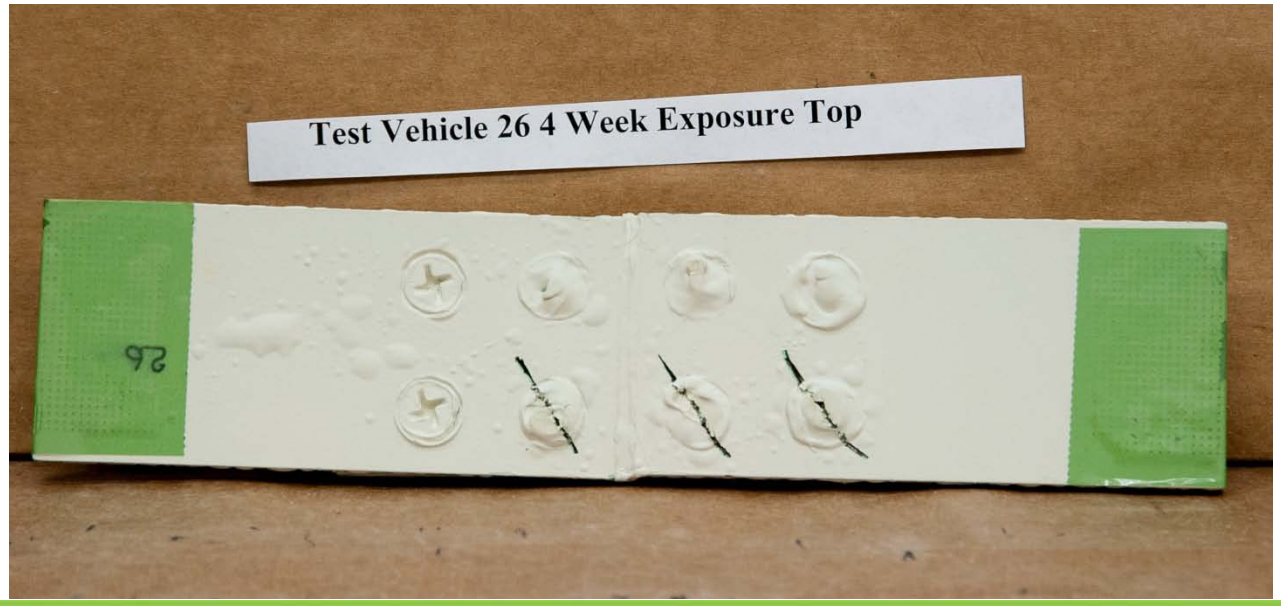
Key Findings from Phase I Efforts

- 7075 alloy had higher corrosion than 6061 alloy for all sealant applications
- Iridite had lower corrosion than hex chrome free conversion coating for most sealant applications
- Countersunk fasteners had more corrosion than protruding fastener heads
- No statistically significant difference in corrosion resistance between hex chrome containing and hex chrome free primers
- Improved corrosion resistance when a topcoat is present
- No statistically significant difference between the corrosion resistance performance of the hex chrome containing and hex chrome free sealants (however, no replicates were provided in the screening level design of experiments)

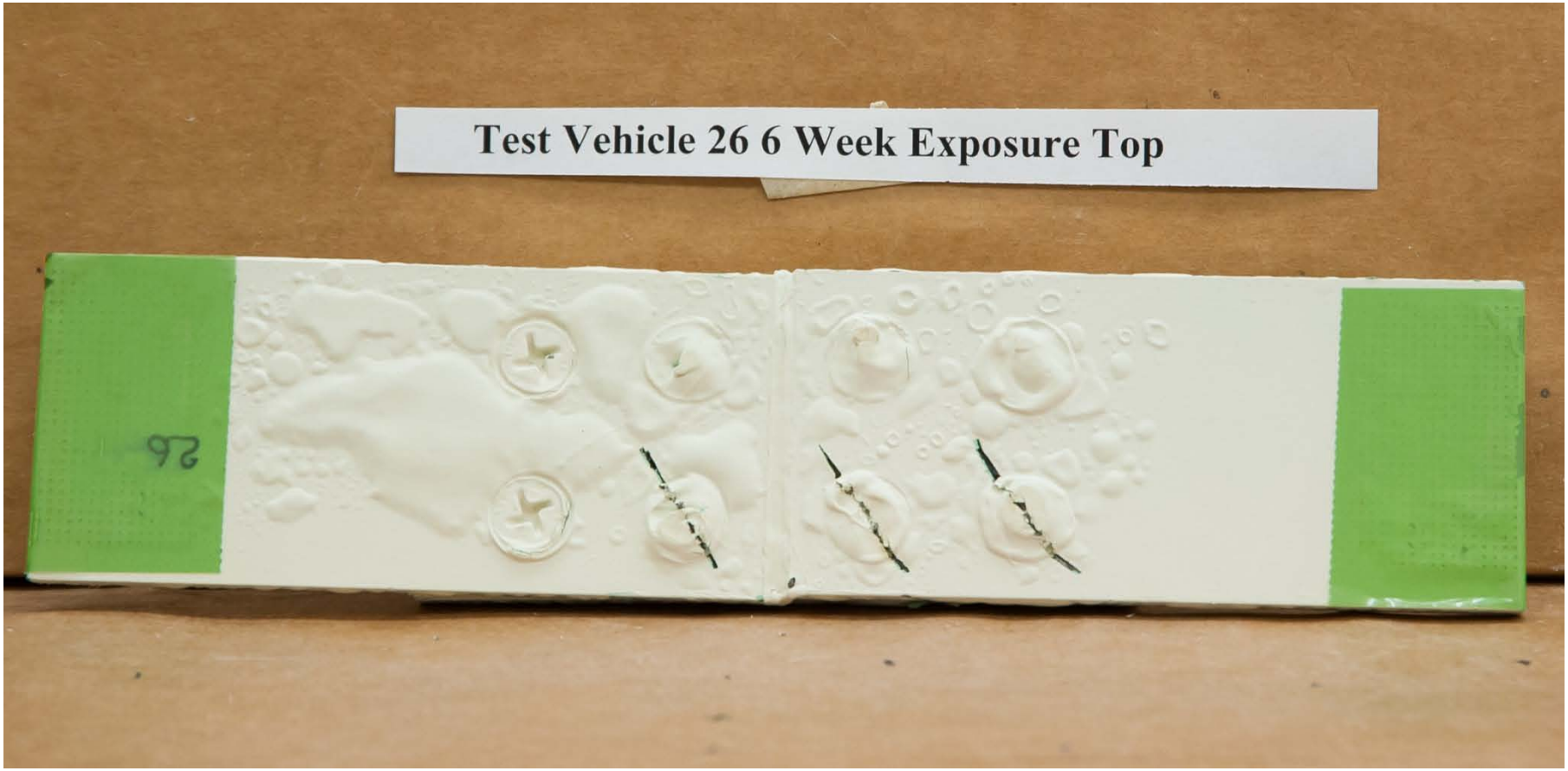
Phase II Corrosion: Ring around Fasteners

TV 26, Exterior Surface

Phase II Corrosion



Phase II Corrosion



Corrosion by Sealant Application

Sealant Area	Average Percent Corrosion for all Six Sealants
1) Faying Surface and Butt Joint Areas	3.2%
Faying Surface	2.9%
Butt Joint	6.6%
2) Fastener Countersunk & Barrel Area	7.1%
Fastener Countersunk Area	17.0%
Fastener Barrel Hole Area	0.9%
3) Ring Around Fastener Areas	6.7%
Top plate surface	16.2%
Bottom plate surface	2.1%

Fastener Hole Area: Data Variability

There was a high level of within group variance for the percent corrosion data for the fastener areas for each sealant type.

For example:
Fasteners 2, 3, and 4 each have sealant and scribing, however, the results had high variability on several test vehicles.

Fastener Counter Sink Area	TV #1 PS-870 Sealant	TV #10 AC-735 Sealant	TV #19 RW-6040-71 Sealant
Fastener 2	3%	0%	100%
Fastener 3	80%	0%	7%
Fastener 4	2%	80%	40%

Fastener Hole Area: Sources of Within Group Variation

Possible causes of within group variance in the percent corrosion results:

- Variability of the depth of the countersink area during machining of plates
- Variability in the application of the sealant (thickness and coverage)
- Variability in the depth of the scribe
- Alignment of fastener head in the countersink area
- Existence of moisture in the hole area prior to testing

Preconditioning

To stress the sealant joints, the test vehicles were mechanically and thermally preconditioned at the NAVAIR facility in Patuxent River, Maryland during September 2013. The preconditioning was conducted according to MIL-PRF-81733D Section 4.8.9.3.1 Cyclic Loading for Class 1 materials. The assemblies were installed vertically in the jaws of a machine and loaded between 0 and 5,000 lb for 250 cycles with a loading rate of 10 inches (254 mm) per minute. The assembly was subjected to 250 cycles at a temperature of -65 °F (-54 °C) following a 30 minute soak time at -65 °F (-54 °C) under no load.

Inspection

Corrosion was only recorded if there was deterioration of the metal (pitting). A rating of 0% would reflect that no corrosion was present and a rating of 100 % would indicate complete corrosion of that area of interest.

For each type of sealant, there were four test vehicles that were averaged together to provide a single corrosion rating.